

ગુજરાત રાજ્યના શિક્ષણવિભાગના પત્ર-ક્રમાંક  
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# CHEMISTRY

## Standard 11

(Semester I)



### PLEDGE

India is my country.

All Indians are my brothers and sisters.

I love my country and I am proud of its rich and varied heritage.

I shall always strive to be worthy of it.

I shall respect my parents, teachers and all my elders and treat everyone with courtesy.

I pledge my devotion to my country and its people.

My happiness lies in their well-being and prosperity.

રાજ્ય સરકારની વિનામૂલ્યે યોજના હેઠળનું પુસ્તક



Gujarat State Board of School Textbooks  
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## PREFACE

The Gujarat State Secondary and Higher Secondary Education Board has prepared new syllabi in accordance with the new national syllabi prepared by N.C.E.R.T. based on N.C.F. 2005 and core-curriculum. These syllabi are sanctioned by the Government of Gujarat.

It is a pleasure for the Gujarat State Board of School Textbooks to place before the students this textbook of **Chemistry Standard 11 (Semester I)** prepared according to the new syllabus.

Before publishing the textbook, its manuscript has been fully reviewed by expert and teachers teaching at this level. Following suggestions given by teachers and experts. We have made necessary changes in the manuscript before publishing the textbook.

The Board has taken special care to ensure that this textbook is interesting, useful and free from errors. However, we welcome any suggestion, from people interested in education, to improve the quality of the textbook.

**Dr. Bharat Pandit    Dr. Nitin Pethani**

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## FUNDAMENTAL DUTIES

It shall be the duty of every citizen of India :\*

- (a) To abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;
- (b) To cherish and follow the noble ideals which inspired our national struggle for freedom;
- (c) To uphold and protect the sovereignty, unity and integrity of India;
- (d) To defend the country and render national service when called upon to do so;
- (e) To promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;
- (f) To value and preserve the rich heritage of our composite culture;
- (g) To protect and improve the natural environment including forests, lakes, rivers and wild life, and to have compassion for living creatures;
- (h) To develop the scientific temper, humanism and the spirit of inquiry and reform;
- (i) To safeguard public property and to abjure violence;
- (j) To strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement ;
- (k) To provide opportunities education by the parent or the guardian, to his child or a ward between the age of 6-14 years as the case may be.

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## BASIC CONCEPTS OF CHEMISTRY

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- 1.1 Introduction
- 1.2 Importance of Study of Chemistry
- 1.3 Nature of Matter
  - 1.3.1 Classification Based on Physical States
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- 1.4 Physical Quantities
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- 1.7 Percentage Composition of Element and Molecular Formula
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- 1.8 Stoichiometry of Chemical Reactions and Calculations
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### 1.1 Introduction

Chemistry is the science of molecules, variety of compounds and transformations.

Chemistry has played a central role in preventing and finding solution of problems of science. Chemistry is associated with the substances formed in environment and the changes taking place in it.

According to Roald Hoffman chemistry is not only the science of 100 elements but diversity of infinite varieties of molecules which are prepared from them. This purpose can be understood and described by the fundamental particles that are atoms and molecules of matter. Is it possible to observe these particles or can they be compared? Can we count the number of atoms or molecules in a definite quantity of matter? Can a quantitative relationship be established by the number of atoms or molecules in a definite quantity of matter? We shall get the answers of many such questions with the help of basic concepts of chemistry discussed in this unit.

Moreover we will also study how to present physical quantity in its numeric form.

### 1.2 Importance of Study of Chemistry

Science is a bridge to understand the nature. In other words, science is a continuous human effort to understand nature using systematic knowledge.

The study of chemistry is so wide and diversified, that it is classified in various disciplines such as inorganic, organic, physical, analytical industrial, biochemistry etc.

Nowadays, study of chemistry becomes very easy due to principle and pro-principle, which are derived from different facts based on their effective interlinking.

Chemistry is the science of occurrence and synthetic composition, structure and properties

of substance. The branches of science like chemistry, physics, biology, geology are interrelated to one another. Chemistry plays an important role in our everyday life. We experience various chemical phenomena from the time we get up in the morning till we go to bed at night. The principles of chemistry are useful in diverse areas, such as functioning of brain, operation of computer, weather patterns, digestion of food etc. Chemical industries manufacturing fertilizers, alkalies, acids, soaps, detergents, salts, polymers, alloys, dyes, drugs and other inorganic and organic chemicals, including new materials contribute in a big way to the national economy.

Chemistry has increased the comforts in the human life. As we know production of fertilizers on large scale and production of pesticides and insecticides are carried out through chemistry. A large group of semisynthetic and synthetic compounds are included in chemistry. Also chemistry has advanced a lot in pharmaceutical field. The discovery of medicines used in cancer and the life saving drugs like 'cisplatin' and 'texol' owe to chemistry.

Like the two sides of a coin, on one side with many advantages due to the development of chemistry, on the other hand there is a possibility of tremendous damage to the human life and environment. In the present circumstances some of the efforts made in chemistry have successfully resulted in solving (abating) the global problems like pollution.

Chlorofluorocarbon (CFC) used in refrigerator and airconditioner are hazardous to ozone layer and the environment. The safer alternatives of CFC have been invented and can be successfully prepared synthetically. Nowadays in refrigerators, instead of CFC, the less hazardous substance to environment known as HFC-134a (1,1,1,2-tetra fluoroethane) is used.

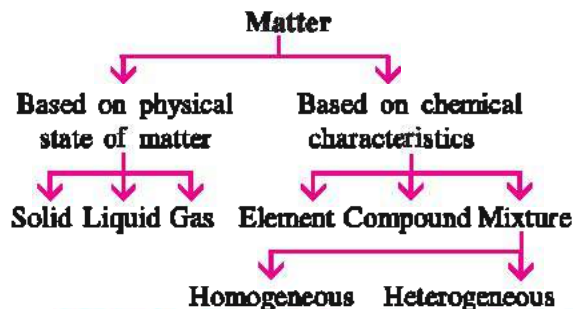
The chemistry involved in production of chemicals without harming the environment is known as Green chemistry.

However, certain challenges like understanding of biochemical reaction, use of enzymes for large scale productions of chemicals, combination of specific types of materials, sources of energy are there before the future generation of chemists. The country needs reputed and creative chemists for the counterattack of such challenges.

### 1.3 Nature of Matter

You have studied about matter in the lower standards. "Anything that has mass and occupies space is matter". Matter is made up of particles.

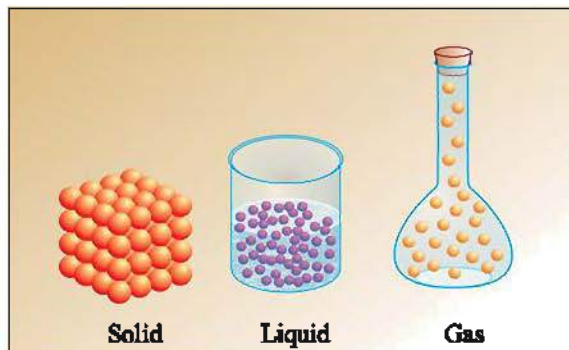
Based on their physical state and chemical characteristics matter is classified as under :



#### 1.3.1 Classification based on physical states :

Natural and man-made, everything around us is made up of matter i.e., pens, clocks, spectacles, air, water, animals are made of matter. They have mass and they occupy space (volume). Matter can exist in three physical states : (1) solid (2) liquid and (3) gas.

These three states can be represented as shown in fig. 1.1.



Arrangement of particles in solid, liquid and gaseous state

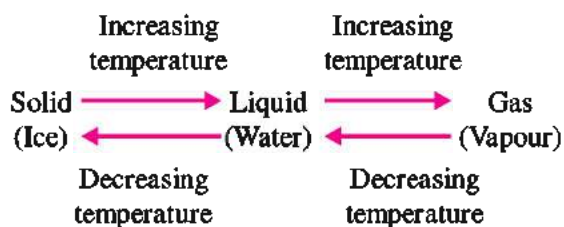
Figure 1.1

**(1) Solid State :** Solids have definite volume and definite shape. In solid, the particles are held very close to each other and the intermolecular attractive forces in their component particles keep them together tightly. They retain their specific shape. e.g. ice, iron etc.

**(2) Liquid State :** Liquids have definite volume but no definite shape. They take shape of the container in which they are poured. In liquid state distances between component particles is more than that in a solid. In liquid state the intermolecular attractive forces between component particles is sufficient enough to keep them together but not enough to keep their places fixed. So liquids are fluids. e.g. water, bromine, benzene etc.

**(3) Gaseous State :** Gases have neither definite volume nor definite shape. They completely occupy the whole space of the container in which they are filled and spread into the entire container. e.g. air, argon etc.

These three states of matter are interconvertible by changing the conditions of temperature and pressure, i.e. they change their state.



### 1.3.2 Classification based on chemical structure :

The matter is classified into three categories, element, compound and mixture, on the basis of their chemical structure.

**(1) Element :** Lavoisier (1743-94) gave the explanation for element. According to him, element consists of only one type of atoms. In different elements, atoms are different. The atoms of one element are different from atoms of the other element. Thus, every element has its own independent property which is not the same in other elements, e.g carbon, sodium, oxygen etc.

**(2) Compound :** When two or more elements combine chemically with one another, a compound is formed. When the compounds are formed, the elements present in them show new type of properties by losing their own individual properties. For example, hydrogen (H) and oxygen (O) are gases, water (H<sub>2</sub>O) formed by their combination is a liquid. Here, hydrogen burns explosively in air and oxygen is a supporter of combustion; but water is used as a fire extinguisher. Thus, hydrogen and oxygen change their properties in water.

**(3) Mixture :** A mixture is a material consisting of two or more kinds of matter, each retaining its own characteristic properties. Mixture can be separated by physical methods. Mixture can be classified in two different categories :

(i) Homogeneous mixture (ii) Heterogeneous mixture

**(i) Homogeneous mixture :** In the homogeneous mixture the components are in same physical state. Solution is a homogeneous mixture. In a homogeneous mixture, composition is uniform throughout and does not separate from definite borderline, e.g. mixture of sugar and water (sugar solution), salt and water (salt solution), oxygen and nitrogen (air), zinc and copper (alloy brass). The components of sugar solution can be separated by evaporation. Oxygen and nitrogen gases are obtained by liquification of the air-mixture.

**(ii) Heterogeneous mixture :** In the heterogeneous mixture the components are different in their physical state. In the heterogeneous mixture the components do not mix with each other. But can be separated by definite boundary of two different physical states. In heterogeneous mixture the composition is not uniform throughout, e.g sodium chloride (NaCl) mixed with iron (Fe) makes heterogeneous mixture. Here, both are in similar solid state but as different entities in mixture and separate from borderline surface.

The component of both the types of mixture can be separated by using physical methods such as filtration, crystallization, distillation etc. For example, to separate the mixture of salt (NaCl) and iron, it is dissolved in water and filtered iron remains as solid on filter paper and solution of NaCl is obtained. The component salt (NaCl) can be separated by using evaporation and iron by filtration.

### 1.4 Physical Quantities

The value of physical quantity is always equal to a definite numeric value and a definite unit. It is necessary to describe the physical quantity with the least possible units. For example, mass of a substance is 5.0 kg. Here, just writing 5.0 carries no meaning, but adding the term kg after 5.0 indicates its mass. In order to express measured or calculated quantity, it is essential to have a suitable system of units. Thus, for the system of units some least number of these quantities are selected in such a way that other quantities can be derived from them. The least value of quantities of units selected are known as fundamental units or basic units. Other units of measurements which can be derived from the fundamental units are known as derived units. For example, mass of piece of iron is 5.0 kg. Here kg is a basic unit of mass. By using this fundamental unit, derived units like density, volume etc. can be obtained.

There are various systems of units for physical measurement which were developed at different times. Some of them are as follows :



- (i) FPS system (Foot, Pound, Second) in the year 1588.
- (ii) CGS system (Centimeter, Gram, Second) in the year (1791-1795).
- (iii) MKS system (Meter, Kilogram, Second) in the year (1791-1795). India accepted (ii) and (iii) in 1956.
- (iv) SI (Le System, International d' Units) in the year 1971.

To solve the difficulties created by a number of methods, IUPAC (International Union of Pure and Applied Chemistry) and IUPAP (International Union of Pure and Applied Physics) have recommended SI method to be used uniformly.

The scientific world requires a method for international dealings. This method should be uniform, reliable, standardised and universally acceptable and should have uniform units.

The International System of units was defined, in 1960 during the 11<sup>th</sup> General Conference of International Bureau of Weights and Measures which was held at Sevres near Paris. The organization created a diplomatic treaty for uniformity in units. International system of units was accepted in 1971. In French, it is called 'Le Systeme International d' Units'. In short, it is called SI system also. In this system seven basic (fundamental) units are defined. These are as under :

**Table 1.1 SI units (Basic units)**

Physical quantity	Symbol for quantity	Symbol of SI units	Name of SI units
Length	<i>l</i>	m	meter
Mass	m	kg	kilogram
Time	t	s	second
Electric current	I	A	ampere
Thermodynamic temperature	T	K	Kelvin
Amount of substance	n	mole	mole
Luminous intensity	<i>I<sub>v</sub></i>	cd	candela

**Table 1.2 Prefixes used in the SI system**

Multiple	Prefix	Symbol
$10^{-15}$	femto	f
$10^{-12}$	pico	p
$10^{-9}$	nano	n
$10^{-6}$	micro	$\mu$
$10^{-3}$	milli	m

$10^{-2}$	centi	c
$10^{-1}$	deci	d
10	deca	da
$10^2$	hecta	h
$10^3$	kilo	k
$10^6$	mega	M
$10^9$	giga	G
$10^{12}$	tera	T
$10^{15}$	peta	p

Definitions of some of the SI units and derived units are mentioned below :

**(1) Mass** : Amount of matter present in a substance is called Mass. Its SI unit is kilogram.

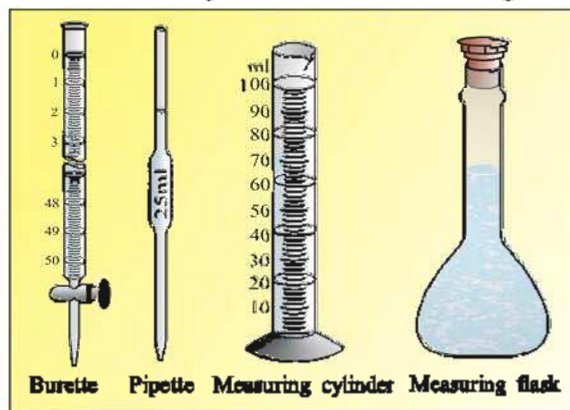
**Kilogram** : The mass of cylinder prepared from platinum-iridium (Pt-Ir) alloy kept in International Bureau of Weight and Measures is called 1 kilogram.

The mass of a substance can be determined in the laboratory by using an analytical balance. However, its fractions—gram, milligram, microgram are used in laboratories due to the smaller amounts of chemicals used in chemical reactions.

**(2) Volume (Derived unit)** : Derived unit of volume by using SI units is (meter)<sup>3</sup>.

$$\begin{aligned}\text{volume} &= \text{length} \times \text{breadth} \times \text{height} \\ &= \text{meter} \times \text{meter} \times \text{meter} \\ &= (\text{meter})^3\end{aligned}$$

In chemistry laboratories, smaller volumes are often denoted in cm<sup>3</sup> or dm<sup>3</sup> units. A common unit liter (L), which is not an SI unit, is used for measurement of volume of liquids. When smaller volume is used, the unit is milliliter (mL). In laboratory, volume of liquids can be measured by cylinder, burette, pipette and volumetric flask. These measuring devices are shown in fig. 1.2.



**Figure 1.2**



$$\begin{aligned}
 1 \text{ Liter (L)} &= 1000 \text{ Milliliter (mL)} \\
 &= 1000 \text{ cm}^3 \\
 &= 1 \text{ (decimeter)}^3 \text{ OR } \text{dm}^3 \\
 &(\because 10 \text{ cm} = 1\text{dm})
 \end{aligned}$$

**(3) Density : (Derived unit) :** Density of a substance is the amount of mass per unit volume. Derived unit of density by using SI units is as under :

$$\begin{aligned}
 \text{Density} &= \frac{\text{mass}}{\text{volume}} = \frac{\text{SI unit of mass}}{\text{SI unit of volume}} \\
 &= \frac{\text{kg}}{\text{m}^3} \\
 &= \text{kg m}^{-3}
 \end{aligned}$$

Smaller unit of density is  $\text{g/cm}^3$  OR  $\text{g cm}^{-3}$  where mass is expressed in gram and volume in  $\text{cm}^3$ .

**(4) Temperature (Basic unit) :** Measurement of temperature is done in the two units-degree Celsius ( $^{\circ}\text{C}$ ) and degree Fahrenheit ( $^{\circ}\text{F}$ ). SI unit of temperature is Kelvin (K). Both the scales can be related to each other by following relationship :

$$^{\circ}\text{F} = \frac{9}{5}(^{\circ}\text{C}) + 32$$

$$\text{K} = ^{\circ}\text{C} + 273.15$$

but normally expressed as

$$\text{K} = ^{\circ}\text{C} + 273$$

$$0^{\circ}\text{C} = 32^{\circ}\text{F} = 273 \text{ K}$$

It should be noted that temperatures below  $0^{\circ}\text{C}$  are possible in Celsius scale but in Kelvin scale negative temperature is not possible.

**(5) Length : (Basic unit) :** SI unit of length is meter. The meter was redefined in 1983 by CGPM (Conference Generale des Poids at Measures).

**Meter :** The distance travelled by light in vacuum in time interval of  $1/299,792,458$  second is called 1 meter.

The meter was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature  $0^{\circ}\text{C}$  as a standard reference.

Dear students, question arises in your mind that why Pt-Ir is chosen ? Because it is highly resistant to chemical attack and its mass or length does not change for a long time.

## 1.5 Laws of Chemical Combination

When two or more substances react chemically a compound is formed.

The following are the laws which govern the formation of chemical compounds :

**1.5.1 Law of Conservation of Mass :** "Matter can neither be created nor destroyed." This law was put forth by Antoine Lavoisier in 1789. He performed carefully experimental studies for combustion reactions for reaching to the above conclusion. This law formed the basis for several later developments in chemistry. In fact this was the result of planned experiments performed by Lavoisier.

**1.5.2 Dalton's Atomic theory :** We know that Dalton's atomic theory can explain the laws of chemical combination. As a result of several experimental studies, John Dalton (1776-1884) was led to a law "Matter is made up of small indivisible particles." These smallest indivisible particles are called atoms. Dalton's atomic theory is helpful to know chemical reaction but during his time the fundamental particles of atom like proton, electron, neutron were not discovered.

In 1808, Dalton published *A New System of Chemical Philosophy* in which he proposed law of chemical combination which provides explanation for existence of atom. Dalton's assumptions are as follows:

- (1) All elements are made up of smallest particles called atoms. Atom is indivisible.
- (2) All the atoms of a given element are identical but are different from those of other elements.
- (3) All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
- (4) Compounds are formed when atoms of different elements combine in a fixed ratio. Atoms present in a compound have a definite composition.
- (5) All the atoms of a given element are identical in mass.
- (6) Compounds are formed by the combination of atoms of two or more elements in the ratio of small whole numbers. The smallest particles formed by chemical combination of two or more atoms are called molecules.
- (7) Chemical reactions involve rearrangement of atoms. These are neither created nor destroyed during chemical reaction.

There is no importance of Dalton's law with reference to nuclear reactions and discovery of isotopes because Dalton's view that atom is indivisible was found wrong. Atom is composed of fundamental particles like proton, electron and neutron.

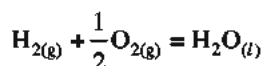
**1.5.3 Law of Constant Proportion :** "A given compound always contains exactly the same proportion of elements by weight".

Joseph Proust (1754-1826) observed that samples of cupric carbonate obtained naturally and prepared synthetically in the laboratory had the same percentage composition of elements.

Cupric carbonate $\text{CuCO}_3$	% of Cu	% of C	% of O
Natural sample	51.35	9.74	38.91
Synthetic sample	51.35	9.74	38.91

Water ( $\text{H}_2\text{O}$ ) produced during the reaction of hydrogen gas with oxygen gas and water obtained by decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has same composition. A given compound of water always contains same proportion. Water ( $\text{H}_2\text{O}$ ) always contains 2.016 g of hydrogen and 16.0 g of oxygen.

The understanding of law of constant proportion is provided by the Dalton's atomic theory. According to this theory, molecules are made up of atoms and the elements for a given compound are same in each of their samples. As the mass of each atom of a given element is same, the mass of its each molecule will always be the same. i.e



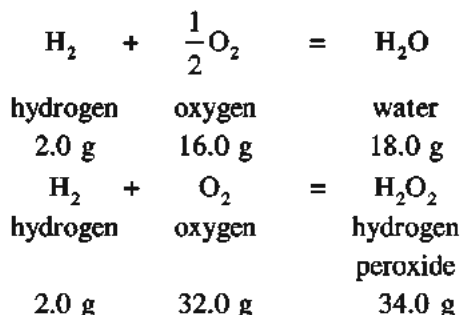
Here simple ratio of volumes of elements H:O in water is 2:1 and ratio 1:8 of the masses for H, (2 g) and O (16 g) which gives fixed mass of  $\text{H}_2\text{O}$  (18 g)

**1.5.4 Law of Multiple Proportion :**

This law was proposed by Dalton in 1803. If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole number.

For example, hydrogen combines with oxygen to form two compounds, water and hydrogen peroxide. The masses of oxygen 16.0 g

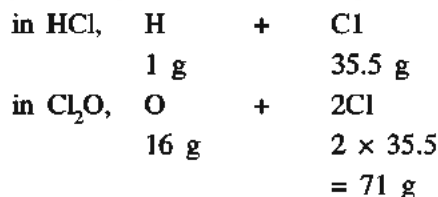
and 32.0g combine with fixed mass of hydrogen 2.0 g in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  respectively.



Here, hydrogen and oxygen combine to form two different compounds. The amount of oxygen that combines with 2.0g of hydrogen in two compounds can be expressed as per the law of multiple proportions as 16:32 bearing simple ratio 1:2.

**1.5.5 Law of Combining Weights :**

According to this law, masses of two elements which separately react chemically with identical masses of a third element are also the masses which react with each other and are in simple multiples of combining weight of an element which is either equal to its atomic weight or simple multiple of it. For example,



Thus, combined masses of Cl (35.5g) in  $\text{Cl}_2\text{O}$  react with 8.0 gram of oxygen. According to the law of combining weights, 35.5 gram of chlorine reacts with 1.008 g and 8.0 g of hydrogen and oxygen respectively in both the compounds. Hydrogen and oxygen combine with each other to form water ( $\text{H}_2\text{O}$ ) where the mass ratio is 2:16 = 1:8.

**1.6 Atomic Mass, Molecular Mass, Molar Mass and Mole Concept**

**(1) Atomic mass :** Dalton proposed "Atoms of every element have their own definite characteristic mass." It is called atomic mass.

Every element has its own characteristic atomic mass. It is very difficult to measure the mass of an extremely small atom. With the help of a modern instrument like mass spectrometer the definite value of atomic mass of an atom can be measured.

However, the present system of atomic masses is based on carbon-12 as the standard and

has been agreed upon in 1961 by IUPAC and IUPAP. Here C-12 is one of the isotopes of carbon and can be represented as  $^{12}\text{C}$ . In this system  $^{12}\text{C}$  is assigned a mass of exactly 12 atomic mass unit (amu) and masses of all other atoms are given relatively to this standard. Mass of an atom of hydrogen is defined as a mass equal to one twelfth of the mass of one  $^{12}\text{C}$  atom.

Nowadays amu is expressed as 'u' as a unit for unified mass.

$$1 \text{ amu} = 1.66056 \times 10^{-24} \text{ g}$$

$$\text{Mass of one hydrogen atom} = 1.6736 \times 10^{-24} \text{ g}$$

$$\begin{aligned} \text{Atomic mass of hydrogen} &= \frac{1.6736 \times 10^{-24} \text{ g}}{1.66056 \times 10^{-24} \text{ g}} \\ &= 1.0078 \text{ amu} \\ &\approx 1.008 \text{ amu} \\ &\approx 1.008 \text{ u} \end{aligned}$$

$$\begin{aligned} \text{Similarly the mass of oxygen} &= 15.995 \text{ amu} \\ &= 15.995 \text{ u} \\ &\approx 16.00 \text{ amu} \approx 16.00 \text{ u} \end{aligned}$$

**(2) Molecular Mass :** Molecular mass can be calculated from the atomic masses of all atoms present in a compound. If we know the molecular formula of any compound, the molecular mass can be found by considering total number of atoms present and adding together their total atomic masses. e.g.,

- (i) Calculate molecular mass of water ( $\text{H}_2\text{O}$ ) molecule

$$\begin{aligned} \text{Molecular mass of } \text{H}_2\text{O} &= 2 (\text{Atomic mass of H}) + 1 (\text{Atomic mass of O}) \\ &= 2(1.008 \text{ u}) + 1 (16.0 \text{ u}) \\ &= 18.016 \text{ u} \end{aligned}$$

- (ii) Calculate molecular mass of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) molecule.

$$\begin{aligned} \text{Molecular mass of } \text{C}_{12}\text{H}_{22}\text{O}_{11} &= 12 (\text{Atomic mass of C}) + 22 (\text{Atomic mass of H}) + 11 (\text{Atomic mass of O}) \\ &= 12 (12 \text{ u}) + 22 (1 \text{ u}) + 11 (16 \text{ u}) \\ &= 144 \text{ u} + 22 \text{ u} + 176 \text{ u} \\ &= 342 \text{ u} \end{aligned}$$

### (3) Molar Mass and Mole Concept :

In SI system, mole is introduced as one of the seven basic quantities for the amount of the

substance. The number of atoms or molecules even in a small amount of any substance is very large. Repeated use of such large numbers would be tedious and leads to inevitable errors in result. Thus, a definite quantity of mass unit of similar magnitude is required in practice. Units like one dozen for 12 items, score for 20 items, gross for 144 items as we use in our daily life, compounds used in laboratory for experiments are mentioned in unit of gram. In this unit there are innumerable atoms. In order to relate the masses of different compounds, scientists have given a unit called 'Mole'. Number of composite particles in 1 mole of molecule, atom or ion =  $6.022 \times 10^{23}$ .

Number of atoms  $6.022 \times 10^{23}$  present in 12 gram of isotope  $^{12}\text{C}$  as a standard, is accepted as Mole. This figure is called Avogadro's number ( $N_A$ ). The mass of a  $^{12}\text{C}$  is found to be equal to  $1.992648 \times 10^{-23}$  gram by spectrometer. To really appreciate largeness of the number let us write it with all the zeros without using any powers of ten. 602213670000000000000000.

Hence, so many entities constitute one mole of a particular substance.

We can, therefore, say that

$$1 \text{ mole of hydrogen atoms} = 6.022 \times 10^{23} \text{ atoms of hydrogen}$$

$$1 \text{ mole of water molecules} = 6.022 \times 10^{23} \text{ molecules of water.}$$

$$1 \text{ mole of sodium chloride} = 6.022 \times 10^{23} \text{ molecules of sodium chloride}$$

Knowing that one mole of carbon weighs 12 gram, the number of atoms in it will be as under :

$$\begin{aligned} \text{Number of atoms of carbon C} &= \frac{\text{mass of 1 mole C}}{\text{mass of 1 atom C}} \\ &= \frac{12 \text{ gram mol}^{-1}}{1.992648 \times 10^{-23} \text{ gram atom}^{-1}} \\ &= 6.022 \times 10^{23} \text{ atom mol}^{-1} \end{aligned}$$

$$\text{Mole} = \frac{\text{Mass of atom or molecule in gram}}{\text{Atomic mass or molecular mass in gram mol}^{-1}}$$

Molar mass of an element or compound is the mass in gram of one mole ( $6.022 \times 10^{23}$  particles) of atoms or molecules contained in it.

**Example 1.1 :** How many moles of 'C' atoms will be there in 100 gram carbon dioxide ( $\text{CO}_2$ ) ? Calculate the number of carbon atoms. (molecular mass of  $\text{CO}_2$  =  $44 \text{ gram-mol}^{-1}$ )

**Solution :**

$$\begin{aligned}\text{Moles of CO}_2 &= \frac{\text{Weight of CO}_2}{\text{Molecular mass of CO}_2} \\ &= \frac{100 \text{ gram}}{44 \text{ gram mole}^{-1}} \\ &= 2.27 \text{ mole}\end{aligned}$$

1 mole molecules of CO<sub>2</sub> contains 1 mole atoms of C

∴ Mole of C atoms = 2.27 mole

The number of carbon atoms

$$\begin{aligned}&= \text{mole of carbon} \times \text{Avogadro number} \\ &= 2.27 \times 6.022 \times 10^{23} \\ &= 13.669 \times 10^{23}\end{aligned}$$

### 1.7 Percentage Composition of Element and Molecular Formula

#### 1.7.1 Percentage Composition of Element :

When compound is formed from two or more elements, the amount of element present in a compound is always proportional to its definite mass. If molecular formula of compound is known, one can calculate the mass percentage of element present in that compound. In contrast to this, if one knows the mass percentage of all elements present in a compound, its molecular formula can be determined.

Mass % of an element

$$= \frac{\text{Mass of the element in the compound} \times 100}{\text{Molar mass of the compound.}}$$

**Example 1.2 :** Calculate the percentage of both elements present in water (H<sub>2</sub>O).

**Solution :**

Atomic mass of H = 1.0 gram mole<sup>-1</sup>

Atomic mass of O = 16.0 gram mole<sup>-1</sup>

Molecular mass of H<sub>2</sub>O = 18.0 gram mole<sup>-1</sup>

$$\begin{aligned}\text{mass \% of Hydrogen} &= \frac{2(1.0 \text{ g mol}^{-1}) \times 100}{18.0 \text{ g mol}^{-1}} \\ &= 11.11\%\end{aligned}$$

$$\begin{aligned}\text{mass \% of Oxygen} &= \frac{(16.0 \text{ g mol}^{-1}) \times 100}{18.0 \text{ g mol}^{-1}} \\ &= 88.89 \%\end{aligned}$$

**Example 1.3 :** Calculate the percentage of each element present in ethanol (C<sub>2</sub>H<sub>5</sub>OH).

**Solution :**

Atomic mass of C = 12.0 gram mole<sup>-1</sup>

Atomic mass of H = 1.0 gram mole<sup>-1</sup>

Atomic mass of O = 16.0 gram mole<sup>-1</sup>

Molecular mass of ethanol (C<sub>2</sub>H<sub>5</sub>OH)

$$\begin{aligned}&= 2(12) + 6(1) + 1(16) \\ &= 24 + 6 + 16 \\ &= 46 \text{ gram mole}^{-1}\end{aligned}$$

$$\text{Mass \% of H} = \frac{6(1.0) \times 100}{46} \approx 13.04\%$$

$$\text{Mass \% of C} = \frac{2(12) \times 100}{46} \approx 52.17\%$$

$$\text{Mass \% of O} = \frac{16 \times 100}{46} \approx 34.78\%$$

#### 1.7.2 Empirical Formula and Molecular

**Formula :** In order to decide the molecular formula of any compound, it is necessary to know the percentage composition of elements in it. From this information simple formula of a compound can be decided. This simple formula indicates the relative proportion of atoms of element. It is a formula showing the relative proportion of component atoms in a compound. Thus, formula which represents the composition of a molecule is an empirical formula. Empirical formula of a compound can be calculated in the following sequence :

- (i) Indicate the symbol of elements present in a compound.
- (ii) Calculate percentage of elements present.
- (iii) Calculate the ratio of percentage of elements and atomic masses of elements which can give ratio of atoms present in element.
- (iv) The ratio of each element is to be divided by the ratio of element having lowest simple integral ratio will be obtained.
- (v) Calculate formula mass of empirical formula.
- (vii) Calculate multiple number (n) from information of empirical formula mass and molecular mass.

$$n = \frac{\text{Molecular mass}}{\text{Formula mass of empirical formula.}}$$

- (viii) The empirical formula is multiplied with 'n' and molecular formula is obtained.  
Molecular formula = n × Empirical formula  
where n = Integral number

**Example 1.4 :** The percentages of carbon, hydrogen and oxygen in an organic substance are 54.55, 9.06, and 36.39 respectively. Find the empirical formula and molecular formula. (Molecular mass of organic substance = 88 gram mole<sup>-1</sup>)



Elements	Atomic mass	Percentage	Atomic ratio	Ratio of simple whole number	Simple(whole) number
C	12	54.55	$\frac{54.55}{12} = 4.55$	$\frac{4.55}{2.27} = 2.0$	2
H	1	9.06	$\frac{9.06}{1} = 9.06$	$\frac{9.06}{2.27} = 3.99$	4
O	16	36.39	$\frac{36.39}{16} = 2.27$	$\frac{2.27}{2.27} = 1.0$	1

∴ Empirical formula =  $C_2H_4O$

∴ The empirical formula mass of organic substance =  $24 + 4 + 16$   
= 44 gram formula weight<sup>-1</sup>

$$\text{Integral number (n)} = \frac{\text{Molecular mass}}{\text{Formula mass}}$$

$$\therefore n = \frac{88}{44} = 2$$

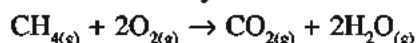
$$n = 2$$

$$\begin{aligned}\text{Molecular formula} &= 2 \times \text{empirical formula} \\ &= 2 \times C_2H_4O \\ &= C_4H_8O_2\end{aligned}$$

### 1.8 Stoichiometry of Chemical Reactions and Calculations

Proper distributions of the element in equation means stoichiometry. Stoichiometry, thus deals with the calculation of masses of the reactants and the products involved in a chemical reaction.

A chemical reaction can be expressed in the form of chemical equation from which we obtain a large amount of qualitative and quantitative information. Quantitative information is available from balanced chemical equation available from stoichiometry of given reaction. A balanced equation for combustion of methane is given below. Let us consider what information is available from stoichiometry.



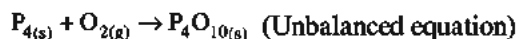
	CH <sub>4</sub>	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
Mole	1 mole	2 moles	1 mole	2 moles
Mole-cules	1 molecule	2 molecules	1 molecule	2 molecules
Volume*	22.4 L	2 × 22.4 = 44.8 L	22.4 L	2 × 22.4 = 44.8 L
Mass	16.00 g	2 × 32 = 64 g	44.0 g	2 × 18 = 36 g
Number of mole-cules	6.022 × 10 <sup>23</sup>	2 × 6.022 × 10 <sup>23</sup>	6.022 × 10 <sup>23</sup>	2 × 6.022 × 10 <sup>23</sup>

\* At STP

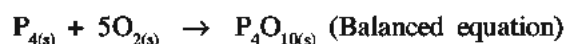
The stoichiometry of the reactants in the above reaction is 1:2 and the stoichiometry of the product is also 1:2. Thus, for a general reaction  $aA + bB \rightarrow cC + dD$  is the stoichiometries of reactants and products are a:b and c:d respectively.

#### 1.8.1 Balancing of a Chemical reaction

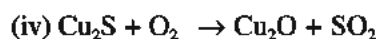
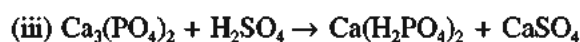
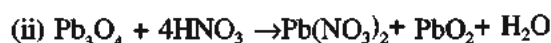
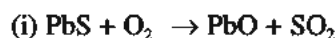
**equation :** According to the law of conservation of mass, a balanced chemical reaction equation has the same number of atoms of each element on both the sides of the equation. If chemical equation is unbalanced, try to balance it by trial and error method with the use of proper multiple number. The method to balance the equation by same number of atoms of each element on both sides is known as method of balancing equation. You have studied in standard 9 the balancing of chemical reaction equation. For example,



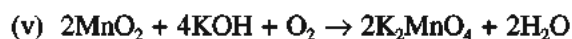
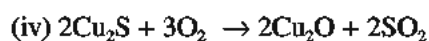
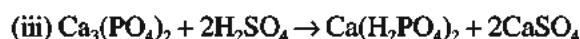
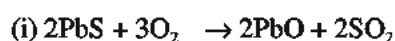
In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance them we must place the multiple 5 on the left of oxygen.



The reactions given below are not balanced :



After balancing the above reactions they are written as



### 1.9 Stoichiometry of Reaction in Solution

A majority of reactions are carried out in solution in the laboratories. Therefore, it is important to understand as how the amount of substance is expressed when it is present in the form of solution. The amount of substance present in its given volume can be expressed in units like normality, molarity, molality, mole fraction, w/w percentage. Let us now discuss and study each one of them in detail.

**(i) Normality (N) :** One litre of solution prepared by dissolving one gram equivalent of a substance is called 1 normal (N) solution or the normality of the solution is 1

$$\begin{aligned}\text{Normality} &= \frac{\text{gram litre}^{-1}}{\text{equivalent weight}} \\ &= \frac{\text{weight of solute in gram}}{\text{equivalent weight} \times \text{volume of solution in litre.}}\end{aligned}$$

$$\begin{aligned}\text{Equivalent weight of acid} &= \frac{\text{Molecular weight of acid (gmol}^{-1}\text{)}}{\text{Basicity of acid}}\end{aligned}$$

$$\begin{aligned}\text{Equivalent weight of base} &= \frac{\text{Molecular weight of base (gmol}^{-1}\text{)}}{\text{Acidity of base}}\end{aligned}$$

**Example 1.5 :** Find the normality of an aqueous solution in which 73 gram hydrochloric acid is dissolved in 500 ml solution.

**Solution :**

Molar mass of HCl = 36.5 gram mole<sup>-1</sup>.

Molar mass and equivalent weight of HCl are equal.

Equivalent weight of HCl = 36.5 gram equi<sup>-1</sup>

Volume of solution 500 ml = 0.5 litre.

Weight of solute HCl in solution = 73 gram

$$\begin{aligned}\text{Normality} &= \frac{\text{weight of solute in gram}}{\text{equivalent weight} \times \text{volume of solution in litre}} \\ &= \frac{73}{36.5 \times 0.5} = 4\text{N}\end{aligned}$$

**(ii) Molarity (M) :** One litre of solution containing one gram mole of a substance is called 1 molar (M) solution or the molarity of solution is 1. It is the most widely used unit.

$$\begin{aligned}\text{Molarity} &= \frac{\text{gram litre}^{-1}}{\text{molecular mass}} \\ &= \frac{\text{weight of solute in gram}}{\text{molecular mass} \times \text{volume of solution in litre}}\end{aligned}$$

Note that normalities and molarities are dependent on temperature because of the change in the volume of solution with temperature.

**Example 1.6 :** Find the molarity of an aqueous solution in which 4 gram NaOH is dissolved in 5 litre aqueous solution.

**Solution :**

Molar mass of NaOH = 40 gram mole<sup>-1</sup>

Volume of solution = 5 liter

Weight of solute NaOH = 4 gram

$$\begin{aligned}\text{Molarity} &= \frac{\text{weight of solute in gram}}{\text{molecular mass} \times \text{volume of solution in litre}} \\ &= \frac{4}{40 \times 5} \\ &= 0.02 \text{ M}\end{aligned}$$

**(iii) Molality (m) :** One gram mole of a solute, when dissolved in 1 kilogram of the solvent, the molality (m) of the solution obtained is 1 molal (m) or it is 1 m solution.

$$\text{Molality} = \frac{\text{weight of solute in gram}}{\text{molecular mass} \times \text{weight of solvent in kilogram}}$$

Note that with the change in temperature the molality does not change because the weight is not affected by temperature.

**Example 1.7 :** Find the molality of the solution when 149 gram of KOH is dissolved in 1.5 kilogram of solvent.

**Solution :**

Molecular mass of KOH = 56 gram mole<sup>-1</sup>

Weight of solute KOH = 149 gram

Mass of solvent = 1.5 kilogram

$$\begin{aligned}\text{Molality} &= \frac{\text{weight of solute in gram}}{\text{molecular mass} \times \text{weight of solvent in kilogram}} \\ &= \frac{149}{56 \times 1.5} \\ &= 1.77 \text{ m}\end{aligned}$$

**(iv) Mole Fraction :** The ratio of the moles of any component to the total moles in a solution is the mole fraction.

Mole fraction of component

$$= \frac{\text{moles of component}}{\text{number of total moles of components in a solution}}$$

The sum of the mole fraction of all the components in a solution is always equal to 1.

**Example 1.8 :** Calculate the mole fraction of NaOH and water in a solution formed by dissolving 4 gram of NaOH in 180 gram of water

**Solution :**

$$\text{Molar mass of NaOH} = 40 \text{ gram mole}^{-1}$$

$$\begin{aligned} \text{Moles of (solute) NaOH} &= \frac{\text{weight}}{\text{molar mass}} \\ &= \frac{4}{40} = 0.1 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Moles of H}_2\text{O (solvent)} &= \frac{\text{weight}}{\text{molar mass}} \\ &= \frac{180}{18} = 10 \text{ mole} \end{aligned}$$

$$\text{Total moles} = 0.1 \text{ mole} + 10 \text{ mole} = 10.1 \text{ mole}$$

Mole fraction of NaOH

$$\begin{aligned} &= \frac{\text{moles of NaOH}}{\text{total moles of solution}} \\ &= \frac{0.1}{10.1} \\ &= 0.0099 \text{ mole} \end{aligned}$$

Mole fraction of H<sub>2</sub>O

$$= \frac{\text{moles of H}_2\text{O}}{\text{total moles of solution}}$$

$$\begin{aligned} &= \frac{10 \text{ mole}}{10.1 \text{ mole}} \\ &= 0.9901 \text{ mole} \end{aligned}$$

∴ Sum of mole fractions =

$$\begin{aligned} &\text{mole fraction of NaOH} + \text{mole fraction of H}_2\text{O} \\ &= 0.0099 + 0.9901 \\ &= 1 \end{aligned}$$

∴ The sum of the mole fractions of all the components is 1

**(v) Percentage by weight : (% w/w)**

The weight of a substance in gram dissolved in 100 gram solution is called percentage by weight (% w/w). Such a solution is called percentage proportion with reference to the weight of solute.

$$\% \text{ w/w} = \frac{\text{weight of solute} \times 100}{\text{weight of solution in gram}}$$

(weight of solution = weight of solute + weight of solvent)

With the change in temperature, the values of molality, mole fraction, percentage w/w do not change.

**Example 1.9 :** How many grams of NaOH will be required to prepare 500 gram solution containing 5% w/w NaOH ?

**Solution :**

$$\% \text{ w/w} = \frac{\text{weight of solute} \times 100}{\text{weight of solution}}$$

$$5\% = \frac{\text{weight of solute} \times 100}{500}$$

$$\begin{aligned} \text{weight of solute} &= \frac{5 \times 500}{100} \\ &= 25 \text{ gram} \end{aligned}$$

## SUMMARY

The study of chemistry is very important because its domain has encompassed to cover every field of life. Chemists have studied the composition and properties of substances and transformations they undergo. The arrangement of constituents in three states of matter is different which indicates its properties. Matter can be classified into element, mixture and compound. If the element is formed, only of one type of constituent,

it can be atom or molecule. When atoms of two or more elements combine with each other in definite proportion, compound is formed. Mixture is formed in different ways.

When the study of properties of a substance is carried out the measurement becomes equally important. At the same time universally accepted unit method is essential. Hence, it is agreed upon that there must be a universally same and general method of measurement. It is known in brief as SI unit.

Atomic analysis is useful in expressing the units of physical quantities in different ways.

The combination of different atoms can be determined from the fundamental laws of chemistry. These laws are law of mass conservation, law of definite proportion, law of multiple proportion; law of combining weights etc. All these laws lead to atomic theory of Dalton.

The atomic weight of an element is related to  $^{12}\text{C}$ . The atomic weight of carbon-12 is 12u. The atomic weights of remaining elements are determined by IUPAC and IUPAP considering this as standard. The molecular mass of a molecule is obtained by calculation and adding atomic masses of all atoms. The molecular formula of a compound, the masses of the different elements present in molecular mass is determined by determination of percentage of elements present and determining empirical formula.

The number of atoms, molecules or any component in any system is expressed with reference to Avogadro constant  $6.0 \times 10^{23}$ . This is known as 1 mole. The quantitative study of reactants and products is called stoichiometry.

Chemical reactions show the chemical changes in different elements and compounds. A balanced chemical reaction equation provides many more informations.

Apart from this, the different methods to express the proportion of the substance in a solution are mole fraction, weight percentage, normality, molarity and molality.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) Which form of classification is not correct for matter on the basis of chemical characteristics ?  
(A) Mixture (B) Gas  
(C) Volume (D) Solid
- (2) Which of the following units is a derived unit ?  
(A) Density (B) A and C  
(C) Volume (D) Time
- (3) What is the SI unit of mass of the matter ?  
(A) kilogram (B) gram  
(C) milligram (D) mole
- (4) Of which alloy the cylinder standardising kilogram value of mass is made of ?  
(A) Pt - Au (B) Pt - Ag  
(C) Pt - Ir (D) Pt - Sn
- (5) What is called the mass of the matter in unit volume ?  
(A) Density (B) Volume  
(C) Weight (D) Pressure



- (6) What degree Fahrenheit will be equivalent to  $25^{\circ}\text{C}$  ?  
(A) 298 F (B) 77 F  
(C) 32 F (D) 248 F
- (7) With which reference there is no importance of Dalton's law ?  
(A) Isotope (B) Isobar  
(C) Isoosmotic (D) Isothermic
- (8) What is the value of one atom of  $^{12}\text{C}$  obtained by mass spectrometer ?  
(A) 12 gram (B)  $1.992648 \times 10^{-23}$  gram  
(C)  $1/12$  gram (D)  $6.022 \times 10^{23}$  gram
- (9) The value of sum of the mole fractions of all the components in a solution will be.....  
(A)  $>1$  (B)  $<1$   
(C)  $=1$  (D)  $=0$
- (10) Which of the following changes with temperature ?  
(A) Molality (B) Molarity  
(C) % w/w (D) Mole fraction
- (11) Molarity means ..... dissolved in one litre solution  
(A) One mole (B) One equivalent  
(C) One gram (D) 1000 gram
- (12) How many decimeter<sup>3</sup> will be equal to 1000 ml ?  
(A) 1 (B) 10  
(C) 100 (D) 0.10
- (13) Which of the following principle or law is not associated with chemical combination ?  
(A) Law of constant proportion (B) Law of combining weight  
(C) Law of multiple proportion (D) Aufbau Principle
- (14) 1 amu is equal to how many grams ?  
(A)  $1.66056 \times 10^{-24}$  gram (B)  $6.022 \times 10^{23}$  gram  
(C)  $9.191 \times 10^{-28}$  gram (D)  $1.992648 \times 10^{-23}$  gram
- (15) Concentration of solution of 2N  $\text{H}_2\text{SO}_4$  is ..... M  
(A) 1 (B) 4  
(C) 0.5 (D) 2

**2. Write the answers of the following questions in short :**

- (1) Write the law of definite proportion.
- (2) Mention the four importances of chemistry.
- (3) Classify matter on the basis of chemical characteristics.
- (4) What is a compound and a mixture ?

- (5) What is heterogeneous mixture ?
- (6) Mention the formula of the relation between the two units of temperature.
- (7) Which are the laws of chemical combination ?
- (8) Find the number of atoms in 1 mole carbon.
- (9) Define : Normality, molarity, molality mole fraction.

**3. Write the answers of the following questions :**

- (1) Mention the differences between homogeneous mixture and heterogeneous mixture.
- (2) Explain in detail the derived units-volume, density and temperature.
- (3) Balance the equations of following reactions :
  - (i)  $\text{HgS} + \text{CaO} \xrightarrow{\Delta} \text{Hg} + \text{CaSO}_4 + \text{CaS}$
  - (ii)  $\text{Na}_2\text{CrO}_4 + \text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}^+ + \text{H}_2\text{O}$
  - (iii)  $\text{MnO}_2 + \text{KOH} + \text{O}_2 \rightarrow \text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
  - (iv)  $\text{Al}_2\text{O}_3 + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}[\text{Al}(\text{OH})_4]$
- (4) Find the percentage mass composition of each element present in  $\text{H}_2\text{C}_2\text{O}_4$ .
- (5) In how many grams of water 36.5 gram HCl should be dissolved so that 10 % w/w solution will be obtained ?
- (6) Find the molality of the solution obtained when 63 gram  $\text{HNO}_3$  is dissolved in 750 gram water.

**4. Write the answers of the following questions in detail :**

- (1) Explain the stoichiometry of chemical reaction by giving example.
  - (2) Write a note on the mole concept.
  - (3) Write a note on SI unit method and explain length and temperature.
  - (4) Mention the hypotheses of Dalton's atomic theory.
  - (5) The percentage proportion of carbon, hydrogen, nitrogen and oxygen in an organic compound are 62.07 %, 10.34 %, 14.0 %, 13.59 %, respectively. Find its empirical formula. If its molecular mass is  $144 \text{ gram mol}^{-1}$ , find its molecular formula.
  - (6) Explain in detail atomic mass and molecular mass by giving examples.
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## STRUCTURE OF ATOM

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- 2.1 Introduction
- 2.2 Fundamental Particles : Proton, Electron and Neutron
  - 2.2.1 Discovery of Electron
  - 2.2.2 Proton and Neutron
- 2.3 Atomic Number, Atomic Mass, Isotope, Isobar and Isotone
  - 2.3.1 Thomson's Model of an Atom and its limitations
  - 2.3.2  $\alpha$ -particle scattering experiment and Rutherford's model of an atom and its limitations
- 2.4 Nature of Electromagnetic Radiation
- 2.5 Emission Spectra of Hydrogen Atom
- 2.6 Bohr's Atomic Model and Its Limitations
- 2.7 Dual Nature of Matter and Radiation
- 2.8 De Broglie's Equation
- 2.9 Heisenberg's Uncertainty Principle
- 2.10 Explanation of Orbit and Orbital
- 2.11 Quantum Numbers.
- 2.12 Shapes of s, p and d-orbitals
- 2.13 Rules for the Electron Arrangement in Orbitals
- 2.14 Stability of Half-filled and Completely Filled Orbitals

### 2.1 Introduction

Different scientists have thought logically about the structure of atom and have given an accepted nuclear model which is known as 'Nuclear model'. This model is derived from the characteristics based on experimental results.

The existence of atom has been proposed since the time of early Indian and Greek philosophers who were of the view that atoms are the fundamental building blocks of matter. According to them atoms are formed due to continuous subdivision of matter into subconstituents which are indivisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncuttable' or indivisible. This ideology could not last long and was revived by scientists in the nineteenth century.

The atomic theory of atom was first proposed in 1808 by a British scientist John Dalton, which is known as Dalton's atomic theory. According to him atom is the ultimate particle of matter.

### 2.2 Fundamental Particles : Proton, Electron and Neutron

Dalton's atomic theory was able to explain the law of conservation of mass, law of constant proportion and law of multiple proportion successfully; but failed to explain some experimental results e.g. when glass is rubbed with silk or ebonite with fur it generates electricity. Thus Dalton's theory was only based on assumptions but it did not have any support of experimental results.

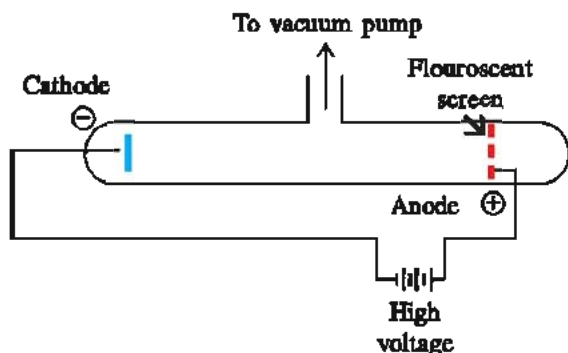
It is proved from modern research that atom is divisible and can be divided into two parts :

- (1) Central part of an atom
- (2) Region other than central part of an atom

**2.2.1 Discovery of Electron :** In 1830, Michael Faraday showed that when electric current is passed through a solution of an

electrolyte, chemical reactions occur at the electrodes which result in the liberation and deposition of matter at electrodes.

An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Michael Faraday studied electrical discharge in an evacuated tube



A cathode ray discharge tube with perforated anode.

Figure 2.1

as shown in figure 2.1. A cathode ray tube is made of glass containing two thin pieces of metal called electrodes, sealed in it. When sufficient electricity at high voltage is passed through sealed electrodes, current starts to flow through a stream of particles moving in the evacuated tube from the negative electrode (cathode) to the positive electrode (anode). They are known as cathode rays or cathode particles. These cathode rays can be examined by allowing them to strike on phosphorescent screen. The characteristic cathode rays (which were later on known as electrons) do not depend upon the material of electrodes or nature of gas in the cathode ray tube. Thus, electrons are fundamental constituents of structure of all atoms.

**2.2.2 Proton and Neutron :** The study of cosmic rays and nuclear reactions of atom proved that atom can be divided into subatomic particles like proton, electron and neutron. These three particles are known as fundamental particles of atom. In addition to these three main subatomic particles, some other subatomic particles like positron, photon, graviton, meson etc. are also present.

It was proved by Faraday's electrolysis experiment and cathode ray discharge tube that proton ( $p^+$ ) remains within the nucleus of an atom while electron ( $e^-$ ) in the outer region of atomic nucleus. The fundamental particles were discovered by different scientists. Proton ( $p^+$ )

was discovered in 1886 by Goldstein while electron ( $e^-$ ) was discovered by J.J Thomson in 1897. Neutron ( $n$ ) was discovered by Chadwick in 1932. Properties of these fundamental particles are given in table 2.1.

Name	Electron	Proton	Neutron
Symbol	$e$	$p$	$n$
Absolute charge	$-1.6022 \times 10^{-19} \text{C}$	$+1.6022 \times 10^{-19} \text{C}$	0
Relative Electric charge	-1	+1	0
Mass (kg)	$9.10939 \times 10^{-31}$	$1.67262 \times 10^{-27}$	$1.67493 \times 10^{-27}$
Mass (u)	0.00054	1.00727	1.00867
Approximate mass (u)	0	1	1

C = coulomb; u = a.m.u.

### 2.3 Atomic Number, Atomic Mass, Isotope, Isobar and Isotone

Atoms (except hydrogen) contain mainly three fundamental particles proton, electron and neutron. Since all elements and compounds have mass; atom also has mass. The total mass of an atom is concentrated in a nucleus which has very small volume (compared to the total volume of the atom). Electrons are arranged in the outer part of nucleus.

The positive charge of nucleus is due to protons (which are positively charged) because neutrons are electrically neutral. The charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus of an atom is called atomic number (Z) e.g. Number of protons in the nucleus of the very first element of periodic table hydrogen atom is one, and therefore, atomic number of hydrogen element is one.

As atom is electrically neutral, number of protons and number of electrons in an atom are always equal.

number of protons in the  
nucleus of atom

Atomic number (Z) = OR

number of electrons  
in a neutral atom.

Mass of nucleus is due to proton and neutron (as mass of the electron is negligible). Protons and neutrons which are present in the nucleus are collectively known as 'nucleons.' Thus mass



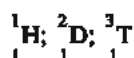
number or atomic mass number (A) of an element is equal to the number of nucleons.)

Mass number or Atomic mass = Number of protons (Z) + Number of neutrons (n)  
 e.g. Atomic mass of sodium is 23. Its atomic number is 11, therefore number of neutrons  
 $= 23 - 11 = 12$

Atomic mass and atomic number of any element (X) are indicated by accepted symbols. Accordingly, element is represented by X with superscript on left hand side as the atomic mass number (A) and subscript (Z) on left hand side as the atomic number.

${}_Z^AX$       A = Atomic mass number  
                     Z = Atomic number  
                     X = Symbol for element.

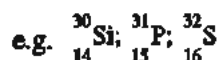
**Isotopes :** Isotopes are species with identical atomic number but different atomic masses. In other words, the difference in atomic mass or mass number in isotopes is due to different number of neutrons present in the nucleus. 99.985% hydrogen contains one proton. This isotope is known as protium  ${}_1^1\text{H}$ . Rest of the percentage of hydrogen atom contains two other isotopes; the one containing 1 proton and 1 neutron which is deuterium  ${}_1^2\text{H}$  or  ${}_1^2\text{D}$  (0.0156%) and the third containing 1 proton and 2 neutrons which is known as tritium  ${}_1^3\text{H}$  or  ${}_1^3\text{T}$  ( $10^{-15}\%$ ). Earth's crust contains very small amount of tritium. These three isotopes of hydrogen can be symbolically represented as



One of the important fact regarding the isotope is that the chemical properties of an atom depends on number of electrons and which are determined by number of protons in the nucleus. Hence, chemical properties of isotopes of a given element are identical.

**Isobars :** Isobars are the species having same mass number (atomic mass) but different atomic number e.g.  ${}_6^{14}\text{C}; {}_7^{14}\text{N}$

**Isotones :** Isotones are species having same number of neutrons but different numbers of atomic mass and atomic number



**Example 2.1 :** Calculate number of protons, electrons and neutrons in  ${}_{15}^{31}\text{P}$

**Solution :**

Atomic number Z = 15 in  ${}_{15}^{31}\text{P}$  and atomic mass A = 31. Number of protons = number of electrons in atom Z = 15

$\therefore$  Number of neutrons = Atomic mass - number of protons  
 $= 31 - 15$   
 $\therefore$  Number of neutrons = 16

**Example 2.2 :** The number of electrons, protons and neutrons in a given species are equal to 15, 10, and 8 respectively. Assign proper symbol to the species.

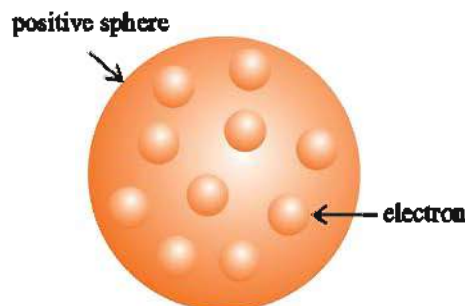
**Solution :**

Number of proton = 8 = Atomic number  
 Therefore the given species is oxygen element  
 Atomic mass = Number of proton + Number of neutrons  
 (mass number) =  $8 + 8 = 16$   
 Atomic mass = 16

The given species is not neutral because number of protons (8) and number of electrons (10) are not equal. Hence it becomes negative ion with two units of negative charge. As a result symbol of this species will be  ${}_{8}^{16}\text{O}^{2-}$ .

### 2.3.1 Thomson's Model of Atom and its limitations :

J.J. Thomson, in 1898, first proposed about the spherical shape (radius approximately  $10^{-10}\text{m}$ ) of an atom, in which the positive charge is uniformly distributed. Electrons are embedded in such a way that they give most stable electrostatic arrangement. Many different names are given to this model, for example, plum pudding, raisin pudding or watermelon.



Thomson's model of an atom  
 Figure 2.2

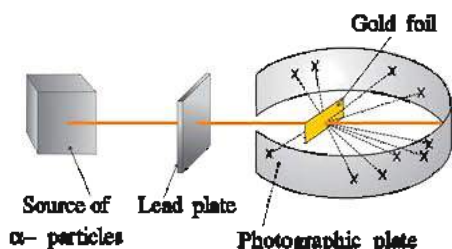
According to this model, positively charged proton and negatively charged electrons are symmetrically distributed over atom. In this model

number of protons and electrons arranged symmetrically are equal. One of the important features of this model is that the total mass of an atom is distributed equally. This model explains overall electrical neutrality of an atom but is not consistent with the experimental results. Thomson was awarded Nobel Prize in physics, in 1906, for theoretical and experimental research on electrical conduction of gases.

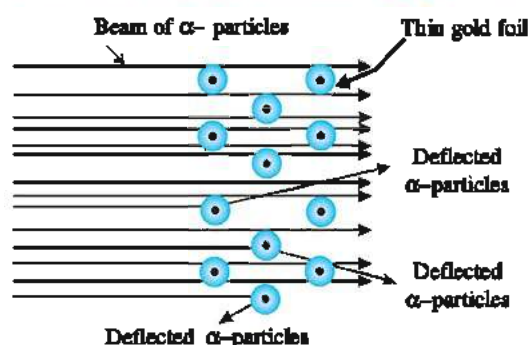
#### Limitations of Thomson's model of an atom :

According to Thomson's model of an atom, we have seen that protons, electrons and neutrons are equally arranged. But from the Rutherford's  $\alpha$ -particle scattering experiment it was noted that most of the space in an atom is empty because most of the  $\alpha$ -particles passed through metal foil without reflection. Thus, Thomson's model of an atom could not explain  $\alpha$ -particle scattering phenomenon.

**2.3.2  $\alpha$ -Particle scattering experiment and Rutherford's model of an atom and its limitations :** Rutherford's model of an atom is also known as nuclear model of an atom. Rutherford and his students Hans Geiger and Ernest Marsden bombarded  $\alpha$ -particle on thin gold foil. This well known  $\alpha$ -particle scattering experiment is shown below :



a. Rutherford's  $\alpha$ -particle scattering experiment



b. Schematic view of Rutherford's  $\alpha$ -particle scattering experiment  
Figure 2.3

High energy  $\alpha$ -particles from radioactive source were directed upon a thin foil (thickness

100 nm) of gold metal. A fluorescent zinc sulphide screen was kept around the thin gold foil. When  $\alpha$ -particles struck this screen they produced fluorescence effect. The result of this experiment was quite unexpected because according to Thomson's model of atom the mass of each gold atom in the foil should have been spread evenly over the entire atom and  $\alpha$ -particles should have sufficient energy to pass directly through such a uniform distribution of mass. According to Thomson, when  $\alpha$ -particles pass through a foil, they would slow down and change directions angularly. It was noted from Rutherford's experiment that.

- (i) Most of the  $\alpha$ -particles passed through the gold foil were undeflected.
- (ii) Very less  $\alpha$ -particles were deflected with angle.
- (iii) A few  $\alpha$ -particles (1 in 20,000) bounced back.

On the basis of the experimental observations, Rutherford drew the following conclusions for atomic model.

- (i) As majority of the  $\alpha$ -particles pass through the foil, most of the space in atom remains empty.
- (ii) A few positively charged  $\alpha$ -particles are deflected which is due to repulsion. The positive charge of atom is concentrated in a very small volume which is responsible for the deflection of positively charged  $\alpha$ -particles. It is known as nucleus of atom.
- (iii) The size of an atomic nucleus is negligible compared to the size of an atom. Atomic radius is about  $10^{-10}\text{m}$  while that of nucleus is  $10^{-15}\text{m}$ .

On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model :

- (i) The positive charge and most of the mass of the atom is concentrated in the center in an extremely small region. This small region was called nucleus by Rutherford.
- (ii) Electrons move around the nucleus with a high speed in a circular path called an orbit.
- (iii) Electrons and nucleus are held together by electrostatic forces of attraction.

#### Drawbacks of Rutherford's atomic model :

The Coulombic force  $k \frac{q_1 q_2}{r^2}$  where  $q_1$  and  $q_2$  are the charges,  $r$  is the distance of separation of the charges and  $k$  is the proportionality constant between electron and the nucleus is mathematically

similar to the gravitational force  $G \frac{m_1 m_2}{r^2}$  where  $m_1$  and  $m_2$  are the masses,  $r$  is the distance between masses and  $G$  is the gravitational constant. The similarity between solar system and nuclear model suggests that electrons should move around the nucleus in some definite orbits. Now, when anything moves in orbit, it accelerates (substance gets accelerated even though moving with a constant speed due to change in the direction). Thus electron in a nuclear model describing planet like orbits also accelerates.

There is no phenomenon of attraction or repulsion in planet (since they are uncharged). But attractive and repulsive forces between positively charged nucleus and negatively charged electrons should be considered.

According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (this feature does not exist for planet since they are uncharged). Therefore, when an electron in orbit emits radiation, the energy of radiation comes from electronic motion. Thus orbit shrinks. Calculation shows that electron takes only  $10^{-8}$  s to get attracted into the nucleus. But this does not happen. Thus Rutherford's model can not explain stability of an atom. Another major drawback of the Rutherford's model is that no information about the electronic structure of atom can be obtained i.e. how electrons are distributed in an atom. The nucleus and energy possessed by them remain unknown.

## 2.4 Nature of Electromagnetic Radiation

Light is known as electromagnetic radiation. To explain the observations of the experiments in this field scientist Max Planck suggested, in 1900, that light has particle nature. Afterwards scientist Huygens proposed the wave nature theory of light on the basis of phenomena like interference and diffraction. Scientist Albert Einestein in 1902 studied the emission of electrons from the surface of the metal by light. This effect of light is known as photoelectric effect. Albert Einstein suggested that quantum properties, absorption and emission can be applied to radiation also. This means that electromagnetic radiation should be made up of particles which are known as photon. The relation between energy ( $E$ ) of photon and the frequency ( $\nu$ ) of light is as follows:

$$E = h\nu$$

The relation between frequency ( $\nu$ ) and wavelength ( $\lambda$ ) of light is as follows:

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

$$\text{Hence, the energy of photon } E = \frac{hc}{\lambda}$$

where,  $E$  = energy of photon

$c$  = velocity of light

$h$  = Planck's constant

$\lambda$  = wavelength

The energy possessed by 1 mole of photon is known as one Einstein.

$$\therefore NE = \frac{Nhc}{\lambda} \quad (\text{where } N = \text{Avogadro number})$$

## 2.5 Emission Spectra of Hydrogen Atom

Light is emitted when high voltage of electricity is applied to hydrogen gas kept in electric discharge tube under controlled conditions and low pressure. This emitted light appears to be of light purple colour. If it is analysed by an instrument called spectrograph, different series of lines at different distances are obtained in the spectrum. These lines obtained in the spectrum are called line spectra. The characteristic line spectra obtained by emission of light from any other element in gaseous state like that in hydrogen is known as atomic spectra.

At the first sight hydrogen spectrum appears to be complicated. The regularity in the positions of the lines in the series is proved. These series are known as Lyman, Balmer, Paschen, Brackett and Pfund series from the names of scientists who have discovered them.

## 2.6 Bohr's Atomic Model and Its Limitations



### Niels Bohr (1885-1962) :

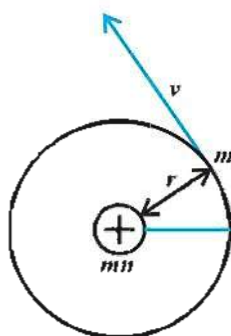
Niels Bohr, the Danish physicist, received Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford

in England in 1913. He returned to Copenhagen where he remained for the rest of his life. In 1920 he became the Director of the Institute of Theoretical Physics. After World War-I Bohr worked enthusiastically for peaceful uses of atomic energy. He received peace award in 1957. Bohr was awarded Nobel Prize in physics in 1922.

From the study of matter, radiation, more information about the structure of atom and models can be obtained. Niels Bohr applied these results to modify Rutherford's model.



Bohr was the first one to propose atomic model for hydrogen atom and it was the first attempt to describe arrangement of electrons in an atom. According to Bohr, hydrogen contains one proton in its nucleus and its one electron continuously revolves around the nucleus in definite path called orbit. Nucleus of the atom gets positively charged due to presence of proton and electron gets negative charge; so a force of attraction is produced between them. As a result possibility of electron to enter in to nucleus arises. If the distance between nucleus and electron (which is also known as radius of orbit) is increased, attraction between them decreases. As a result energy of electron also decreases.

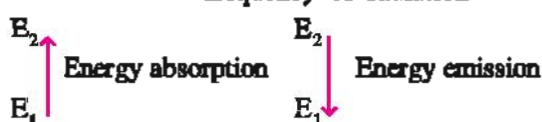


Bohr's model of an atom  
Figure 2.4

To explain hydrogen spectrum Bohr gave following postulates :

- (i) Electron revolves around the nucleus in certain accepted (permissible) energy states (orbits). Even though electron continuously revolves around the nucleus in some definite orbit, its energy remains constant. The path of electron revolution where its energy remains constant is known as stationary state or stationary orbit. Thus, energy is neither absorbed nor emitted when electron revolves in stationary orbit.
- (ii) Electron can move from one stationary orbit to another either by absorbing or emitting energy. The amount of energy absorbed or emitted by electron remains constant
 
$$E_1 + h\nu \rightarrow E_2 \text{ Absorption of energy}$$

$$E_2 \rightarrow E_1 + h\nu \text{ Emission of energy.}$$
 where,  $E_1$  = lower energy stationary orbit  
 $E_2$  = higher energy stationary orbit  
 $h$  = Planck's constant  
 $\nu$  = frequency of radiation



- (iii) Electron can revolve only in such orbit in which its angular momentum  $h/2\pi$  is an integral multiple of  $n$  where  $n$  is any positive integral number  $n = 1, 2, 3, \dots, n$ . This type of orbit is called accepted or permissible orbit.

$$\text{Angular momentum} = mvr = \frac{nh}{2\pi} \quad 2.1$$

where,  $m$  = mass of electron

$v$  = velocity

$r$  = radius of orbit (distance between electron and nucleus)

$n$  = positive integer number

$h$  = Planck's constant

- (iv) Energy of electron revolving in accepted or permissible orbit,  $E$ , can be given by Bohr's equation

$$E = \frac{-2e^4 \pi^2 Z^4 m}{n^2 h^2} \quad 2.2$$

where,  $E$  = energy of electron

$h$  = Planck's constant

$e$  = charge of electron

$Z$  = atomic number

$m$  = mass of electron

$n$  = any positive integer number

The negative sign in the above equation indicates that energy of electron in an atom is less than energy of free electron. Free electron remains at far distance from the nucleus and its energy is considered to be zero. For hydrogen atom, energy states  $n > 1$  are considered as excited states of electron.

- (v) The most important property associated with the electron is the energy of its stationary state which is given by following equation :

$$E_n = -R_H \left( \frac{1}{n^2} \right) \quad n = 1, 2, 3 \quad 2.3$$

where  $R_H$  = Rydberg's constant =  $2.18 \times 10^{-18} \text{ J}$   
 $n = 1, 2, 3, \dots, n$

The energy of the lowest state also called the ground state is,

$$E_1 = -2.18 \times 10^{-18} \left( \frac{1}{1^2} \right) \text{ J}$$

$$E_1 = -2.18 \times 10^{-18} \text{ J}$$

The energy of the stationary state for  $n = 2$ , will be

$$E_2 = -2.18 \times 10^{-18} \left( \frac{1}{2^2} \right) \text{ J}$$

$$E_2 = -0.545 \times 10^{-18} \text{ J}$$



- (vi) Electron can move from one energy state to another either by absorption of energy or emission of energy. The energy difference is  $\Delta E$  which can be given as

$$\Delta E = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\Delta E = 2.18 \times 10^{-18} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

where,  $R_H$  = Rydberg's constant

$n_i$  = initial energy state

$n_f$  = final energy state.

Frequency associated with energy absorption or emission can be given as

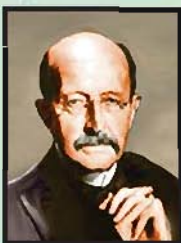
$$\Delta E = h\nu = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad 2.4$$

$$\therefore \nu = \frac{\Delta E}{h} = \frac{R_H}{h} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\therefore \nu = \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34}} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\therefore \nu = 3.29 \times 10^{15} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ Hz} \quad 2.5$$

**Max Planck (1858-1947) :**



Max Planck, the German physicist, received degree of Ph.D. in theoretical physics from the University of Munich in 1879. In 1888, he was appointed as Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel prize in physics, in 1918, for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics.

**Example 2.3 :** Calculate change in energy of a photon emitted during a transition of electron from  $n = 4$  state to  $n = 2$  state.

**Solution :**

The initial energy state ( $n_i = 4$ ) and the final energy state ( $n_f = 2$ ).

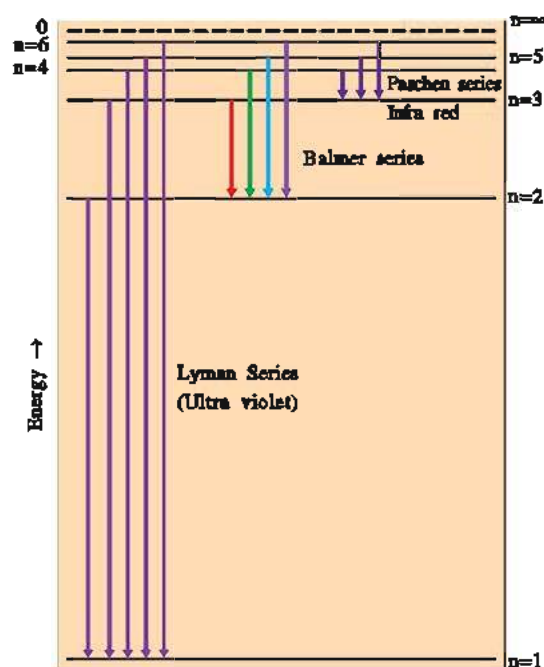
$$\Delta E = 2.18 \times 10^{-18} \times \left( \frac{1}{4^2} - \frac{1}{2^2} \right)$$

$$\therefore \Delta E = -4.076 \times 10^{-19} \text{ J}$$

Explanation of the hydrogen spectrum from Bohr's assumption can be given as follows :

**Table 2.2 The spectral lines for atomic hydrogen**

Series	$n_i$	$n_f$	Range of Spectrum
Lyman	1	2,3,....	Ultraviolet
Balmer	2	3,4,....	Visible
Paschen	3	4,5,....	Infrared
Brackett	4	5,6,....	Infrared
Pfund	5	6,7,....	Infrared



**Figure 2.5**

### Limitations of Bohr's Atomic Model :

Bohr's model of the hydrogen atom is considered as an improvement over Rutherford's nuclear model because it accounts for the stability of atom or ion. Limitations of Bohr's atomic model are as follows :

- Bohr's atomic model failed to explain the atomic spectrum of atoms other than hydrogen atom.
- Bohr's model could not give better explanation of hydrogen spectrum because it could not explain the spectrum when two spectral lines are very close to each other (i.e. doublet)
- It failed to explain Zeeman effect i.e. splitting of spectral lines under the influence of magnetic field.
- It could not explain the ability of atoms to form molecule by chemical bonds.

## 2.7 Dual Nature of Matter and Radiation

James Maxwell (1870) was the first to give comprehensive information about the interaction between the charged substances and the behaviour of electric and magnetic fields on macroscopic level. He suggested that when electrically charged particles move with acceleration, electric and magnetic fields are produced and transmitted. These fields are transmitted in wave forms which are known as electromagnetic waves or electromagnetic radiations.

During time of Newton it was believed that light is made up of particles but in 19<sup>th</sup> century the wave nature of light was established. Electromagnetic waves are of many types.

### Dual Nature of Radiation :

Particle nature of light confused scientists. On one hand it could explain black body radiation and photoelectric effect satisfactorily but on the other hand failed to explain well known phenomena of light like interference and diffraction. To resolve this confusion it was necessary to accept the idea that light possesses both particle and wave like properties, i.e, light has dual behaviour. From the experiment it was decided that light acts as a wave and as a stream of particles.

**Example 2.4 :** Calculate energy of one mole of photon whose frequency of radiation is  $4 \times 10^{14}$  Hz.

**Solution :** Energy of one photon can be calculated as follows :

$$E = h\nu$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\nu = 4 \times 10^{14} \text{ s}^{-1}$$

$$E = (6.626 \times 10^{-34} \text{ Js}) \times (4 \times 10^{14} \text{ s}^{-1})$$

$$\therefore E = 2.6496 \times 10^{-19} \text{ J}$$

Now, energy of one mole photon

$$(E_{\text{mol}} = NE)$$

$$E_{\text{mol}} = (2.6496 \times 10^{-19} \text{ J}) \times (6.022 \times 10^{23} \text{ mol}^{-1})$$

$$E_{\text{mol}} = 159.0 \text{ kJ mol}^{-1}.$$

**Example 2.5 :** When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of  $1.68 \times 10^5 \text{ J mol}^{-1}$ . What is the minimum energy needed to remove an electron from sodium ? What is the maximum wavelength that will cause a photoelectron to be emitted ?

**Solution :** The energy (E) of a 300 nm photon is given by

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{300 \times 10^{-9} \text{ m}}$$

$$E = 6.626 \times 10^{-19} \text{ J}$$

The energy of one mole of photons

$$E_{\text{mol}} = 6.626 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$E_{\text{mol}} = 3.99 \times 10^5 \text{ J mol}^{-1}$$

The minimum energy to remove one mole of electrons from sodium =  $(3.99 - 1.68) \times 10^5 \text{ J mol}^{-1}$

$$= 2.31 \times 10^5 \text{ J mol}^{-1}$$

The minimum energy for removal of electron

$$E = \frac{2.31 \times 10^5 \text{ J}}{6.022 \times 10^{23}}$$

$$\therefore E = 3.84 \times 10^{-19} \text{ J}$$

$$\therefore \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{3.84 \times 10^{-19} \text{ J}}$$

$$\therefore \lambda = 517 \text{ nm}$$

This value of  $\lambda = 517 \text{ nm}$  corresponds to green light.

## 2.8 De Broglie's Equation

In 1924, French physicist, de Broglie proposed that matter, like radiation also exhibits a dual behaviour. Matter and radiation act both as particle and wave. They possess both particle and wave nature. We know that photon has momentum and wavelength, electrons must also possess momentum and wavelength.

de Broglie gave the following equation relating wavelength and momentum of matter-particle.

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad 2.6$$

where, h = Planck's constant

p = momentum

m = mass of particle

v = velocity of particle

de Broglie's dual character or duality principle was confirmed experimentally. It was found that an electron beam undergoes diffraction which is characteristic of wave. The electron microscope is based on the wave like nature of electron while ordinary microscope utilizes the wave nature of light. Electron microscope achieves a magnification of about 15 million times.

According to this principle, every object in motion has wave character. The wavelengths of

ordinary object are so short that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles with very small mass can be detected experimentally.

**Example 2.6 :** Calculate wavelength of a ball of mass 0.2 kg whose velocity is  $10 \text{ ms}^{-1}$

**Solution :** According to de Broglie's equation

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ Js}}{(0.2) \text{ kg} \times (10 \text{ ms}^{-1})}$$

$$\lambda = 3.313 \times 10^{-34} \text{ m} = 3.313 \times 10^{-25} \text{ nm}$$

**Example 2.7 :** Calculate wavelength of wave associated with electron whose velocity is  $10^8 \text{ cm sec}^{-1}$ . (Mass of electron =  $9.1 \times 10^{-31} \text{ kg}$ )

**Solution :**  $\lambda = \frac{h}{p} = \frac{h}{mv}$

$$\text{Now, } h = 6.62 \times 10^{-34} \text{ J}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$v = 10^8 \text{ cm sec}^{-1} = 10^6 \text{ m s}^{-1}$$

$$\therefore \lambda = \frac{6.62 \times 10^{-34} \text{ Js}}{9.1 \times 10^{-31} \text{ kg} \times 10^6 \text{ m s}^{-1}}$$

$$\lambda = 7.27 \times 10^{-10} \text{ m}$$

$$\lambda = 0.727 \text{ nm}$$

## 2.9 Heisenberg's Uncertainty Principle

In 1927, German physicist Werner Heisenberg gave uncertainty principle as a consequence of dual behaviour of matter and radiation. It is as follows :

The position and momentum of moving microscopic particle cannot be determined simultaneously and precisely.

When position of electron is measured by electron microscope, the radiation bombarded on electron (radiation possesses energy) is absorbed by the electron and changes its momentum. Similarly, uncertainty in its position is produced when momentum of electron is measured accurately.

A mathematical relationship between uncertainty in position ( $\Delta x$ ) and momentum ( $\Delta p$ ) was given by Heisenberg in the form of equation

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \quad 2.7$$

where,

$\Delta x$  = uncertainty in position of electron

$\Delta p$  = uncertainty in momentum of electron

Now momentum  $p = m \times v$

where,  $m$  = mass of electron

$v$  = velocity of electron

Therefore the above equation can also be written as :

$$\Delta x \cdot m\Delta v \geq \frac{h}{4\pi} \quad 2.8$$

Importance of Heisenberg's uncertainty principle is only for moving microscopic object. This can be explained from the following example :

Suppose Heisenberg's principle is applied to an object having mass of  $10^{-8} \text{ kg}$ .

$$\Delta v \cdot \Delta x = \frac{h}{4\pi m}$$

$$\Delta v \cdot \Delta x = \frac{6.62 \times 10^{-34} \text{ Js}}{4 \times 3.141 \times 10^{-8} \text{ kg}}$$

$$\Delta v \cdot \Delta x = 0.53 \times 10^{-26} \text{ m}^2 \text{ s}^{-1}$$

Thus the value of  $\Delta v \cdot \Delta x$  is extremely small and has no significance. Therefore, one can say that when the mass of any object is of one milligram or more or less, then the uncertainties in momentum or position associated are hardly of any significance.

Particles like electron whose mass is  $9.11 \times 10^{-31} \text{ kg}$ , the product  $\Delta v \cdot \Delta x$  is more and hence for such particles this principle is significant.

$$\begin{aligned} \Delta v \cdot \Delta x &= \frac{h}{4\pi m} \\ &= \frac{6.0626 \times 10^{-34} \text{ Js}}{4 \times 3.141 \times 9.11 \times 10^{-31} \text{ kg}} \end{aligned}$$

$$\Delta v \cdot \Delta x = 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

Therefore, statement of Heisenberg's position and momentum uncertainty is replaced by probability function which is seen in quantum mechanical model of an atom.

**Example 2.8 :** The position of electron located at  $1\text{Å}$  with microscope. Calculate uncertainty in the velocity of electron.

**Solution :** According to Heisenberg's uncertainty principle,

$$\Delta x \cdot \Delta p = \frac{h}{4\pi}$$

$$\text{or } \Delta x \cdot m\Delta v = h/4\pi$$

$$\therefore \Delta v = \frac{h}{4\pi \Delta x m}$$

$$\Delta v = \frac{6.626 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 1 \times 10^{-10} \text{ m} \times 9.11 \times 10^{-31} \text{ kg}}$$

$$\Delta v = 5.79 \times 10^5 \text{ ms}^{-1}$$

## 2.10 Explanation of Orbit and Orbital

The circular planar path of rotation of electron around the nucleus is called an orbit. The region around the nucleus of an atom, where probability of finding the electron is maximum, is called an orbital.

Thus orbital shows probability of finding electron while orbit shows position of electron, its energy and distance of electron from nucleus. Different orbits can be represented by principal quantum number ( $n$ ).

## 2.11 Quantum Numbers

In order to describe electron of an atom in detail, quantum numbers are used. The energy levels of electron in atom is mentioned by the use of positive integer number which is known as Principal Quantum Number ( $n$ ).

Large number of orbitals are possible in an atom. These orbitals can be classified (distinguished) by their size, shape and orientation. Every orbital can be represented mainly by three quantum numbers  $n$ ,  $l$ , and  $m_l$ . A new quantum number, i.e. spin quantum number is also introduced based on the rotation of electron around the nucleus as well as spinning on its own axis.

### Principal quantum number ( $n$ ) :

Principal quantum number  $n$  is positive integer which is represented by  $n$ . Its value may be 1, 2, 3, ...  $n$ . It mainly decides size of orbit and energy up to some extent. Size of orbit and energy of orbit of hydrogen atom and species like hydrogen atom depend only on principal quantum number ( $n$ ). Number of allowed orbitals increase with increase in  $n$  values which are given by  $n^2$ . Every orbital for a given value of ' $n$ ' constitutes a single shell. They are represented as follows.

$n = 1 \quad 2 \quad 3 \quad 4 \quad \dots$

Shell = K L M N  $\dots$

Energy of orbit increases with increase in the value of ' $n$ '

### Angular Momentum Quantum Number (or Azimuthal Quantum Number) ( $l$ ) :

Angular momentum or Azimuthal quantum number is represented as ' $l$ '. It is also known as subsidiary quantum number. It decides geometrical shapes of orbitals. For a given value of  $n$ ,  $l$  can have values ranging from 0 to  $n-1$  i.e. for a given value of  $n$  the possible values of  $l$  are  $l = 0, 1, 2, \dots (n-1)$ .

e.g.  $n = 1, \quad l = (n-1) = 1 - 1 = 0$

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

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

Each shell constitutes one or more subshells or sublevels.

The number of subshells in a principal shell is equal to the value of  $n$ ; e.g. for  $n = 1$  there is only one subshell i.e.  $l = 0$ . For  $n = 2$ , there are two subshells i.e.  $l = 0, 1$  and so on. Subshells corresponding to  $n$  and  $l$  are listed in table 2-3, Angular momentum quantum number decides shapes of orbitals,

Value of  $l \quad : \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5, \dots$

Notation for sub shell : s p d f g h, ...

Table 2.3 shows  $n$  and  $l$  subshell notation.

Table 2.3

$n$	$l$	Symbol of sub shell
1	0	1s
2	0	2s
2	1	2p
3	0	3s
3	1	3p
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4f

### Magnetic Quantum Number $m_l$ :

Any charged particle (like electron), when is in motion, produces magnetic field which is due to its orbital motion (velocity). The magnetic field value is represented by magnetic quantum number  $m_l$ . It indicates orientation of orbitals in space under magnetic field. For a given value of  $l$ ,  $m_l$  values indicate number of specific orbitals i.e. values of  $m$  are dependent on  $l$  which is given by the following relationship :

e.g. ( $m_l = -l \dots 0 \dots +l$  (i.e.  $2l + 1$ )

$l = 0, \quad m_l = 0$  (s-orbital)

$l = 1 \quad m_l = -1, 0, +1$ , (p-orbital)

$l = 2 \quad m_l = -2, -1, 0, +1, +2$  (d-orbital)

$l = 3 \quad m_l = -3, -2, -1, 0, +1, +2, +3$  (f-orbital)



### Spin Quantum Number 's' :

The above three quantum numbers  $n$ ,  $l$  and  $m$  are not enough to explain the line spectra observed in the case of multi-electron atom or ion. e.g. some of the lines occurred in spectrum as doublet or triplet.

In 1925, George Uhlenbeck and Samuel Goudsmit gave the fourth quantum number known as rotational or spin quantum number 's'.

Electron has two types of motion. Orbital motion in which electron rotates around the nucleus in its own definite orbit. Axial motion is one in which electron spin on its own axis. Velocity of electron around the nucleus is called orbital velocity, but velocity of electron spinning on its axis is known as axial velocity. Electron spin on its own axis either in clockwise or in anticlockwise direction. Hence, value of spin quantum number is taken as  $+1/2$  or  $-1/2$ .

**Example 2.9 :** Find out orbitals associated with principal quantum number  $n = 3$ .

**Solution :**

For  $n = 3$  the possible values of  $l$  are 0, 1 and 2. Therefore, there is one 3s-orbital ( $n = 3$ ,  $l = 0$ ,  $m = 0$ ). There are three 3p-orbitals ( $n = 3$ ,  $l = 1$ ,  $m_1 = -1, 0, +1$ ). There are five 3d-orbitals ( $n = 3$ ,  $l = 2$ ,  $m = +2, +1, 0, -1, -2$ ). Thus there are total number of orbitals =  $1 + 3 + 5 = 9$ .

(This can also be obtained by using the relation : number of orbitals =  $n^2$  and  $l = 3^2 = 9$ )

**Example 2.10 :** Using s, p d and f orbitals, describe the orbitals with the following quantum numbers :

- (a)  $n = 2$ ,  $l = 1$ , (b)  $n = 4$ ,  $l = 3$ , (c)  $n = 5$ ,  $l = 0$   
(d)  $n = 3$ ,  $l = 2$

**Solution :**

	$n$	$l$	orbital
(a)	2	1	2p
(b)	4	3	4f
(c)	5	0	5s
(d)	3	2	3d

### 2.12 Shapes of s, p and d-orbitals

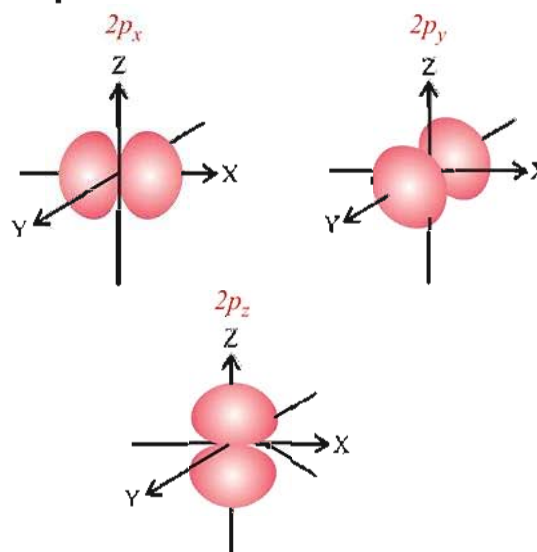
Schrodinger deduced in 1926 the equation for the energy of electron moving around the nucleus which is known as Schrodinger's wave equation : This equation is as follows :

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

$x$ ,  $y$ , and  $z$  in the above equation are cartesian co-ordinates showing the position of electron in atom.  $m$  = mass of electron,  $E$  = total energy of electron-proton system,  $V$  = potential energy,  $h$  = Planck's constant,  $\psi$  is known as wave function which represents similarity with amplitude of normal wave. There is no physical significance of orbital wave function  $\psi$  of electron. It is only the mathematical function of electron co-ordinate.

As s-orbital is spherically symmetrical, the probability of finding electron in s-orbital is also symmetrical. All the energy levels, having  $l=0$  value, have one spherical orbital which is expressed by symbol  $ns$ .

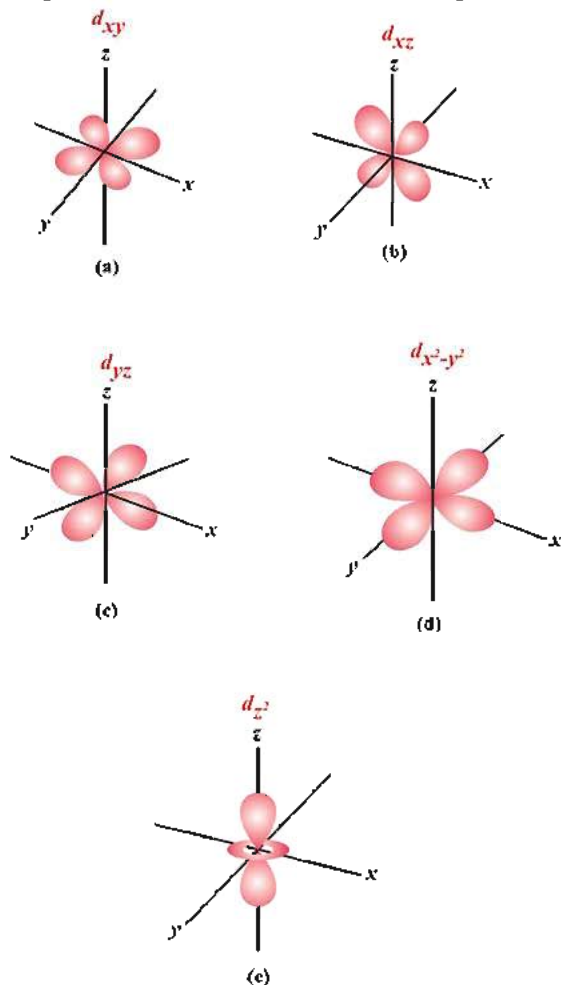
Surface of the orbital where the value of probability function decreases to zero (i.e. probability of finding the electron becomes zero). Such surface is called nodal plane or 'node.'  $(n-1)$  indicates number of nodes in  $ns$  orbitals. e.g. for  $n = 1$  in 1s orbital there is no node and  $n = 2$  in 2s orbital has 1 node. Boundary surface plot for p orbital ( $l = 1$ ) is not spherical, but are seen as dumbbell shape. Every p-orbital is divided into two parts which are known as lobes which remain on either side of the plane passing from centre. The probability function is zero at a point where two lobes meet each other. The size, shape and energy of all the three orbitals are equal. They only differ in their orientation. They are named as  $p_x$ ,  $p_y$  and  $p_z$  depending upon the lobes lying on  $x$ ,  $y$  or  $z$  coordinate. The values of  $m_l$  are  $-1$ ,  $0$  and  $+1$  respectively.



Boundary surface diagram of the three 2p orbitals

Figure 2.6

Orbitals generated by  $l = 2$  values are known as d-orbitals where minimum value of  $n = 3$ . It has five equal energy orbitals which are also known as degenerate orbitals. They are named as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$ . The boundary surface diagrams for d-orbital are shown in fig. 2.8.



Boundary surface diagram of the five 3d-orbital

Figure 2.7

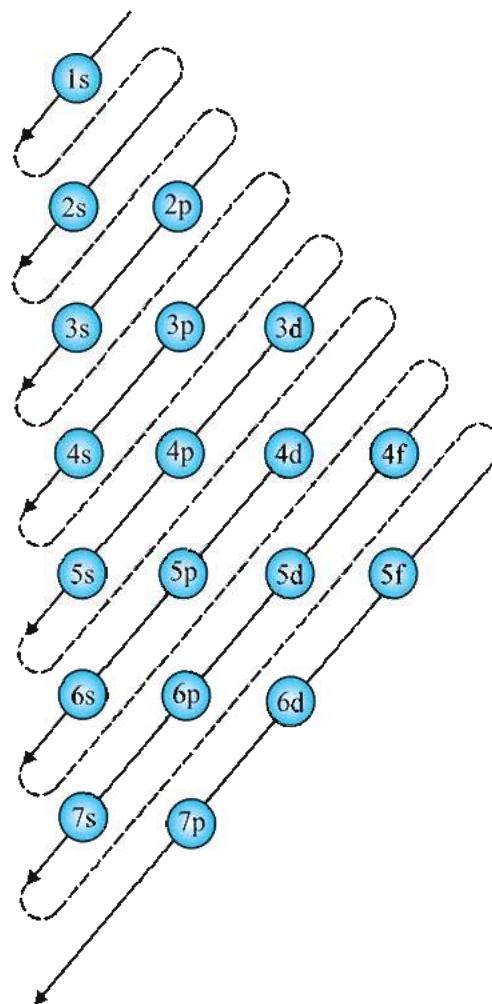
### 2.13 Rules for the Electron Arrangement in Orbitals

Each atom has definite electron arrangement depending upon the number of electrons present. The distribution of electrons in an atom, in different atomic orbitals is based on some rules, which is known as electron configuration. Electron configuration of atom is mainly followed by three rules :

(i) Aufbau principle (ii) Pauli's exclusion principle (iii) Hund's rule (ie Hund's rule of maximum multiplicity or maximum spin)

**(i) Aufbau Principle :** The German word Aufbau means 'building up'. We shall use this word in the arrangement of electron in the different orbitals according to their energy.

According to this rule, electron of an atom first enters into the empty orbital of lowest energy. When the lowest energy orbitals are completely filled electron then enters into the orbital of higher energy and this way electrons are arranged in other orbitals based on their energy. Therefore, it is necessary to know the order of energy levels for different orbitals which is shown in the figure 2.8.



Order of filling of orbitals

Figure 2.8

The order of energy levels of orbitals for H-atom is as follows :

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \dots$$

The order of energy levels for the orbitals of atoms other than hydrogen (more than one electron) is as follows :

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

The arrangement of electrons in orbitals of atom can be given by  $n + l$  rule. If  $(n + l)$  value is same for different orbitals, the orbital with higher value of 'n' has higher energy as shown in table 2.4.

**Table 2.4 Arrangement of orbitals with increasing energy on the basis of  $(n + l)$  rule.**

Orbital	Value of $n$	Value of $l$	Value of $(n + l)$	
1s	1	0	$1 + 0 = 1$	
2s	2	0	$2 + 0 = 2$	
2p	2	1	$2 + 1 = 3$	2p ( $n = 2$ ) has lower energy than 3s
3s	3	0	$3 + 0 = 3$	3s ( $n = 3$ )
3p	3	1	$3 + 1 = 4$	3p ( $n = 3$ ) has lower energy than 4s
4s	4	0	$4 + 0 = 4$	4s ( $n = 4$ )
3d	3	2	$3 + 2 = 5$	3d ( $n = 3$ ) has lower energy than 4p
4p	4	1	$4 + 1 = 5$	4p ( $n = 4$ )

**(ii) Pauli's Exclusion Principle :** The number of electrons to be filled in various orbitals is restricted by the Pauli's exclusion principle. According to this principle, all the four quantum numbers of two electrons in the same atom are not equal. This rule can also be presented in other words:

Only two electrons can remain in the same orbital with their spins opposite to each other. This principle helps in calculating the capacity of electron to be present in any subshell e.g. subshell is comprised of two electrons and thus the maximum number of electrons present in 1s subshell can be two. As there are three subshells for p-orbital maximum six electrons can be accommodated. Similarly, d-orbital can accommodate maximum of ten electrons as it has five subshells and f-orbital can accommodate fourteen electrons as it has seven subshells.

The following table shows the arrangement of electrons.

Principal Quantum number(n)	Symbol of orbital	Orbital in orbit				No. of orbitals $n^2$	Total No. of electrons $2n^2$
		s	p	d	f		
1	K	1	-	-	-	1	2
2	L	1	3	-	-	4	8
3	M	1	3	5	-	9	18
4	N	1	3	5	7	16	32

**(iii) Hund's Rule of Maximum Multiplicity :**

This rule indicates arrangement of electrons in equal energy subshell of any orbital. Subshell of some orbitals having equal energy are known as degenerate orbitals, e.g. p-orbitals have three subshells of equal energy named  $p_x$ ,  $p_y$  and  $p_z$ . According to this rule, when electron enters into the orbital of equal energy subshells, they are arranged in such a way that the direction of their spins remains parallel and the value of spin quantum number remains maximum. When all the sub-shells are occupied with electrons having parallel spin attains the half filled subshell electron configuration there after pairing of electrons occur. Hund's rule can be explained by the following illustrations in table 2.5.

**Table 2.5**

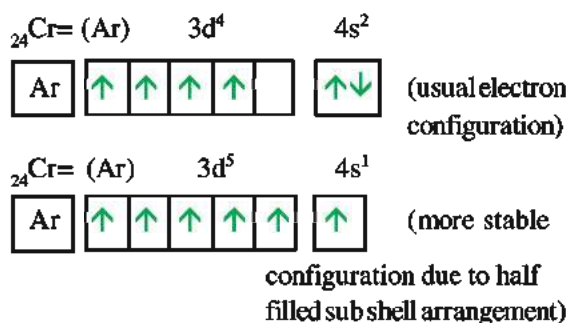
Atomic number	Element	Electronic configuration				
		1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>
5	Boron	↑↓	↑↓	↑		
6	Carbon	↑↓	↑↓	↑	↑	
7	Nitrogen	↑↓	↑↓	↑	↑	↑
8	Oxygen	↑↓	↑↓	↑↓	↑	↑
9	Fluorine	↑↓	↑↓	↑↓	↑↓	↑
10	Neon	↑↓	↑↓	↑↓	↑↓	↑↓

**2.14 Stability of Half Filled and Completely Filled Orbitals**

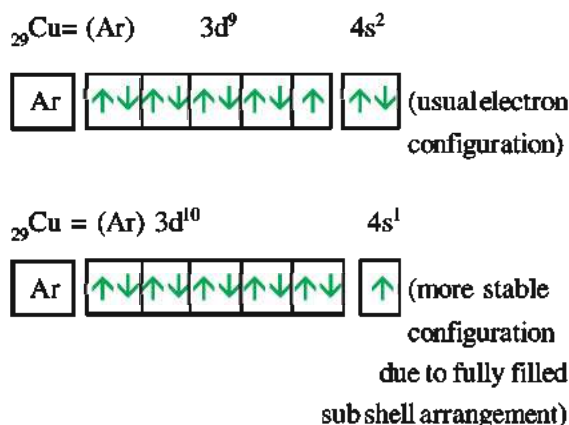
The ground state electron configuration of an element always corresponds to the state of lowest energy. Electron configuration of atoms strictly follows the three rules as studied earlier. Even though in some cases like Cr and Cu where two subshells (4s and 3d) differ slightly in their energy, then electron shifts from a subshell of lower energy (4s) to a sub-shell of



higher energy (3d) provided such shift results in all orbitals of the subshells of higher energy getting either completely filled or half filled configuration and thereby attains maximum stability. Because of this electron configuration of chromium is (Ar)3d<sup>5</sup> 4s<sup>1</sup> instead of (Ar)3d<sup>4</sup> 4s<sup>2</sup> and electron configuration of copper is (Ar)3d<sup>10</sup> 4s<sup>1</sup> instead of (Ar)3d<sup>9</sup> 4s<sup>2</sup>. Such configurations will add extra stability.



Similarly more stable configuration of copper is given as



We shall study about such types of abnormality later on.

### SUMMARY

Atoms are constitutional species of element. They are the smallest species of element taking part in chemical reaction. In 1808, Dalton put forward the theory that atom is indivisible. Then it was discovered that atom can be divided into three fundamental particles like proton, electron and neutron.

Thomson, in 1898, presented atomic model. According to this, positive charge (proton) and negative charge (electron) are equally distributed in the surface of atom. The idea of isotopes, isobars etc. was also given. From the Rutherford's  $\alpha$ -particle scattering experiment, it was proved that atom contains small positively charged centre called nucleus i.e. centre of atom contains positively charged protons while negatively charged electrons are arranged around the centre.

Thomson's model of an atom was not accepted because limitations exposed due to Rutherford's particle scattering experiment. Rutherford's atomic model was accepted to certain extent. Bohr gave modern model of an atom to explain some experimental phenomenon of light radiation. According to him, the total mass of an atom remains in the centre i.e. proton and neutrons are in the nucleus while electron with negligible mass rotates around the nucleus in some definite path known as an orbit. Bohr suggested that energy of the electron remains constant as far as it remains in some definite orbit. Such states are known as stable or stationary states.

Electron can go from one stable state to another one either by absorption or emission of energy. As a result spectrum is obtained. Different lines were obtained in hydrogen spectrum.

There were some defects in the Bohr's model of atom. Later on energy of orbitals, their shapes, sub-shells of orbit and spins of electron revolving around its own axis were also shown.

Thus, as a whole discovery of fundamental species of atom, theories regarding different models of atoms, modification, final model of atom were established. Explanation of orbit, orbital and electron configuration of atoms were also studied.

Position and momentum of electron cannot be measured simultaneously and precisely. Heisenberg gave uncertainty principle and de Broglie gave wave particle duality principle. The arrangement of electrons in an orbit is governed by three rules. But before this, quantum mechanics gave idea about quantized energy and four quantum numbers  $n$ ,  $l$ ,  $m$ , and  $s$ . Each of them has its own significance and thereby electron arrangement in orbits. The three rules: Aufbau principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity helped to write electron arrangement (configuration) of element. From Hund's rule stability of half filled subshells and completely filled subshells can be explained.



## EXERCISE

## 1. Select the proper choice from the given multiple choices :

- (1) How many electrons are present in  $A^+$  ion having eleven protons ?  
 (A) 11 (B) 12  
 (C) 10 (D) 9
- (2) Which is the correct electronic configuration of  $Na^+$  ion ?  
 (A)  $[Ne]$  (B)  $[Ne] 3s^1$   
 (C)  $1s^2 2s^2 2p^5$  (D)  $[Ar]$
- (3) Where is the zero probability of finding the electron ?  
 (A) Node (B) Near the nucleus  
 (C) Orbit (D) Antinode
- (4) From which of the following it was proved that nucleus of atom contains positive charge ?  
 (A) Thomson's model of an atom (B) Bohr's atomic model  
 (C) de Broglie's principle (D)  $\alpha$ -particle scattering experiment
- (5) Which of the following is the accepted electron configuration of chromium ?  
 (A)  $[Ar]3d^5 4s^1$  (B)  $[Ar] 4s^2 4p^4$   
 (C)  $[Ar] 3d^4 4s^2$  (D)  $[Ar] 4s^1 4p^5$
- (6) Which of the following is the correct order of energy levels of atomic orbitals ?  
 (A)  $1s < 2s < 2p < 3s < 3p$  (B)  $1s < 2p < 3s < 3p < 2s$   
 (C)  $3p < 3s < 2p < 2s < 4s$  (D)  $1s < 2s < 3s < 2p < 3p$
- (7) Which of the following is the relation between momentum and the wave length of moving particle according to de Broglie's principle ?  
 (A) Inversely proportional (B) Proportional  
 (C) Square root (D) No relation
- (8) Which of the following is the correct formula for one Einstein ?  
 (A)  $\frac{Nc}{\lambda}$  (B)  $\frac{hc}{\lambda}$  (C)  $\frac{Nhc}{\lambda}$  (D)  $\frac{Nh}{\lambda c}$
- (9) Which of the following is a correct pair :  
 (a) Aufbau principle (1) mvr  
 (b) Angular momentum (2) Orientation of electron in orbital  
 (c) Hund's rule (3) order of orbital energy  
 (A)  $b \rightarrow 1$  (B)  $a \rightarrow 1$  (C)  $c \rightarrow 1$  (D)  $b \rightarrow 3$
- (10) Which of the following electronic configuration is not possible ?  
 (A)  $2p^6$  (B)  $3s^1$  (C)  $2p^5$  (D)  $3f^{12}$
- (11) From which of the following equations atomic mass can be known ?  
 (A)  $Z + n$  (B)  $Z + e^-$  (C)  $N + e^-$  (D)  $Z + N$
- (12) How many 'nodes' are there in 3s orbital ?  
 (A) 3 (B) 2 (C) 1 (D) Zero.
- (13) Spin multiplicity value of Nitrogen element is :  
 (A) 4 (B) 3 (C) 2 (D) 1.5

- (14) How many subshells are associated with  $n = 4$  ?  
 (A) 16 (B) 15 (C) 8 (D) 18
- (15) How many unpaired electrons are present in the electron configuration of phosphorous ?  
 (A) 5 (B) 3 (C) 2 (D) 1

**2. Write the answers of following questions in short :**

- (1) Explain the difference between orbit and orbital.
- (2) Give the statement of de Broglie's principle.
- (3) Conclusion drawn from the  $\alpha$ -particle scattering experiment.
- (4) Drawbacks of Bohr's model of an atom.
- (5) Order of energy levels of atomic orbitals.
- (6) Irregularities observed in the electron configuration of chromium and copper.
- (7) Importance of quantum numbers.
- (8) Shapes of p and d-orbitals.
- (9) What is called nodal surface ?
- (10) Ground and excited state of atom.

**3. Write the answers of the following questions :**

- (1) Absorption and Emission spectra.
- (2) Spectral lines produced in atomic spectra of hydrogen.
- (3) What is photon ? Write equation for energy of photon.
- (4) Explain magnetic quantum number.
- (5) Explain Aufbau principle.
- (6) Draw the shapes of p and d-orbitals. Write the values of angular momentum quantum number ?
- (7) Why spin quantum number is introduced ?
- (8) Explain Heisenberg's uncertainty principle.
- (9) Write a brief account of Thomson's atomic model.
- (10) Position of proton, electron and neutron in atomic structure.

**4. Write the answers of the following questions in detail :**

- (1) Explain Pauli's exclusion principle giving suitable example.
- (2) Explain hydrogen spectrum.
- (3) Calculate number of proton, electron and neutron in the following :  
 ${}^{32}_{16}\text{S}^{2-}$  ;  ${}^{23}_{11}\text{Na}^{+}$
- (4) Explain Isotope, Isobar and Isotone.
- (5) Calculate wave frequency of yellow colour radiation whose wavelength is  $5800 \text{ \AA}$ .
- (6) Calculate mass of a photon having  $3.6 \text{ \AA}$  wavelength.
- (7) What is the total number of orbitals associated with  $n = 3$  ? How many electrons can be accommodated in them ?
- (8) Explain by giving suitable example the stability of half filled subshell and completely filled subshell of orbital.
- (9) Write Ritz's equation for the frequency of radiation. Explain each term involved in it.
- (10) Calculate wavelength of electron having  $2.05 \times 10^{-7} \text{ ms}^{-1}$  velocity.

## CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

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- 3.1 Introduction
- 3.2 Necessity of Classification of Elements
- 3.3 History of the Development of Periodic Table
- 3.4 Modern Periodic Law and Modern Periodic Table
- 3.5 Nomenclature of Elements With Atomic Numbers > 100
- 3.6 Electronic Configurations of Elements and Periodic Table
- 3.7 Electronic Configuration and Types of Elements : s, p, d, f - blocks
  - 3.7.1 The s- block elements
  - 3.7.2 The p- block elements
  - 3.7.3 The d- block elements
  - 3.7.4 The f- block elements
- 3.8 Periodic Trends in Properties of Elements
  - 3.8.1 Periodic Trends in Physical Properties
    - 3.8.1.1 Atomic radius
    - 3.8.1.2 Ionic radius
    - 3.8.1.3 Ionization enthalpy
    - 3.8.1.4 Electron gain enthalpy
    - 3.8.1.5 Electronegativity
  - 3.8.2 Periodic Trends in Chemical Properties
    - 3.8.2.1 Periodicity of Oxidation State or Valence

### 3.1 Introduction

You have got preliminary knowledge about periodic table for the classification of elements in Standard 9. According to scientist Glenn T. Seaborg, the periodic table is the most important concept in chemistry. It always supports the students, suggests new avenues of research and presents the entire branch of chemistry in brief. In this unit, we will study the history of periodic table and modern periodic law. Moreover, we will understand the periodic classification and some of the periodic trends in the physical and chemical properties of the elements.

### 3.2 Necessity of Classification of Elements

In 1800, only 31 elements were known. In 1865, number of known elements became 63. Due to increasing number of elements, it became difficult to study the chemical properties of elements and their innumerable compounds individually. To solve this problem, scientists classified the elements. This classification was not only for understanding of chemical properties of elements but was also helpful in prediction of new elements. On account of this 114 elements are known to us today. Out of these, 92 elements are found in nature and rest are synthetic elements which are man-made. Efforts to synthesise new elements are continuing even today.

### 3.3 History of the Development of Periodic Table

The German chemist, Johann Dobereiner, in early 1800, was the first to consider the idea of trends among properties of elements. In 1829, he arranged many of the elements into triads (group of three) based on their physical and chemical properties. For example, lithium, sodium and potassium were grouped together as being soft and reactive metals. Dobereiner also observed that when these elements were arranged according to their atomic weights, the atomic weight of middle element was roughly the average of the atomic weights of first and

third (table 3.1). This relationship was known as the Law of Triads, but this was found in few elements and so it was rejected by considering it as a coincidence.

**Table 3.1 Dobereiner's Triads**  
(For information only)

Element	Atomic Weight	Element	Atomic Weight	Element	Atomic Weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

In 1862, French geologist, A.E.B. de Chancourtois published first probable periodic table. He arranged known elements in cylindrical form (chart) in terms of increasing order of their atomic weights. He was first to find out that the properties of an element repeat after every seventh element. He was able to predict stoichiometry of some metal oxides using this chart. This work has also not attracted attention of anyone. The English chemist, John Newlands presented a research paper, in 1863, in which he classified 56 elements in 11 groups based on their physical properties. In 1865, Newlands published his version of periodic table and presented Law of Octaves. This law suggests that any element in periodic table shows similar behaviour with its eighth element (Table 3.2). He linked this law to the octaves of music (Sa, Re, Ga, Ma, Pa, Dha, Nee,... Sa...). This law of octaves proposed by Newlands was found to be true up to calcium. Even at that time this concept was also not accepted widely. Dmitri Mendeleev and Lothar Meyer published their periodic tables independently in 1869 and 1870, respectively. They both constructed their tables in a similar manner, by arranging the elements in a row or column in order of atomic weight and started with a new row or column when the characteristics of elements began to repeat. The credit for development of periodic law, that we know today, goes to the Russian chemist, Dmitri Mendeleev (1834-1907) and the German chemist Lothar Meyer (1830-1895). But Mendeleev was first to publish the periodic law. It can be stated as follows :

“The properties of the elements are periodic function of their atomic weights.”

Mandeleev was more courageous than Meyer. He assumed that if a measured atomic weight of an element is placed in the wrong

place in the periodic table, the atomic weight must be wrong. In some cases this was true. For example, previously assigned atomic weight of indium was nearly 76. But this could not be placed in the periodic table between arsenic (atomic weight 75) and selenium (atomic weight 79). Mendeleev suggested that its atomic weight should be 114 instead of 76. It was nearer to the currently accepted value 114.82. Besides chemical properties of indium it was inconsistency with the group pattern defined by the known properties of aluminium and thallium. It supported Mendeleev. In the same way though the atomic weight of K(39.10) was less than atomic weight of Ar (39.95), Mendeleev placed Ar before K, because Ar possessed properties similar to elements of group 0 and K possessed properties similar to elements of group I.

**Table 3.2 Newlands' Octaves**

Elements	Li	Be	B	C	N	O	F
Atomic weight	7	9	11	12	14	16	19
Elements	Na	Mg	Al	Si	P	S	Cl
Atomic weight	23	24	27	29	31	32	35.5
Elements	K	Ca					
Atomic weight	39	40					

Subsequent studies about periodic system have shown that the arrangement of elements is not in order strictly according to atomic weight. For example, atomic weight of iodine is less than that of tellurium (group VI). It was placed along with fluorine, chlorine and bromine in group VII because they showed similar properties (Fig. 3.1). Thus at that time, the basic concept of Mendeleev was to arrange the elements having similar properties in the same group. When Mendeleev published periodic table, gallium and germanium were not known. He left the gaps for unknown elements below the aluminium and the silicon. Mendeleev named these elements as “Eka-Aluminium” and “Eka-Silicon” (in Sanskrit ‘eka’ means ‘next’), respectively. Quite similarities in some properties were predicted by Mendeleev for these elements and the properties experimentally observed were found (Table 3.3). On these bases Mendeleev named “gallium” to “Eka-Aluminium” and “germanium” to “Eka-silicon”. Thus development of periodic table took place. Mendeleev's periodic table published in 1905 is shown in Fig. 3.1.



**Table 3.3 Mendeleev's predictions about properties of Eka-aluminium and Eka-silicon elements and experimental results**

(For information only)

Property	Eka-aluminium (Predicted)	Gallium (found)	Eka-Silicon (Predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density ( $\text{gcm}^{-3}$ )	5.9	5.94	5.5	5.36
Melting point (K)	Low	302.93	High	1231
Formula of oxide	$\text{E}_2\text{O}_3$	$\text{Ga}_2\text{O}_3$	$\text{EO}_2$	$\text{GeO}_2$
Formula of chloride	$\text{ECl}_3$	$\text{GaCl}_3$	$\text{ECl}_4$	$\text{GeCl}_4$

**Periodic system of the elements in groups and series**  
(For Information Only)

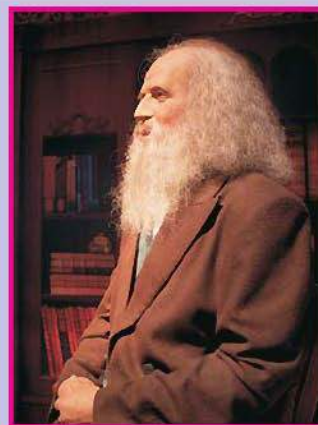
	0	I	II	III	IV	V	VI	VII	VIII
1	Helium He 4.0	Hydrogen H 1.008	Beryllium Be 9.1	Boron B 11.1	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
2		Lithium Li 7.03						Chlorine Cl 35.45	
3		Sodium Na 23.5	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06		
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	Nickel Ni 59
6		Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 96.6	Niobium Nb 94.0	Molybdenum Mo 96.0	Iodine I 126.9	Rhodium Rh 103.3
7	Krypton Kr 81.8	Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 128.0	Tellurium Te 127.6		Palladium Pd 106.5
8	Xenon Xe 128	Cesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140				
9									
10									
11		Gold Au 197.2	Mercury Hg 200.0	Thallium Tl 204.1	Lead Pb 206.9	Bismuth Bi 208	Tungsten W 184		Osmium Os 191
12			Radium Ra 224		Thorium Th 232		Uranium U 239		Iridium Ir 193
	R	$\text{R}_2\text{O}$	RO	$\text{R}_2\text{O}_3$	$\text{RO}_2$ $\text{RH}_4$	HIGHER SALINE OXIDES $\text{R}_2\text{O}_5$ $\text{R}_2\text{O}_3$ HIGHER GASEOUS HYDROGEN COMPOUNDS $\text{RH}_3$ $\text{RH}_2$		$\text{RO}_4$	Platinum Pt 194.9

Mendeleev's periodic table published earlier (1905)

Figure 3.1

Dmitri Mendeleev was born in Tobolsk of Siberia in Russia. He received his Master's degree (M.Sc.) in chemistry in 1856 and the Doctoral degree (Ph.D.) in 1865.

He joined as professor of chemistry at the university of St. Petersburg in 1867. Preliminary work for his great text book *Principles of Chemistry* led Mendeleev to propose the periodic law and to construct his periodic table of elements. Mendeleev's periodic law gave encouragement to several areas of research during the subsequent decades. Periodic law and periodic table became the key to the discovery of uranium, thorium, noble gases and transuranium elements. Mendeleev invented an accurate barometer. He resigned from the professorship in 1890. Mendeleev passed away in 1907. To appreciate the work of Mendeleev, G. T. Seaborg suggested to give name Mendelevium to the element 101 discovered by him.



Dmitri Evanesvich Mendeleev  
(1834-1907)

### 3.4 Modern Periodic Law and Modern Periodic Table

When Mendeleev developed periodic table, chemists had no knowledge about internal structure of atom. However, principles about subatomic particles were developed in the beginning of 20th century. In 1913, the English physicist, Henry Moseley observed regularity in the characteristics of X-ray spectra of the elements. He plotted two types of graphs  $\sqrt{\nu}$  (where  $\nu$  is frequency of X-rays emitted) against atomic number and against atomic weight. First graph was found to be a straight line but second graph was not found to be a straight line. It indicated that atomic number was the fundamental property and not the atomic weight. As a result, periodic law of Mendeleev was corrected by putting the word 'atomic number' instead of 'atomic weight'. It is known as modern periodic law. It can be stated that

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

We know that atomic number is equal to the nuclear charge (i.e., number of protons) or number of electrons in a neutral atom. Many forms of periodic table have been considered from time to time. Some forms emphasise the electronic configuration of elements, whereas the other forms emphasise the chemical reactions and valence. "Long form" of periodic table of elements is known as modern periodic

table (Fig. 3.2) which is used widely. The elements having similar electronic configuration in their outermost orbit, are arranged in vertical column of periodic table known as group or family. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the numbering of groups is from 1 to 18 instead of numbers which are given by old method IA..... VII A, VIII, IB..... VII B and 0.

The horizontal rows in periodic table are called periods. There are altogether total seven periods. To identify the periods, numbers are given from the top of periodic table. Thus, period 3 is the third row of elements and period 4 is the fourth row of elements. First period has two elements. Following periods have 8, 8, 18, 18 and 32 elements respectively, whereas seventh period is the incomplete period. Period 1 is known as a very small period, period 2 and 3 are known as first and second small periods respectively, periods 4 and 5 are known as first and second long periods respectively, periods 6 and 7 are known as first and second very long periods respectively. List of 14 elements of both sixth and seventh periods are mentioned separately at the bottom in this form of periodic table.

Thus, we have seen the classification of elements in group, development of periodic law and periodic table are results of sincere efforts of many scientists.

Representative elements		Representative elements										Noble gases	
GROUP NUMBER		GROUP NUMBER										18	
1												0	
1A													
2A													
3A													
4A													
5A													
6A													
7A													
8A													
9A													
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### 3.5 Nomenclature of Elements with Atomic Numbers > 100

Scientist who discovers element can give the name to the newly discovered element by traditional method. This suggested name is approved by IUPAC. But nomenclature by this method created some problems. Because of the competition for discovery of new elements, scientists, before collecting the reliable data about new element, got tempted to claim for its discovery. For example, Americans and Soviets claimed for discovery of element 104. Americans named it as Rutherfordium whereas Soviets named it as Kurchotavium. The systematic nomenclature is suggested to avoid such types of problems. To use the numerals for number 0 and 1 to 9 in systematic nomenclature are shown in Table 3.4. The numerals are put together in order of digits which make up the atomic number and 'ium' is added at the end. This creates the name of an element. The nomenclature of elements with atomic number above 100 are shown in Table 3.5.

Table 3.4

Notation for IUPAC nomenclature of elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

Table 3.5

Nomenclature of elements with atomic numbers above 100

Atomic Number	Name	Sym-bol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf

105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununillium	Uun	Darmstadtium	Ds
111	Unununnium	Uuu	Rontgenium	Rg*
112	Ununbium	Uub	*	*
113	Ununtrium	Uut	+	
114	Ununquadium	Uuq	*	*
115	Ununpentium	Uup	*	
116	Ununhexium	Uuh	*	*
117	Ununseptium	Uus	+	
118	Ununoctium	Uuo	+	

\* Official IUPAC name yet to be announced

+ Elements yet to be discovered

Let us think about IUPAC name and symbol of element 119, according to Table 3.4, numerals of digit 1 and 9 are un and enn respectively. Therefore, the symbol of element (119) will be Uue and name will be Ununennium. Thus three letters consisting a symbol and a temporary name are given to the new element. Afterwards the permanent name and symbol are given to the element according to opinion of IUPAC representatives from each country. Permanent name is given considering the contribution of well known scientist or the country in which the element is discovered. For example, name Mendelevium is given to element with atomic number 101 for appreciation of Mendelev's work. This name was suggested by American scientist Glenn T. Seaborg who discovered this element. In this manner naming the element with atomic number 106 as Seaborgium is to honour the Nobel Prize winner scientist Glenn T. Seaborg.

### 3.6 Electronic Configuration of Elements and the Periodic Table :

We have learnt in previous unit about four quantum numbers which explain the characteristics of electrons, energy levels (shells) (K, L, M...), atomic orbitals (s, p, d, f) and electronic configuration of elements. Now we shall study about relation between electronic configuration of elements and long form of periodic table.

#### (a) Electronic configuration in periods :

The period number indicates value of n for outer orbit or valence shell. This can be understood from Table 3.6.



Table 3.6 Electronic configuration of elements in periods

Period number	Elements of the period and electronic configuration in their outermost orbit	Number of outermost orbits
First	Hydrogen ( $1s^1$ ) to Helium ( $1s^2$ ) ${}_1\text{H}$ to ${}_2\text{He}$	1
Second	Lithium ( $2s^1$ ) to Neon ( $2s^2 2p^6$ ) ${}_3\text{Li}$ to ${}_{10}\text{Ne}$	2
Third	Sodium ( $3s^1$ ) to Argon ( $3s^2 3p^6$ ) ${}_{11}\text{Na}$ to ${}_{18}\text{Ar}$	3
Fourth	Potassium ( $4s^1$ ) to Krypton ( $4s^2 4p^6$ ) ${}_{19}\text{K}$ to ${}_{36}\text{Kr}$	4
Fifth	Rubidium ( $5s^1$ ) to Xenon ( $5s^2 5p^6$ ) ${}_{37}\text{Rb}$ to ${}_{54}\text{Xe}$	5
Sixth	Cesium ( $6s^1$ ) to Radon ( $6s^2 6p^6$ ) ${}_{55}\text{Cs}$ to ${}_{86}\text{Rn}$	6
Seventh	Francium ( $7s^1$ ) to incomplete period ${}_{87}\text{Fr}$ to incomplete period	7

As shown in Table 3.6, the electronic configuration of the outermost orbit of the atom of every first element of each period is  $ns^1$  where as the electronic configuration of the outer most orbit of the last element is  $ns^2 np^6$  except that of the first period.

**(b) Electronic configuration in groups :** Electronic configuration in outermost orbit is similar in all elements of any group. Therefore, these elements show similar properties. For example, electronic configuration of outermost orbit of all elements of group 1 is  $ns^1$  as mentioned in Table 3.7. In same way electronic configuration of outermost orbit of all elements of halogen group is  $ns^2 np^5$ .

Table 3.7 Electronic configuration of elements of group 1

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ or $[\text{He}] 2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ or $[\text{Ne}] 3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[\text{Ar}] 4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ or $[\text{Kr}] 5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ or $[\text{Xe}] 6s^1$
87	Fr	$[\text{Rn}] 7s^1$

### 3.7 Electronic Configuration and Types of Elements : s-, p-, d-, f- blocks

Classification of elements into different blocks in periodic table is made easy due to electronic configuration of atom. It can be classified as elements in s-block, p-block, d-block, f-block based on the orbital of element filled with electron lastly as mentioned in Fig 3.3. In having such types, hydrogen and helium are found to be exceptions. Due to electronic configuration of helium it will be the element of s-block, but its place may be considered in group 18 of p-block in periodic table. This is because it has properties

similar to the other elements (noble gases) of group 18 due to its completely filled valence shell. Electronic configuration of hydrogen is  $1s^1$ . So it can be placed in group 1 but it can achieve the electronic configuration of noble gas helium by gaining one electron. Thus, its behaviour is similar to elements of group 17 (the halogen group). So H can be placed in group 1 or in group 17 but hydrogen is placed separately in the middle at the top of the periodic table as shown in Fig 3.2 and Fig 3.3. Now we will classify the elements in s-, p-, d- and f- blocks.

<i>f</i> -BLOCK														
Lanthanoids <i>4f</i>	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Actinoids <i>5f</i>														

**METALS** (     ), **NON METALS** (   ) and **METALLOIDS** (  )

The types of elements in the periodic table based on the orbitals that are being filled

**3.7.1 The s-block elements :** The electrons are filled at last in s orbital in elements of group 1 (alkali metals) and group 2 (alkaline earth metals). Electronic configuration of these orbitals are  $ns^1$  and  $ns^2$ , respectively. Therefore, these elements are known as s-block elements. They are reactive metals with low ionization enthalpy.

**3.7.2 The p-block elements :** The elements in which the p-orbital is filled at last are called p-block elements. In elements of groups 13 to 18 the last electron is filled in p orbital so, they are included in p-block. Electronic configuration of outermost orbit of elements of each period varies from  $ns^2 np^1$  to  $ns^2 np^6$ . All orbitals of valence shell of elements of group 18 are completely filled with electrons. It is stable configuration. These elements do not gain or lose electrons. These gaseous elements, are known as noble gases. These elements do not participate in chemical reaction. It means that they remain inert so they are known as inert gases.

Groups 16 and 17 are known as chalcogens and halogens, respectively. Elements of s and p-block are called representative elements and main group elements.

**3.7.3 The d-block elements : Transition elements :** Elements in which the last electron is filled in d-orbital are known as d-block elements. In elements of groups 3 to 12 the last electron is filled in d-orbital so these elements are called d-block elements. General outer electronic configuration of these elements is  $(n-1)d^{1-10} ns^{1-2}$ . These elements are transition metals.

**3.7.4 The f-block elements : Inner-transition elements :** Elements in which the last electron is filled in f-orbital are called f-block elements. Elements of two horizontal rows i.e. Ce(Z = 58)–Lu(Z = 71) (Lanthanoids) and Th(Z = 90)–Lr(Z = 103) (Actinoids) which are kept at bottom of periodic table, have electronic configuration as  $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$  in their outermost orbit. In every element of these two series, the last electron is filled in f-orbital so these elements are called f-block elements. They are also known as innertransition elements. They all are metals.

Metals appear on the left side of periodic table whereas non metals appear at the top right hand side of the periodic table. The change from metallic to non metallic character is not abrupt as shown by the thick zig-zag line in Fig : 3.3.

These elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the periodic table show properties of both metals and nonmetals, so these elements are called semimetals or metalloids.

### 3.8 Periodic Trends in Properties of Elements

Many patterns in physical and chemical properties of elements are observed in periodic table as we move from left to right in a period or from top to bottom in a group. For example, in same period, chemical reactivity trend is high in metals of group 1, low in middle elements of periodic table and increases to maximum in nonmetals of group 17. In the same way reactivity increases when we go down in group 1 whereas reactivity decreases as we go down in group 17. Why do chemical and physical properties of elements show this trend ? How can we explain the periodic trend in properties ? Here we will try to get answers of these questions.

**3.8.1 Periodic Trends in Physical properties :** We find periodic deviation in many physical properties of elements. Here we will discuss about atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy and electronegativity.

**3.8.1.1 Atomic radius :** As we know atom is a very minute particle, therefore, it is very difficult to measure the radius of individual atom. Nevertheless, an estimate for the atomic radius can be given by knowing the distance between the atoms in a molecule. Atomic radius can be measured by X-rays or other spectroscopic methods. Average half value of distance between nuclei of two atoms in covalent molecule is considered as atomic radius. It is known as covalent radius of element. For example, the bond distance in chlorine molecule ( $Cl_2$ ) is 198 pm. The half value (99 pm) of this distance is taken as atomic radius of chlorine. Average half value of distance of nucleus between two adjacent atoms in metallic crystal is called radius of metal element. It is known as metallic radius. For example, the distance between two adjacent copper atoms in solid copper is 256 pm so, metallic radius of copper will be 128 pm.

Atomic radius is related with electronic configuration of atoms. As shown in Table 3.8 (a) the positive charge increases with increase in atomic number of elements when we move from left to right in the period.



On the other hand number of electrons increases in outermost orbit. The number of outermost orbit (principal quantum number  $n$ ) does not increase so the distance of electron from nucleus does not increase. As a result the force of attraction acting on the electron towards the nucleus increases which causes shrinking in the atomic orbital, hence the atomic radius decreases. It is shown in Fig. 3.4 (a) for the elements of the second period. There is a negligible change in the atomic radius of d-block and f-block elements present in the middle of the long period.

**Table 3.8 (a) Atomic radius in periods (pm)\***  
(For information only)

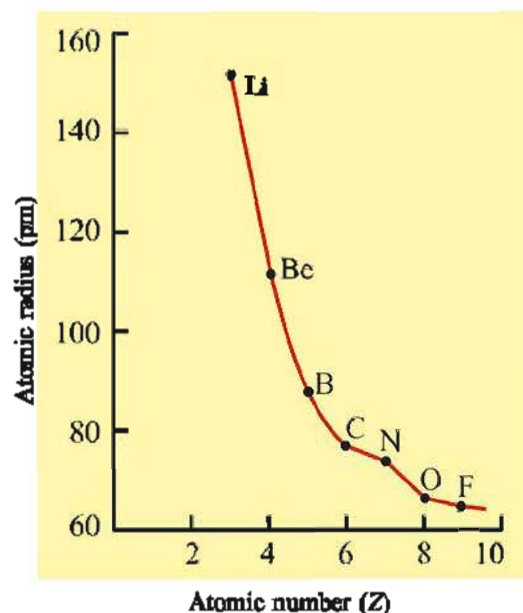
Atom (Period II)	Li	Be	B	C	N	O	F
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Atomic radius	186	160	143	117	110	104	99

pm\* = Picometer =  $10^{-12}$  meter

As shown in table 3.8(b) when we move from top to bottom in a group, principal quantum number ( $n$ ) increases with increase in atomic number, so valence electrons are farther away from the nucleus. Therefore, the positive charge of nucleus increases despite of decreasing of the attraction on electrons towards nucleus. Thus orbits expand and the atomic radius increases. It is explained in Fig. 3.4 (b) for alkali metals and halogen group.

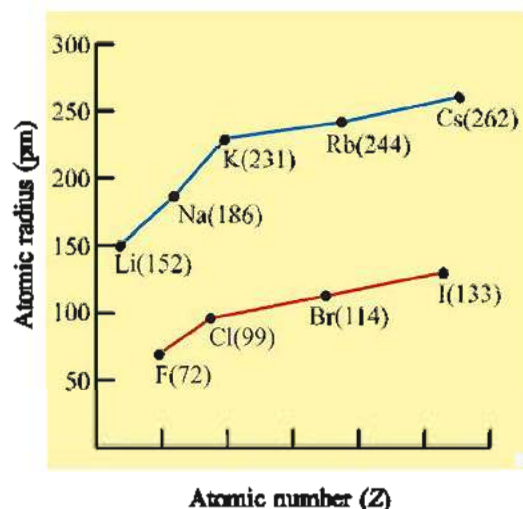
**Table 3.8 (b) Atomic radius (pm) in group**  
(For information only)

Atom (Group 1)	Atomic radius	Atom (Group 17)	Atomic radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140



Variation of atomic radius with atomic number across the second period

Figure 3.4 (a)



Variation of atomic radius with atomic number for alkali metals and halogens.

Figure 3.4 (b)

In the end of above discussion we will try to arrange three elements viz. Al, C and Si in ascending order of their atomic radii. The sequence becomes  $C < Si < Al$ . It is because atomic radius decreases when we move from left to right in same period. Al ( $Z=13$ ), Si ( $Z=14$ ) belong to same period (third period), Therefore sequence of their atomic radius is  $Si < Al$ ; where as C ( $Z=6$ ) and Si ( $Z=14$ ) belong to group 14. We know that the atomic radius increases when we move from top to bottom in a group. Hence the sequence becomes  $C < Si$ ,



**3.8.1.2 Ionic radius :** Generally atom forms positive ion by loss of electron and negative ion by gain of electron. Ionic radius can be measured by measuring the distance between positive ion and negative ion in ionic crystals. The positive ion is smaller than its parent atom because it has less electrons, whereas their positive charges are similar. This means that effective nuclear charge is higher in positive ion than its parent atom. For example, 11 protons attract 11 electrons in Na, whereas 11 protons attract 10 electrons in  $\text{Na}^+$ , so ionic radius of  $\text{Na}^+$  is 95 pm and atomic radius of Na is 186 pm. The size of negative ion is bigger than its parent atom because it has more electrons whereas their positive charges are same. Hence the effective nuclear charge is lower in negative ion than its parent atom. For example, 9 protons attract 9 electrons in F. Whereas 9 protons attract 10 electrons in  $\text{F}^-$ . Ionic radius of  $\text{F}^-$  is 136 pm and atomic radius of F is only 64 pm. Ionic radii of elements show similar trend to the atomic radii in periodic table.

We also find equal number of electrons in some atoms and ions. They are known as isoelectronic species. For example,  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  all have equal number of electrons (10). Their radii are different because they have different nuclear charges. Effective nuclear charge is increased due to higher positive charge in a positive ion so its radius will be small, the effective nuclear charge is decreased due to higher negative charge in a negative ion which results in bigger radius.

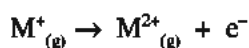
Now, we will think about size of Mg,  $\text{Mg}^{2+}$ , Al and  $\text{Al}^{3+}$  species. The Mg has the largest size and  $\text{Al}^{3+}$  has the smallest size. It is so because Mg and Al belong to the same period (period 3) and in the same period atomic radius decreases when we move from left to right so that  $\text{Al} < \text{Mg}$ . In isoelectronic species when the positive charge increases then the radius decreases. Hence  $\text{Al}^{3+} < \text{Mg}^{2+}$ . Moreover size

of positive ion is smaller than its parent atom. Therefore,  $\text{Mg}^{2+} < \text{Mg}$  and  $\text{Al}^{3+} < \text{Al}$ . Besides this, because of higher effective nuclear charge in  $\text{Mg}^{2+}$  than Al, it becomes  $\text{Mg}^{2+} < \text{Al}$ .

**3.8.1.3 Ionization enthalpy :** The minimum energy required for formation of positive ion from gaseous neutral atom (M) by removing electron, is called ionization enthalpy (energy). First ionization enthalpy is the energy required to remove first electron. In other words first ionization enthalpy of an element M is the difference of enthalpy ( $\Delta_i H_1$ ) for the reaction shown by the following equation

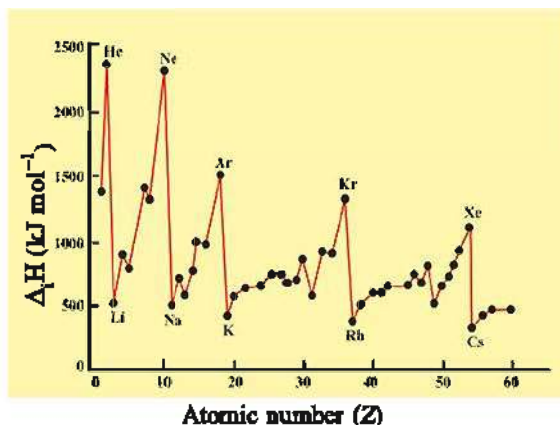


The ionization enthalpy is expressed in units of  $\text{kJ mol}^{-1}$ . Energy required to remove the second electron from element M is called second ionization enthalpy ( $\Delta_i H_2$ ).



The second ionization enthalpy will be higher than the first ionization enthalpy because of increased effective nuclear charge. The force of attraction of outermost electron towards the nucleus increases with increase in effective nuclear charge. Removal of electrons having higher force of attraction towards the nucleus requires more energy. Thus, ionization enthalpy also increases with increased effective nuclear charge. The energy required to remove the third electron is called third ionization enthalpy ( $\Delta_i H_3$ ). Its value is found higher than the second ionization enthalpy. Thus, the value of next ionization enthalpy increases gradually as  $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3, \dots$

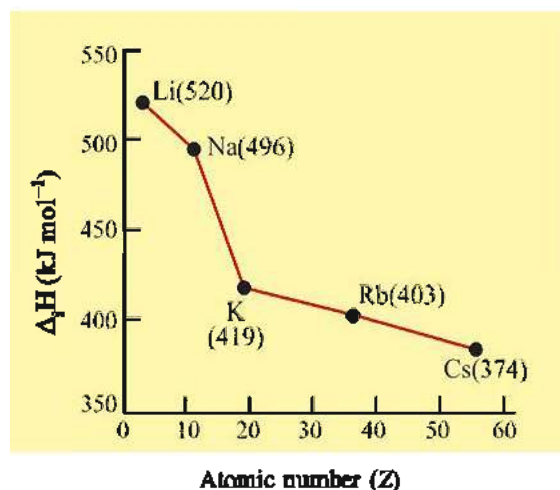
Relation between atomic number and first ionization enthalpy of elements having atomic numbers 1 to 60 is shown in Fig. 3.5. It indicates that values of first ionization enthalpy of noble gases are maximum. Whereas these values are minimum for alkali metals because the outermost orbit of noble gases is completely filled which gives higher stability. It is more difficult to remove electron from noble gases, whereas less energy is required to remove electrons from alkali metals due to their high reactivity.



Relation between first ionization enthalpies and atomic number with  $Z = 1$  to 60

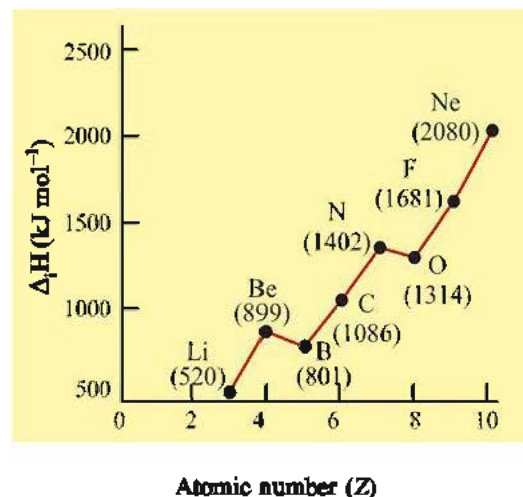
Figure 3.5

The inner orbital electrons of an element fulfil the need to shield or screen valence electrons and causes decreased attraction of valence electrons towards the nucleus. It results in decreased ionization enthalpy of valence electrons. This effect is called shielding or screening effect. When shielding effect increases then ionization enthalpy decreases. So, in any group when we move from top to bottom then ionization enthalpy decreases with increase in atomic number. This type of trend is clearly observed in representative elements. This can be seen in the graph of first ionization enthalpy of alkali metal elements and their atomic numbers as shown in Fig. 3.6 (a).



Relation between first ionization enthalpies of alkali metals elements and their atomic number

Figure 3.6 (a)



Relation between first ionization enthalpies of second period elements and their atomic number

Figure 3.6 (b)

In a period, when we move from left to right then ionization enthalpy increases with increase in atomic number. As shown Fig 3.6 (b) the ionization enthalpy increases from Li to Ne. In elements of same period as the atomic number increases positive charge of nucleus also increases. The outermost orbit remains the same for elements of the same period. This means that the distance of electrons of outermost orbit from nucleus does not increase, so the shielding effect for outer electrons also does not increase. That is why the force of attraction on electrons towards the nucleus increases due to increase in positive charge of nucleus. It results in the increase of enthalpy required to remove an electron from atom.

It can be seen from Fig 3.6(b) that boron ( $Z = 5$ ) has higher nuclear charge than beryllium ( $Z = 4$ ), even then its value of ionization enthalpy is low. What can be the reason for this? Let us think about it. Electronic configurations of beryllium and boron are  $1s^2 2s^2$  and  $1s^2 2s^2 2p^1$ , respectively. The electron to be removed is in  $2s$  orbital in beryllium and in  $2p$  orbital in boron. Therefore, more energy is required to remove the electron from beryllium than boron. The  $s$  type electron is in spherical orbital, hence it is nearer to nucleus than the electron of  $p$ ,  $d$  and  $f$  orbital of same orbit. The  $s$ -type electron which is nearer to nucleus remains highly attracted towards nuclear charge and so it is more difficult to remove it. If all the factors remain same then the ionization enthalpy decreases as we go from  $s \rightarrow p \rightarrow d \rightarrow f$  orbital with same principal quantum number.

Like boron and beryllium, the anomaly is also found in nitrogen and oxygen. The first ionization enthalpy is lower in oxygen than that of nitrogen as shown in Fig 3.6 (b). Electronic configuration of nitrogen ( $Z = 7$ ) and oxygen ( $Z = 8$ ) are  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  and  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ , respectively. In oxygen the electron-electron repulsion value increases due to two electrons filled in  $2p_x$  orbital. So it is easy to remove the fourth electron from the  $2p$  orbital in oxygen than the removal of any one electron out of three electrons from  $2p$  orbital in nitrogen.

The first ionization enthalpies of the elements Na, Mg and Si of third period are 496, 737, and 786  $\text{kJ mol}^{-1}$ , respectively. Will the first ionization enthalpy of Al be closer to 575 or 760  $\text{kJ mol}^{-1}$ ? Let us think about it.

Electronic configuration of Na ( $Z = 11$ ) is  $[\text{Ne}] 3s^1$

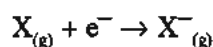
Electronic configuration of Mg ( $Z = 12$ ) is  $[\text{Ne}] 3s^2$

Electronic configuration of Al ( $Z = 13$ ) is  $[\text{Ne}] 3s^2 3p^1$

Electronic configuration of Si ( $Z = 14$ ) is  $[\text{Ne}] 3s^2 3p^2$

As mentioned in the question, probable value of ionization enthalpy of Al (575 or 760  $\text{kJ mol}^{-1}$ ) is nearer to the value of ionization enthalpy of Mg (737  $\text{kJ mol}^{-1}$ ). Thus we will have to study carefully about the electron configuration of Al and Mg. This suggests that less energy is required to remove an electron from  $3p$  orbital of Al than to remove an electron from  $3s$  orbital of Mg, so the value of first ionization enthalpy of Al will be 575  $\text{kJ mol}^{-1}$ .

**3.8.1.4 Electron gain enthalpy :** Addition of an electron to neutral gaseous atom (X) converts it into negative ion which results in change of enthalpy. This is known as electron gain enthalpy ( $\Delta_{\text{eg}}H$ ).



The reaction of adding an electron to the atom may be either exothermic or endothermic; it depends on corresponding element. When an electron is added to the atom then energy is released, so the value of electron gain enthalpy is negative. For example, elements of group 17 (halogens) have very high negative electron gain enthalpy. It is because they accept an electron and achieve the stable

electronic configuration similar to nearest noble gas element. The noble gas elements have more positive values of electron gain enthalpy because the added new electron enters in the next higher energy level orbit. Therefore, it becomes very unstable configuration. Thus, when the value of electron gain enthalpy is more negative than negative ion is easily formed which is more stable.

Generally if effective nuclear charge increases then trend of attraction of added electron towards nucleus increases. The elements with small size can easily show this trend. Therefore, in a period when we move from left to right the effective nuclear charge increases as the atomic number increases and the value of electron gain enthalpy becomes more negative. This trend is not exactly so. For example when  $\text{Be}^-$  is formed then added electron enters the energy orbital ( $2p$ ) which is higher than the valence orbital ( $2s$ ). This is not a stable state because the value of electron gain enthalpy becomes less negative. In the same way, generally the nitrogen atom also does not show the trend to accept electron because when an electron is added to it then  $2p_x$  orbital gains two electrons. This causes increased electron-electron repulsion due to which it becomes unstable.

In a group when we move from top to bottom then the added electron is found farther away from the nucleus due to increased atomic size. This results in decreased attraction of added electron towards the nucleus. Hence, the trend of atom to become negative ion by accepting electron, decreases gradually. Thus, generally, when we go from top to bottom the value of electron gain enthalpy becomes more negative (Table 3.9) but the electron gain enthalpy of O or F is less negative than that of the succeeding elements of the same group (S or Cl respectively) (Table 3.9). This is because in O or F, the added electron takes place in lower energy level  $n = 2$  which is already having 6 or 7 electrons. This results in more electron-electron repulsion which decreases the stability of negative ion, whereas in S and Cl added electron takes the place at higher energy level  $n = 3$ . Therefore, less electron-electron repulsion occurs.

**Table 3.9 Values of electron gain enthalpy ( $\text{kJ mol}^{-1}$ ) of some representative elements (For information only)**

Group 1	( $\Delta_{\text{eg}}\text{H}$ )	Group 16	( $\Delta_{\text{eg}}\text{H}$ )	Group 17	( $\Delta_{\text{eg}}\text{H}$ )	Group 18	( $\Delta_{\text{eg}}\text{H}$ )
						He	+48
Li	-60	O	-141	F	-328	Ne	+116
Na	-53	S	-200	Cl	-349	Ar	+96
K	-48	Se	-195	Br	-325	Kr	+96
Rb	-47	Te	-190	I	-295	Xe	+77
Cs	-46	Po	-174	At	-270	Rn	+68

Now to make the firm discussion about electron gain enthalpy stronger we have to get solution of the question- 'among P, S, Cl and F which one has the most negative and which one has the least negative electron gain enthalpy ?' Generally, in a period, when we move from left to right then the electron gain enthalpy becomes more negative. So the order of negative value of electron gain enthalpy for P, S and Cl elements of third period is  $\text{P} < \text{S} < \text{Cl}$ . F and Cl are members of group 17. Added new electron takes place in 2p orbital in F and in 3p orbital in Cl. As we know, repulsion between electron-electron in 2p orbital is higher than in 3p orbital. So the electron can enter easily in 3p orbital. Therefore, order of negative value of electron gain enthalpy is  $\text{F} < \text{Cl}$ . Thus, Cl has the most negative electron gain enthalpy and P has the least negative electron gain enthalpy.

**3.8.1.5 Electronegativity :** The ability of an atom in a chemical compound to attract shared electrons of bond towards itself is called electronegativity. It is not possible to measure its absolute value, unlike ionization enthalpy and electron gain enthalpy. Although many numerical scales of electronegativity of elements have been developed such as Pauling Scale, Mulliken-Jaffe Scale and Alfred Rochow Scale. Out of these, the Pauling scale is widely used. In 1922, an American scientist Linus Pauling assigned arbitrarily the value for electronegativity. He considered to have studied the concept of

ability to attract electrons for fluorine and suggested the value of 4.0 to fluorine. As an another option, accepting the electronegativity of lithium atom as unity, the value of electronegativity of F becomes 4.0 which supports the electronegativity concept of Pauling. As we have understood previously, when the atomic radius of atom increases then, attraction of electrons of outermost orbit towards nucleus decreases. On the contrary when the atomic radius decreases then the attraction of electrons of outermost orbit towards nucleus increases. This means that the electronegativity of atom (small size) having small atomic radius is higher than that of the atom (big size) having more atomic radius. Thus in a period when we move from left to right then the electronegativity increases as the atomic radius of atom decreases (Table 3.10 (a)).

**Table 3.10 (a) Electronegativity values (on Pauling scale) in periods**

Atom (Period II)	Li	Be	B	C	N	O	F
Electro-negativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electro-negativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

In a group when we move from top to bottom the electronegativity decreases because atomic radius of the atom increases.

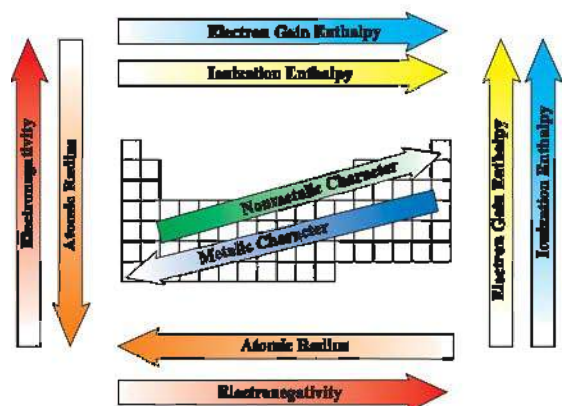


**Table 3.10 (b) Electronegativity values (on Pauling scale) in group**

Atom (Group 1)	Electro-negativity	Atom (Group 17)	Electro-negativity
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

We know that the non-metallic elements have strong tendency to gain electron. Thus, there is a direct relation of electronegativity with the non-metallic properties. In other words, there is an inverse relation of electronegativity with the metallic properties. Thus, in a period when we move from left to right the non-metallic character increases and the electronegativity also increases. In a group when we move from top to bottom the electronegativity and non-metallic properties decrease. So, in a period when we move from left to right the electropositivity decreases and electronegativity increases.

The periodic trends in physical properties of elements are shown in brief in Fig. 3.7.



The periodic trends in physical properties of elements in the periodic table

Figure 3.7

### 3.8.2 Periodic Trends in Chemical

**Properties :** Most of the trends in chemical properties of elements such as diagonal relationship, inert pair effect, effect of lanthanoid contraction etc. will be explained along with the discussion of each group in later units. Here,

we will study about the valence or state of oxidation elements.

#### 3.8.2.1 Periodicity of Oxidation State or Valence :

The valence is the important property of an element. It can be easily understood by electronic configuration of an element. The valence of representative elements is usually equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of outermost electrons. This can be mentioned below :

Group	1	2	13	14	15	16	17	18
Number of valence electron	1	2	3	4	5	6	7	8
valence	1	2	3	4	3,5	2,6	1,7	0,8

The word oxidation state is also used for valence. Let us consider two compounds containing oxygen- $\text{OF}_2$  and  $\text{Na}_2\text{O}$ . The order of electronegativity of elements present in these compounds is  $\text{F} > \text{O} > \text{Na}$ . Electronic configurations of outermost orbits of O, F, and Na are  $2s^2 2p^4$ ,  $2s^2 2p^5$  and  $3s^1$  respectively. In  $\text{OF}_2$ , fluorine atom shares one electron with oxygen atom, fluorine being more electronegative element contains  $-1$  oxidation state whereas O atom shares two electrons with fluorine atoms, so oxidation state of O is  $(+2)$ . In  $\text{Na}_2\text{O}$  oxygen being more electronegative accepts two electrons from two sodium atoms. Because of this its oxidation state is  $(-2)$ . On the other hand sodium atom loses one electron from  $3s$  orbital which shows its  $(+1)$  oxidation state. Thus the oxidation state of an element in a particular compound is the charge acquired by its atoms from other atoms on the basis of electronegativity consideration in molecule. Table 3.11 shows some periodic trends in valence of elements.

**Table 3.11 Periodic trends in valence of elements  
(as formulae of compounds of elements)**

Group	1	2	13	14	15	16	17
Formula of hydride	LiH	CaH <sub>2</sub>	B <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> O	HF
	NaH		AlH <sub>3</sub>	SiH <sub>4</sub>	PH <sub>3</sub>	H <sub>2</sub> S	HCl
	KH			GeH <sub>4</sub>	AsH <sub>3</sub>	H <sub>2</sub> Se	HBr
				SnH <sub>4</sub>	SbH <sub>3</sub>	H <sub>2</sub> Te	HI
Formula of oxide	Li <sub>2</sub> O	MgO	B <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>6</sub> , P <sub>4</sub> O <sub>10</sub>	SeO <sub>3</sub>	
	K <sub>2</sub> O	SrO	Ga <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub> , As <sub>2</sub> O <sub>5</sub>	TeO <sub>3</sub>	
		BaO	In <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>5</sub>		
				PbO <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>		

Now let us see, what would be the formula of compound formed from Si and Br ? The answer is SiBr<sub>4</sub> because Si is the member of group 14 so its valence becomes (+4) and Br is the member of group 17 so its valence becomes (-1). Similarly the

formula of compound formed from Al and S becomes Al<sub>2</sub>S<sub>3</sub> because the valence of Al is (+3) and that of S is (-2).

We shall study later on about the transition and innertransition elements containing different valence or oxidation states.

### SUMMARY

In early 1800 several efforts were made to classify newly invented and existing elements of the world. In which Dobereiner, A.E.B. De Chancourtois, John Newlands, Lothar Meyer and Mendeleev contributed elegantly. Modern periodic table exists on the basis of atomic number which is developed from the Mendeleev's old periodic table considering the atomic weight as the fundamental property. Modern periodic table is classified into 18 groups and 7 periods. Because of the same number of electrons in outermost orbit of element of the same group, they show similar chemical properties. Elements of same period have same quantum number (n) of outermost orbit. Classification of elements of periodic table in s, p, d, and f- blocks is based on filling of last electron in that orbital of element. Elements of s and p blocks are known as representative elements or main group elements; d-block elements as transition elements and; f-block elements as innertransition elements. When we move from left to right in a period in the periodic table, then, due to increase in atomic number of element, ionization enthalpy, negative value of electron gain enthalpy and value of electronegativity increase. On the other hand atomic radius and metallic property decrease. When we move from top to bottom in a group, then, due to increase in atomic number of element, ionization enthalpy, negative value of electron gain enthalpy and value of electronegativity decrease. On the other hand atomic radius and metallic property increase.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) By which name the Eka-silicon element is known after its discovery ?  
 (A) Gallium (B) Germanium  
 (C) Tellurium (D) Indium

- (2) Uub means.....  
(A) element having atomic number 111 (B) element having atomic number 112  
(C) element having atomic number 113 (D) element having atomic number 114
- (3) Who suggested "Mendelevium" name for the element having atomic number 101 ?  
(A) Mendeleev (B) Dobereiner  
(C) Seaborg (D) Newlands.
- (4) Which electronic configuration from the following would be the element of third period ?  
(A)  $[\text{Ar}] 3d^7 4s^2$  (B)  $[\text{Ne}] 3s^2 3p^4$   
(C)  $[\text{Ar}] 3d^1 4s^2$  (D)  $[\text{Ar}] 3d^3 4s^2$
- (5) Which group contains the element having electronic configuration  $[\text{Ne}] 3s^2 3p^2$  ?  
(A) 14 (B) 15  
(C) 16 (D) 17
- (6) Which electronic configuration from the following is of s-block element ?  
(A)  $[\text{Ar}] 3d^2 4s^2$  (B)  $[\text{Ar}] 4s^2$   
(C)  $[\text{Ar}] 3d^3 4s^2$  (D)  $[\text{Xe}] 4f^4 5d^0 6s^2$
- (7) Which elements have the electronic configuration  $ns^2 np^6$  in their outermost orbit ?  
(A) Alkali metals (B) Transition metals  
(C) Noble gases (D) Innertransition metals
- (8) What is not consistent about atomic radius ?  
(A) Decreases when we move from left to right  
(B) Increases when we go from top to bottom  
(C) Increases with increase in principal quantum number  
(D) Increases with increase in positive charge of nucleus
- (9) Which is true from the following ?  
(A) Size of  $\text{Al}^{3+} < \text{Size of Al}$  (B) Size of  $\text{Al}^{3+} > \text{Size of Al}$   
(C) Size of  $\text{F}^- < \text{Size of F}$  (D) Size of  $\text{Na}^+ = \text{Size of Na}$
- (10) For which element the highest shielding effect for outermost electron is observed ?  
(A) Element of group 13 and period 2 (B) Element of group 13 and period 3  
(C) Element of group 13 and period 4 (D) Element of group 13 and period 5
- (11) Which one is the descending order of atomic radius of elements of third period.  $\text{Na}(Z = 11)$ ,  $\text{Mg}(Z = 12)$ ,  $\text{Al}(Z = 13)$  and  $\text{Si}(Z = 14)$  ?  
(A)  $\text{Si} > \text{Al} > \text{Mg} > \text{Na}$  (B)  $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$   
(C)  $\text{Na} < \text{Mg} < \text{Al} < \text{Si}$  (D)  $\text{Na} > \text{Al} > \text{Mg} > \text{Si}$
- (12) Which order is true with reference to size of species ?  
(A)  $\text{Pb} < \text{Pb}^{2+} < \text{Pb}^{4+}$  (B)  $\text{Pb}^{4+} > \text{Pb}^{2+} > \text{Pb}$   
(C)  $\text{Pb} > \text{Pb}^{2+} > \text{Pb}^{4+}$  (D)  $\text{Pb}^{2+} < \text{Pb} < \text{Pb}^{4+}$

**2. Write the answers of the following questions in brief :**

- (1) Who gave the law of triads ?
- (2) Mention the temporary name of element having atomic number 114.
- (3) Write the general electronic configuration of f-block elements.
- (4) Which periods are called very long periods ?
- (5) Which electronic configuration occurs in outermost orbit of element of group 17 and period 3 ?
- (6) Which one has the largest size among  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ , and  $\text{Cr}$  ?

### 3. Write the answers of the following questions :

(1) Give definitions :

- |                         |                             |
|-------------------------|-----------------------------|
| (1) Modern periodic law | (8) Semimetal               |
| (2) Group               | (9) Covalent radius         |
| (3) Period              | (10) Metallic radius        |
| (4) Elements of s-block | (11) Ionization enthalpy    |
| (5) Elements of p-block | (12) Shielding effect       |
| (6) Elements of d-block | (13) Electron gain enthalpy |
| (7) Elements of f-block | (14) Electronegativity      |

(2) Describe the efforts of following scientists about the classification of elements :

- |                             |                      |
|-----------------------------|----------------------|
| (1) Johann Dobereiner       | (4) Lothar Meyer     |
| (2) A. E. B.de Chancourtois | (5) Dmitri Mendeleev |
| (3) John Newlands           |                      |

- (3) Why is the size of positive ion smaller than its parent atom ?
- (4) Why is the size of negative ion larger than its parent atom ?
- (5) Mention the oxidation state of Ba and O in the compound BaO formed from Ba(group 2) and (group 16).
- (6) Arrange in decreasing order of size of  $K^+$ ,  $Cl^-$ ,  $S^{2-}$ ,  $Ca^{2+}$ . Give reason.
- (7) Arrange in increasing order of size :  $Na^+$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $F^-$ ,  $O^{2-}$ ,  $C^{4-}$ . Give reason.
- (8) Out of Na and K which one has lower value of ionization enthalpy ? Why ?
- (9) Which element from Na, I, Cl and Ar can form stable negative ion by easily gaining one electron ?
- (10) Which element from Li, B, N, O, and C has the highest electronegativity ? Why ?

### 4. Write the answers of the following questions in detail :

- (1) Describe the history of development of periodic table.
- (2) Mention the outline of modern periodic table.
- (3) Discuss the classification of elements in s, p, d, and f- block.
- (4) Explain the change in atomic radii when we move from left to right in a period.
- (5) In a group when we move from top to bottom the atomic radii of elements increase. Explain giving reasons.
- (6) What is ionization enthalpy ? In a group when we move from top to bottom, the values of ionization enthalpies decrease. Explain giving reasons.
- (7) In a period, when we move from left to right, the values of ionization enthalpies increase. Explain giving reasons.
- (8) Why the value of third ionization enthalpy of element is more than that of the second ionization enthalpy which is more than that of first ionization enthalpy ?
- (9) What is electron gain enthalpy ? The values of electron gain enthalpy become more negative as we move from left to right in the period ? Explain giving reasons.
- (10) In the same group with the increase in atomic number the values of electron gain enthalpies are found to be less negative ? Why ?
- (11) Explain the changes in electronegativity when we move from top to bottom in the same group and when we move from left to right in the same period.
- (12) What is an oxidation state ? Explain by giving an example.



## REDOX REACTIONS

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### 4.1 Introduction

#### 4.2.1 Oxidation and Reduction

#### 4.2.2 Oxidation - Reduction and Electron Transfer Methods

### 4.3 Competitive Electron Transfer Reaction

### 4.4 Oxidation Number

#### 4.4.1 Rules for the calculation of Oxidation Number

#### 4.4.2 Calculation of Oxidation Number

#### 4.4.3 Oxidation Number and Redox Reaction

### 4.5 Oxidation Number and Nomenclature

### 4.6 Equation of Redox Reaction

### 4.7 Balancing of Redox Reaction Equation

#### 4.7.1 Balancing of Redox Reaction equation using Oxidation Number Method.

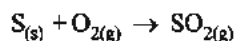
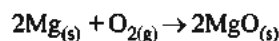
#### 4.7.2 Balancing of Redox Reaction equation using Half Reaction equation Method

### 4.1 Introduction

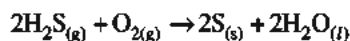
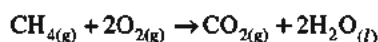
In chemical reaction when there is oxidation reaction, there is always reduction reaction. Hence, study of redox reactions are essential. Many phenomena are included in chemistry. One of them is the change from one phenomenon to the other one, substance is converted to the other substance at the end of chemical reaction. One of them is redox reaction. Redox reactions are related to physical and biological phenomena. The wider use of this reaction is found in different fields like pharmaceutical science, biology, industrial metallurgy, agriculture etc. The redox reactions are included in obtaining household energy in the use of different types of fuels for commercial purpose, production of compounds like caustic soda. In recent time hydrogen as an economy energy source and also holes in ozone layer are notable redox reactions.

#### 4.2.1 Oxidation and Reduction :

Basically the word oxidation is used to describe addition of oxygen to the substance. Many substances combine with oxygen because of its presence in atmosphere (nearly 20%). Because of this reason generally they are found in the form of oxides, the following reactions indicate oxidation :

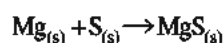
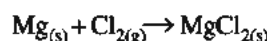
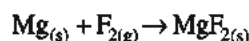


In the above reactions, by addition of oxygen to  $\text{Mg}_{(s)}$  and  $\text{S}_{(s)}$  oxidation reactions take place.

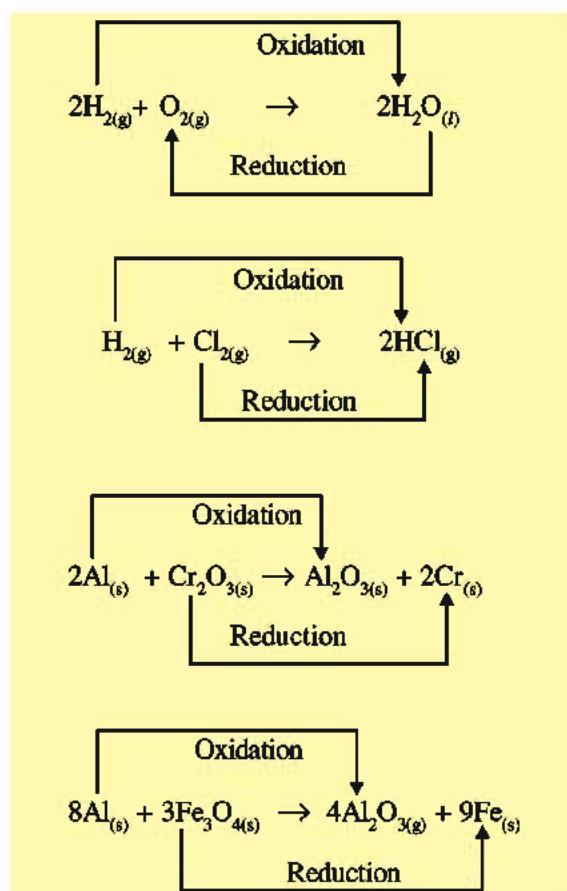


In the above reactions, with addition of oxygen, hydrogen is removed. Removal of hydrogen is called oxidation.

As mentioned in the following reactions Mg metal, reacts with difluorine, dichlorine and sulphur and experiences oxidation.



The reaction, in which oxygen is added or hydrogen is removed, is known as oxidation reaction but the reaction in which hydrogen is added or oxygen is removed is known as reduction. Hence, oxidation and reduction are reactions opposite to each other.

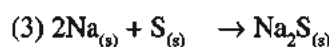
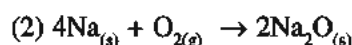
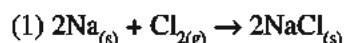


The substance which loses oxygen or gains hydrogen is called oxidizing agent.

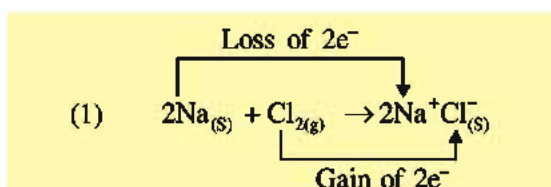
Oxidizing agent is reduced in the above reaction. Oxygen, chlorine, chromium trioxide, ferrous ferric oxide ( $\text{Fe}_3\text{O}_4$ ) are oxidizing agents. The substance which loses hydrogen or gains oxygen is called reducing agent. In the above reactions hydrogen and aluminium are reducing agents. During the reaction, reducing agent is oxidized.

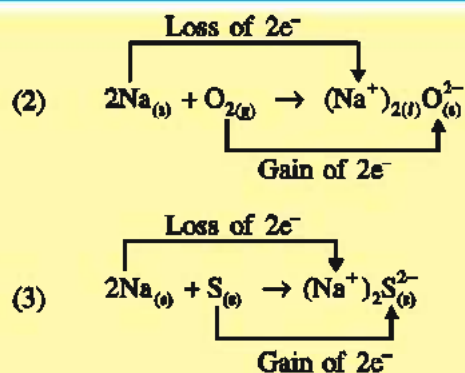
During the complete redox reaction oxidizing agent is reduced and the reducing agent is oxidized. Simultaneous oxidation reduction reactions are called redox reactions. Some methods are used to explain redox reactions, in which oxygen or hydrogen may not be taking part in the reaction.

#### 4.2.2 Oxidation-Reduction and Electron Transfer Method :

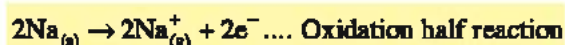


Above are redox reactions because sodium (Na) is converted into sodium chloride, sodium oxide and sodium sulphide. During this, the oxidation of sodium occurs with the addition of electronegative elements. Chlorine, oxygen and sulphur are reduced. All these elements are reacted with positively charged sodium ion.  $\text{NaCl}$ ,  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{S}$  are ionic compounds, they can be written as  $\text{Na}^+\text{Cl}^-$ ,  $(\text{Na}^+)_2\text{O}^{2-}$  and  $(\text{Na}^+)_2\text{S}^{2-}$ . The above equations can be written in ionic forms as follows :

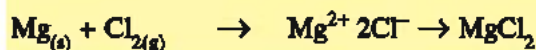
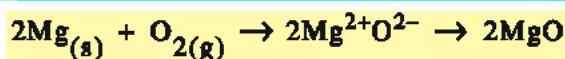




To make it simple, the above reactions can be divided into two independent steps. In the first step electron is lost and in the second step electron is gained. Electron exchange reactions can be written as.



Above reactions are called oxidation and reduction half reactions. Both the half reactions indicate the path of flow of electrons. The combination of these two reactions indicate the complete redox reaction. The reactions of magnesium with oxygen and chlorine can be explained by showing their outermost orbital electrons and the complete reaction can be written as.



In the above reactions one atom of magnesium gives two electrons to one oxygen atom and two electrons to two chlorine atoms. As the number of electrons decreases in magnesium some positive charge is produced, and the number of electrons in oxygen atom and chlorine atom increases and so negative charge is produced on these atoms. Both these examples are the reduction-oxidation or redox reactions.

Redox reaction is such a reaction in which the exchange of electrons takes place from one reactant to the other reactant. Positively charged ion is obtained by loss of electron during oxidation reaction; while in reduction reaction there is decrease in positive charge and if the reactant is neutral, then it gives negative ion. The reactant which receives the electron and gets reduced is called oxidizing agent. Similarly, the reactant which loses electron and gets oxidized is called reducing agent. In the above reactions Mg loses the electrons and so it becomes reducing agent; while chlorine receives the electrons and so becomes oxidizing agent.

#### 4.3 Competitive Electron Transfer Reaction

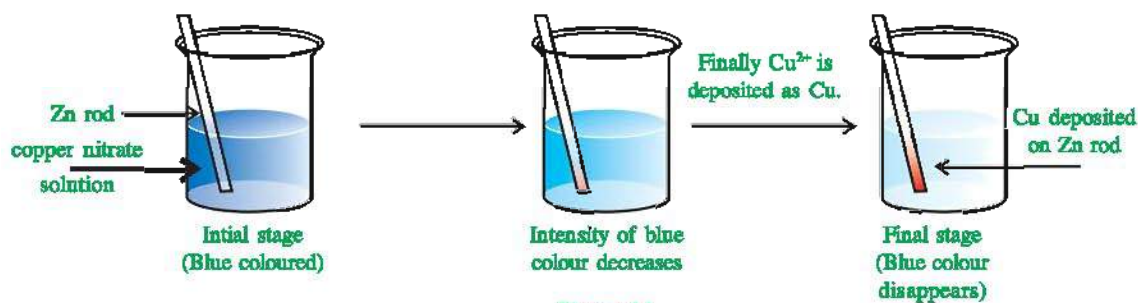


Figure 4.1

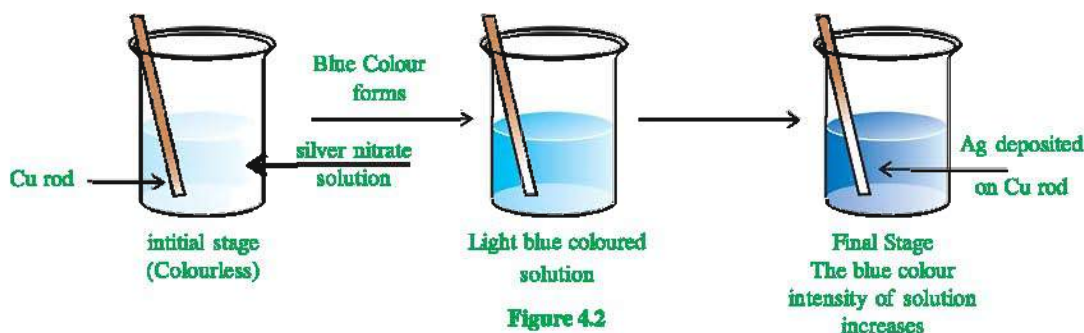
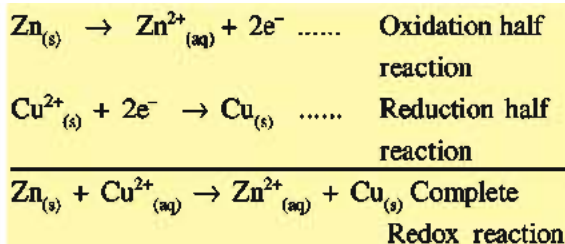
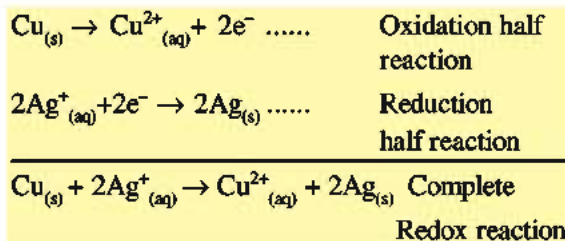


Figure 4.2

As shown in Fig. 4.1 when a rod of zinc (Zn) is placed in a solution of copper nitrate for some time, it is observed that the blue colour of copper nitrate solution disappears and reddish coloured copper (Cu) metal is deposited. As the  $\text{Cu}^{2+}$  ions are reduced in the solution, copper (Cu) is deposited on zinc (Zn) rod and the blue colour of solution disappears and a solution containing  $\text{Zn}^{2+}$  ions is formed which is colourless. The chemical reactions occur as follows :

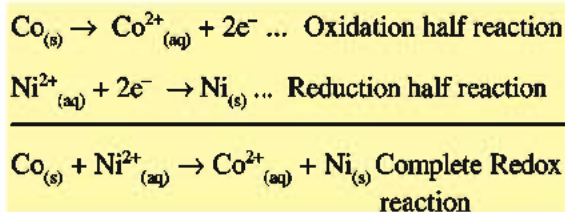


As shown in Fig. 4.2 when copper rod is placed in a solution of silver nitrate ( $\text{AgNO}_3$ ) for some time, and observed, it is found that the  $\text{Ag}^+$  ions in the solution are reduced and silver metal is deposited on copper rod. The copper rod is oxidized to  $\text{Cu}^{2+}$  ions so that the colour of solution becomes blue. The chemical reactions are as follows :



Redox reactions are shown by such type of two reactions. Hence the number of electrons lost and the electrons received in the complete reaction are equal. It is always necessary to balance the redox reactions.

Similarly, the redox reaction between cobalt metal and nickel sulphate solution occurs as follows :



#### 4.4 Oxidation Number

Some redox reactions can be explained by electron exchange method but some of the reactions cannot be clearly explained by electron exchange method. In the study of this type of

redox reactions the explanation of oxidation number is very important.

Any element or a compound is neutral while the element in certain compounds are not neutral but they possess positive or negative electrical charge. Hence, the oxidation number of element present in simple ionic compounds is equal to the electric charge on that element.

The oxidation number is expressed on the basis of number of electrons lost or gained by an element, molecule or ion. Thus oxidation state indicates the electrical charge of that atom.

##### 4.4.1 Rules for Calculation of Oxidation Number :

- The oxidation number of each neutral atom molecule or compound is considered zero e.g Na, Mg, Ca, Ba,  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{P}_4$ ,  $\text{S}_8$ , NaCl, CaO,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$
- The oxidation number of free ions which are of the same atom as well as in their ionic compounds is considered same as the electric charge on the ion e.g.  
 In  $\text{MgCl}_2$   $\text{Mg}^{2+} = +2$  and  $\text{Cl}^- = -1$   
 In NaCl  $\text{Na}^+ = +1$  and  $\text{Cl}^- = -1$   
 In CaO  $\text{Ca}^{2+} = +2$  and  $\text{O}^{2-} = -2$   
 In  $\text{AlCl}_3$   $\text{Al}^{3+} = +3$  and  $\text{Cl}^- = -1$   
 In FeS  $\text{Fe}^{2+} = +2$  and  $\text{S}^{2-} = -2$   
 In  $\text{Sb}_2\text{S}_3$   $\text{Sb}^{3+} = +3$  and  $\text{S}^{2-} = -2$
- The oxidation number of negative ions is same as their electric charge and oxidation number of positive ion is equal to its electric charge e.g.  
 $\text{NH}_4^+$  has +1  
 $\text{PH}_4^+$  has +1  
 $\text{NO}_2^-$  has -1                       $\text{CN}^-$  has -1  
 $\text{CH}_3\text{COO}^-$  has -1                 $\text{CO}_3^{2-}$  has -2  
 $\text{SO}_4^{2-}$  has -2                       $\text{PO}_4^{3-}$  has -3  
 $\text{ClO}_3^-$  has -1                       $\text{BO}_3^{3-}$  has -3
- In compounds of hydrogen the oxidation number of hydrogen is +1 but as an exception in metallic hydride compounds it is considered as -1. The oxidation number of hydrogen is +1 e.g.  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$   
 Similarly in metallic hydride like  $\text{BeH}_2$ ,  $\text{LiH}$ ,  $\text{NaH}$ ,  $\text{AlH}_3$ ,  $\text{CaH}_2$  the oxidation number of hydrogen is -1.



- (5) In most of the compounds of oxygen the oxidation number of oxygen is -2

e.g. in  $\text{H}_2\text{O}$  oxidation number of O = -2

in  $\text{H}_2\text{SO}_4$  oxidation number of O = -2

in  $\text{KMnO}_4$  oxidation number of O = -2

**Exception :** In peroxide (O-O) compounds the oxidation number of oxygen is considered as -1 e.g. in  $\text{K}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{BaO}_2$ ,  $\text{H}_2\text{O}_2$ , the oxidation number of oxygen is -1

**Exception :** In the compounds of superoxide the oxidation number of oxygen is considered -0.5 (-1/2) e.g.  $\text{KO}_2$ ,  $\text{CsO}_2$

**Exception :** In the compounds of fluorine with oxygen, the oxidation number of oxygen should be considered positive because the electronegativity of F is more than that of oxygen. Hence oxygen possesses positive (+ve) oxidation number.

In  $\text{O}_2\text{F}_2$  oxidation number of O = +1

$\text{OF}_2$  oxidation number of O = +2

- (6) In halide compounds, the oxidation number of halogen (F, Cl, Br, I) is considered -1 e.g.

In  $\text{HF}$ , F = -1, in  $\text{BaCl}_2$ , Cl = -1,

in  $\text{NaBr}$ , Br = -1, in  $\text{KI}$ , I = -1

**Exception :** In oxides and oxyacids of halogens (except F) the oxidation number of halogen is considered positive (+ve) e.g.

In  $\text{Cl}_2\text{O}_6$  the oxidation number of Cl = +6

In  $\text{HClO}_2$  the oxidation number of Cl = +3

In  $\text{HBrO}_3$  the oxidation number of Br = +5

In  $\text{HIO}_4$  the oxidation number of I = +7

- (7) In organic compounds possessing covalent bonds, more electronegative atom is assigned negative oxidation number and other having less electronegativity is assigned positive oxidation number, e.g. in  $\text{CCl}_4$  the oxidation number of more electronegative atom chlorine is -1 and oxidation number of less electronegative atom carbon is +4 and the oxidation number of carbon becomes (-4), in  $\text{CH}_4$ .
- (8) The algebraic sum of oxidation number of all elements in a polyatomic neutral molecules is zero which can be understood by examples given 1, 2, 3, 4, 5, 6... as mentioned in 4.4.2

- (9) The algebraic sum of oxidation number of atoms present in polyatomic ion is equal to its electrical charge, which can be understood as mentioned in 4, 7 as in 4.4.2

- (10) The oxidation number of alkali metals in its compounds is taken as +1 and the oxidation number of alkaline earth metal in its compounds is taken as +2. In fluoride compounds oxidation number of fluorine is always taken -1.

Thus, on the whole, the oxidation number of any neutral atom can be considered as zero, the oxidation number of any element in it can be calculated on the basis of above rules.

#### 4.4.2 Calculation of Oxidation Number :

The oxidation number of molecule, ion or compound is calculated on the basis of the above rules.

- (1) In  $\text{H}_2\text{S}$  molecule : Two atoms of hydrogen are present. The oxidation number of hydrogen is +1. As the oxidation number of  $\text{H}_2\text{S}$  is zero, the oxidation number of S will be -2 in  $\text{H}_2\text{S}$

2 (oxidation number of H atom)

+ (oxidation number of S atom) = 0

$\therefore 2(1) + x = 0; \therefore x = -2$

Hence oxidation number of S = -2

- (2) In  $\text{H}_2\text{SO}_4$  the oxidation number of S = x  
 $\therefore 2$  (oxidation number of H atom) + (oxidation number of S atom) + 4 (oxidation number of O atom)

$\therefore 2(1) + x + 4(-2) = 0$

$\therefore 2 + x - 8 = 0 \therefore x = +6$

Hence oxidation number of S atom is + 6

- (3) In  $\text{K}_3\text{PO}_4$  the oxidation number of P = x  
 3(oxidation number of K) + (oxidation number of P) + 4(oxidation number of O) = 0

$\therefore 3(1) + x + 4(-2) = 0$

$\therefore 3 + x - 8 = 0 \therefore x = 5$

Hence oxidation number of P is +5

- (4) In  $\text{ClO}_3^-$  The oxidation number of Cl = x  
 (oxidation number of Cl) + 3(oxidation number of O) = -1

$x + 3(-2) = -1$

$x - 6 = -1 \therefore x = +5$

Hence oxidation number of Cl is + 5

- (5) In  $\text{CH}_2\text{Cl}_2$  molecule oxidation number of C = x  
(oxidation number of C) + 2 (oxidation number of H) + 2 (oxidation number of Cl) = 0

$$x + 2(1) + 2(-1) = 0$$

$$x + 2 - 2 = 0 \quad \therefore x = 0$$

Hence, oxidation number of C is 0.

- (6) In  $\text{SiO}_2$  The oxidation number of Si = x  
(oxidation number of Si) + 2 (oxidation number of O) = 0

$$x + 2(-2) = 0$$

$$x - 4 = 0 \quad \therefore x = +4$$

Hence, oxidation number of Si is +4

- (7) In  $\text{CrO}_4^{2-}$  oxidation number of Cr = x  
(oxidation number of Cr) + 4(oxidation number of O) = -2

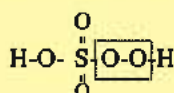
$$x + 4(-2) = -2$$

$$x - 8 = -2 \quad \therefore x = +6$$

Hence, oxidation number of Cr is +6

- (8) Calculate some exceptional oxidation numbers of elements :

- (1)  $\text{H}_2\text{SO}_5$  per mono sulphuric acid (Caro's acid). In per monosulphuric acid,



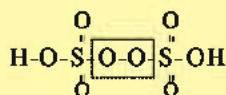
oxidation number of S = x

$$\therefore 2(\text{oxidation number of H}) + 2(\text{oxidation number of O atoms of peroxide}) + (\text{oxidation number of S}) + 3(\text{oxidation number of oxygen}) = 0$$

$$\therefore 2(+1) + 2(-1) + x + 3(-2) = 0$$

$$\therefore x = +6$$

- (2)  $\text{H}_2\text{S}_2\text{O}_8$  perdisulphuric acid (Marshall's acid). In perdisulphuric acid



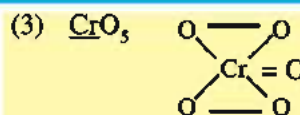
$\therefore$  oxidation number of S = x

$$\therefore 2(\text{oxidation number of H atom}) + 2(\text{oxidation number of O atoms of peroxide}) + 2(\text{oxidation number of S atom}) + 6(\text{oxidation number of O atoms}) = 0$$

$$\therefore 2(+1) + 2(-1) + 2x + 6(-2) = 0$$

$$\therefore 2x = +12$$

$$\therefore x = +6$$



In the given substance  $\text{CrO}_5$  it possesses two peroxy rings, where oxidation number of O atom will be -1

suppose oxidation number of Cr = x in  $\text{CrO}_5$

$$\therefore x + 4(\text{oxidation number of O of peroxide}) + 1(\text{oxidation number of O atom}) = 0$$

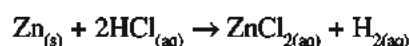
$$\therefore x + 4(-1) + (-2) = 0$$

$$\therefore x = +6$$

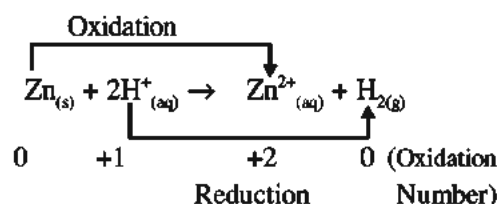
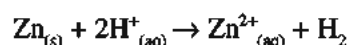
#### 4.4.3 Oxidation Number and Redox Reaction:

The reaction in which there is change in oxidation number of reactants is called redox reaction. The reaction in which, there is increase in oxidation number of reactant is called oxidation and the reaction in which there is decrease in oxidation number of reactant is called reduction reaction.

By the study of reaction between zinc and hydrochloric acid it is found that

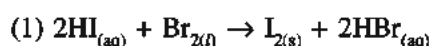


OR



In this reaction zinc is converted to  $\text{Zn}^{2+}$  ion by loss of two electrons. So, it undergoes oxidation while  $\text{H}^+$  ions are reduced by gain of electrons. Hence, zinc (Zn) is a reducing agent and  $\text{H}^+$  ion is an oxidizing agent. Looking this reaction from oxidation number point of view the oxidation number zero (0) of Zn is increased to +2 and the oxidation number of  $\text{H}^+$  ion is decreased from +1 to zero. Hence, it can be said that in oxidation reaction the oxidation number of one reactant increases and in reduction the oxidation number of other reactant decreases.

The following redox reaction can be explained by calculation of oxidation number :



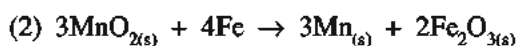
Change in oxidation number

I = 0 from -1 (increase of 1 in oxidation number)

Br = -1 from 0 (decrease of 1 in oxidation number)

H = +1 from +1 (No change in oxidation number and so it is considered as spectator ion)

In the reaction iodide ion is oxidized and bromine is reduced



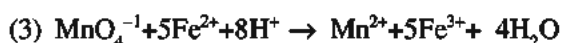
The change in oxidation number

Mn = 0 from +4 (Decrease in oxidation number by 4)

Fe = +3 from 0 (Increase in oxidation number by 3)

O = -2 from -2 (No change in oxidation number - Spectator ion)

In this reaction oxidation of iron and reduction of manganese ion take place.



change in oxidation number

Mn = +2 from +7 (Decrease in oxidation number by 5)

Fe = +3 from +2 (Increase in oxidation number by 1)

O = -2 from -2 (No change in oxidation number - spectator ion)

H = +1 from +1 (No change in oxidation number - spectator ion)

In this reaction oxidation of ferrous ion and reduction of manganese of  $\text{KMnO}_4$  take place.

#### 4.5 Oxidation Number and Nomenclature

Roman scientists used the oxidation state of element in the nomenclature of metal compounds. This nomenclature method is known as "Stock notation" in which the oxidation number of metal is expressed with Roman number in the bracket. The oxidation number of Cu in  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are +1 and +2 respectively. These two compounds are known as copper (I) oxide and copper (II) oxide. In the same way, oxides of iron  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are known as iron (II) oxide and iron (III) oxide.

Stock notation method is used in type of metals which have more than one oxidation states e.g.

- (1)  $\text{FeSO}_4$  as iron (II) sulphate
- (2)  $\text{Fe}_2(\text{SO}_4)_3$  as iron (III) sulphate
- (3)  $\text{Na}_2\text{CrO}_4$  as sodium chromate (VI)
- (4)  $\text{K}_2\text{CrO}_7$  as Potassium dichromate (VI)
- (5)  $\text{Cr}_2\text{O}_3$  as Chromium (III) oxide
- (6)  $\text{Mn}_2\text{O}_7$  as Manganese (VII) oxide
- (7)  $\text{V}_2\text{O}_5$  as Vanadium (V) oxide

Generally Stock notation is used for metals but not for non metals.

#### 4.6 Equation of Redox Reaction

Some general rules must be obeyed while showing redox reaction equation :

- (1) The molecular formulas of reactants and products must be known.
- (2) All the electrons released during oxidation half reaction, should be used in the reduction half reaction that is to say, change of electron in the reaction, should be the same.
- (3) The law of conservation of mass must be obeyed. The number of atoms or elements on both the sides of equation should be the same.

Redox reactions can occur in acidic, basic or neutral media. For reactions in acidic medium the requirement of oxygen is fulfilled by using  $\text{H}_2\text{O}$  and using  $\text{H}^+$  for hydrogen. In basic medium the requirement of oxygen is fulfilled by  $\text{H}_2\text{O}$  and  $\text{OH}^-$  ions are used to fulfill requirement of hydrogen.

#### 4.7 Balancing of Redox Reaction Equation

Two methods are used for the balancing of redox reaction equation.

- (1) Oxidation number method
- (2) Oxidation number and half reaction equation method.

##### 4.7.1 Balancing of Redox Reaction equation using Oxidation Number Method :

In balancing of redox reaction equation, the balance is carried by difference in oxidation number of reactants and products. It can be balanced in different media like acidic or basic. The balanced equation is obtained in redox equation equilibrium by using following points in sequence :

##### Points :

- (1) Write oxidation number of all the elements in the redox equation.
- (2) Balance the atoms of reactants and products in which oxidation numbers are changing. If one reactant is experiencing both oxidation and reduction reactions, it should be mentioned twice.
- (3) Determine oxidation and reduction reactions on the basis of change of oxidation numbers and write the change in oxidation number.
- (4) Multiply the oxidation and reduction reactions with proper coefficient for balancing the change in oxidation digit number.
- (5) Obtain the balanced equation by adding  $\text{H}_2\text{O}$  to balance oxygen atoms by adding  $\text{H}^+$  or  $\text{OH}^-$  on the basis of medium of reaction and the electric charge of reactants and products. Each spectator atom must also be balanced. If the medium is acidic, add

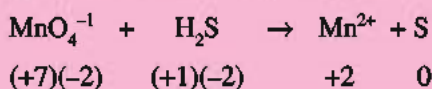


$\text{H}^+$  and  $\text{H}_2\text{O}$  and if the medium is basic, add  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . The electric charges of reactants and products in the equation must be mentioned and that should be balanced.

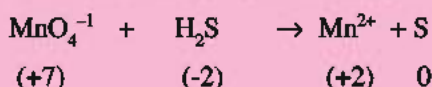
**Example 4.1 :** Balance the following reaction by oxidation number method :



- (1) Write oxidation number of elements

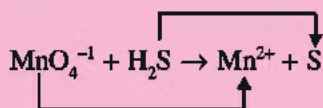


- (2) Balance the number of atoms of the elements in which oxidation number changes

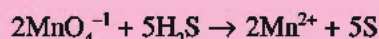


- (3) Decide the oxidation and reduction reaction on the basis of difference of oxidation number.

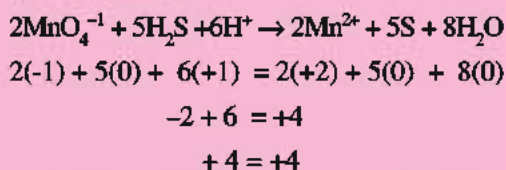
Increase in oxidation number by 2(Oxidation)



- (4) On multiplying oxidation reaction by 5 and reduction reaction by 2 to balance the change in oxidation number.

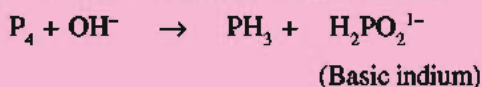


- (5) Balance the electric charge and atoms which do not change in oxidation number (spectator ion).

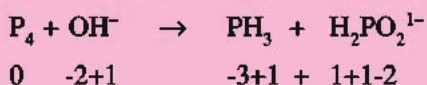


In the above reaction the reactants and products are balanced in terms of electric charge and mass equivalence.

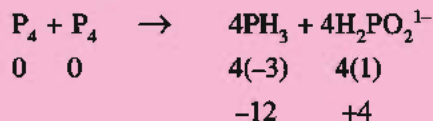
**Example 4.2 :** Balance the following redox reaction by oxidation number method.



- (1) Write oxidation numbers of elements



- (2) Balance the atom of elements and write the change in oxidation number.



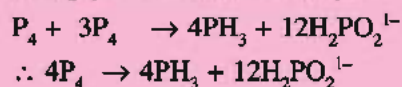
- (3) Decide the oxidation and reduction reaction on the basis of change in oxidation number.

Increase in oxidation number by  $4(+1) = +4$  (oxidation)

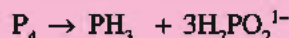


Decrease in oxidation number by  $4(-3) = -12$  (Reduction)

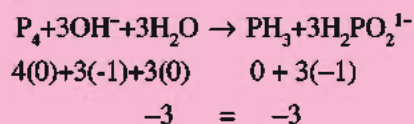
- (4) To balance the change in oxidation number multiply oxidation reaction by 3



Dividing by common factor 4



- (5) To balance the electric charge and atoms which do not change in oxidation number (Spectators)



The above reaction is balanced in terms of electric charge and mass equivalence.

#### 4.7.2 Balancing of Redox Reaction equation using Half Reaction equation

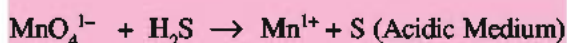
**Method :** The balanced equation is obtained by using following points in sequence.

**Points :**

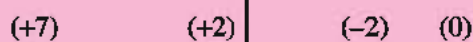
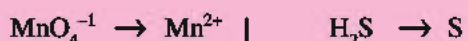
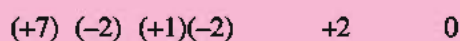
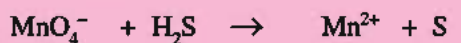
- (1) Find the elements whose oxidation numbers change and write half reactions.
- (2) Separate both the half reactions in which oxidation numbers change and balance their atoms.
- (3) Put number of electrons equivalent to the oxidation numbers in both half reactions.
- (4) On the basis of total electric charge in both the half reactions and the medium of the reaction, add  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{H}_2\text{O}$  and balance the equation.
- (5) Obtain the balanced equation by equalizing both the half reactions by number of electrons and then add up.



**Example 4.3 :** Balance the following redox reaction by half reaction equation :



(1) Write the Oxidation number of elements and half reaction



Decrease in oxidation number

∴ Reduction half reaction

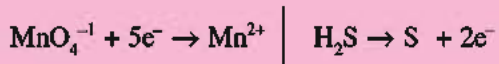
Increase in oxidation number

∴ Oxidation half reaction

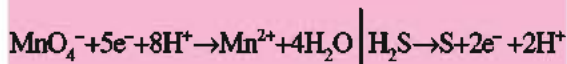
(2) Balance the atoms of elements in both half reactions



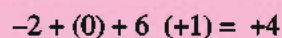
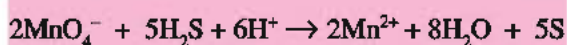
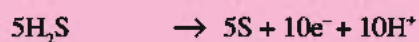
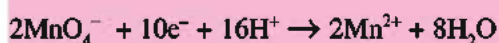
(3) Add electrons on the basis of change in oxidation number in both half reaction



(4) Add  $\text{H}^+$  and  $\text{H}_2\text{O}$  on the basis of acidic medium to balance electric charge in both half reactions.

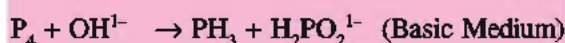


(5) To equalize the number of electrons in both half reactions, oxidation half reaction is multiplied by 5 and reduction half reaction by 2 and then adding up both the half reactions.

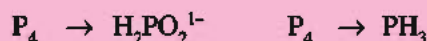


The above reaction is balanced in terms of electric charge and mass equivalence.

**Example 4.4 :** Balance the following redox reaction by half reaction method :



(1) Write oxidation number of elements and half reaction



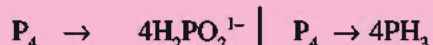
Increase in oxidation number.

∴ Oxidation half reaction

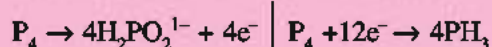
Decrease in oxidation number

∴ Reduction half reaction

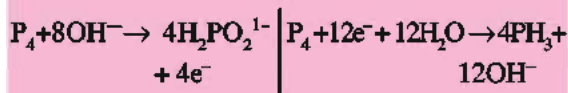
(2) Balance the atoms of elements in both half reactions.



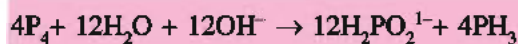
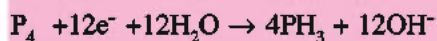
(3) Add electrons on the basis of change in oxidation number in both half reactions.



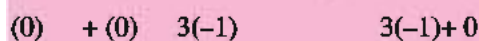
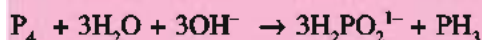
(4) Add  $\text{OH}^-$  and  $\text{H}_2\text{O}$  on the basis of basic medium to balance the electric charge in both half reactions.



(5) To equalize the number of electrons in both half reactions, multiply oxidation reaction by 3 and adding up both half reactions.



dividing by common factor 4



The above redox reaction is balanced in terms of electric charge and mass equivalence.

### SUMMARY

The form of redox reaction is such an important reaction in which oxidation and reduction reactions occur simultaneously. The points involved in are electron transfer, oxidation number etc. An attempt is made to give a deep explanation of these points. The concepts of oxidation, reduction, oxidizing agents, reducing agent are given in sequence. To find out oxidation number rules are also given in sequence which may be followed and oxidation number can be calculated.

The nomenclature, in compounds of metals, Stock notation can be used. To balance the reaction equation, two methods (i) Oxidation Number Method (ii) Half Reaction Equation Method can be used which are explained in both acidic and basic medium with illustration.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) What is the reaction called in which hydrogen is added during the reaction ?  
 (A) Oxidation (B) Reduction  
 (C) Redox (D) All the given
- (2) In the reaction  $\text{H}_{2(g)} + \text{Br}_{2(g)} \rightarrow 2\text{HBr}_{(g)}$  which substance undergoes oxidation ?  
 (A)  $\text{H}_2$  (B)  $\text{Br}_2$   
 (C)  $\text{HBr}$  (D)  $\text{H}_2$  and  $\text{Br}_2$
- (3) Which of the following statements is correct ?  
 (A) Reducing agent is reduced.  
 (B) Oxidising agent is oxidized.  
 (C) Reducing agent is oxidized.  
 (D) Oxidation or reduction does not occur in the reaction.
- (4) Which substance is the oxidizing agent in redox reaction ?  

$$\text{R-CHO} + 2\text{CuO} \rightarrow \text{Cu}_2\text{O} + \text{R-COOH}$$
 (A)  $\text{CuO}$  (B)  $\text{R-CHO}$   
 (C)  $\text{Cu}_2\text{O}$  (D)  $\text{R-COOH}$
- (5) Which of the following reactions is a redox reaction ?  
 (A)  $\text{NaOH}_{(aq)} + \text{HCl}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$   
 (B)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$   
 (C)  $\text{K}_2\text{SO}_{4(aq)} + \text{BaCl}_{2(aq)} \rightarrow 2\text{KCl}_{(aq)} + \text{BaSO}_{4(s)}$   
 (D)  $\text{H}_2\text{S}_{(aq)} + 3\text{H}_2\text{SO}_{4(aq)} \rightarrow 4\text{SO}_{2(g)} + 4\text{H}_2\text{O}_{(l)}$

- (6) In which order is oxidation number of underlined elements in  $\underline{\text{Ba}}\text{O}_2$  and  $\underline{\text{Si}}\text{O}_2$  ?  
(A) +2,+4 (B) +2, +2  
(C) +4, +2 (D) +4, +4
- (7) Which substance is the reducing agent in the reaction ?  
 $\text{CH}_3\text{CHO}_{(s)} + \text{Ag}_2\text{O}_{(s)} \rightarrow \text{CH}_3\text{COOH} + 2\text{Ag}$   
(A)  $\text{CH}_3\text{CHO}$  (B)  $\text{Ag}_2\text{O}$   
(C)  $\text{CH}_3\text{COOH}$  (D)  $\text{Ag}$
- (8) What is the oxidation number of N in  $\text{N}_3\text{H}$  ?  
(A) 2 (B) 1  
(C)  $-\frac{1}{3}$  (D) 0
- (9)  $\text{K}_2\text{Cr}_2\text{O}_7 + (\text{a})\text{SO}_2 + (\text{b})\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + (\text{c})\text{H}_2\text{O}$  In the reaction what will be the respective number of coefficients (a), (b), and (c).  
(A) 1,1,3 (B) 3,1,1  
(C) 1,3,1 (D) 3,1,3
- (10) Which of the following atoms can have positive and negative oxidation number in their compounds ?  
(A) F (B) Na  
(C) Ar (D) Cl
- (11) Mention the values of a, b, c and d respectively for the balanced chemical reaction  
 $\text{BrO}_3^- + (\text{a})\text{Br}^- + (\text{b})\text{H}^+ \rightarrow (\text{c})\text{Br}_2 + (\text{d})\text{H}_2\text{O}$   
(A) 5,6,3,3 (B) 5,4,3,4  
(C) 3,5,6,3 (D) 3,3,6,5
- (12) In which reaction,  $\text{H}_2\text{SO}_4$  acts as an oxidizing agent ?  
(A)  $2\text{KOH} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$   
(B)  $2\text{HCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$   
(C)  $\text{Ba}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{H}_2\text{O}$   
(D)  $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$

**2. Write the answers of the following questions in short :**

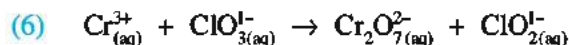
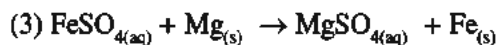
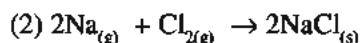
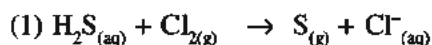
- (1) What is oxidation reaction ?  
(2) What is reduction reaction ?

- (3) Give an example of oxidation reaction.
- (4) Give an example of reduction reaction.
- (5) What is an oxidizing agent ?
- (6) What is a reducing agent ?
- (7) What is an oxidation number ?
- (8) What is Stock notation method ? To what it is applied ?
- (9) Calculate oxidation number of S in  $\text{H}_2\text{SO}_5$ .
- (10) Write the chemical reaction when Cu rod is placed in solution of silver nitrate.
- (11) Write chemical reaction when Zn rod is placed in solution of  $\text{H}_2\text{SO}_4$ .
- (12) Write the name of  $\text{K}_2\text{Cr}_2\text{O}_7$  according to Stock notation.

**3. Write the answers of the following questions :**

- (1) Explain oxidation reduction (Redox) reaction.
- (2) Find oxidation number of carbon in following compounds :  
 $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$
- (3) Find oxidation number of nitrogen in following compounds.  
 $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{NaNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$

- (4) Explain Stock notation method with example.
- (5) Are the following reactions-redox or not ? Explain :



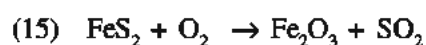
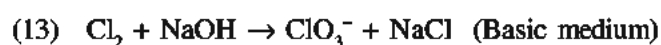
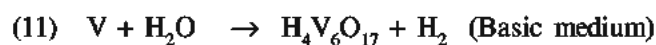
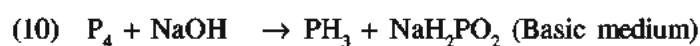
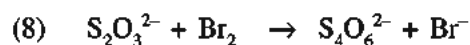
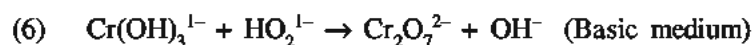
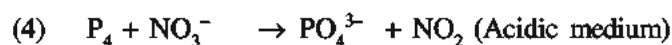
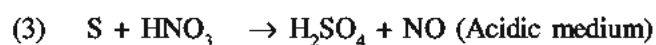
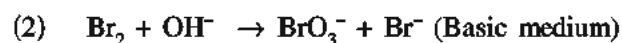
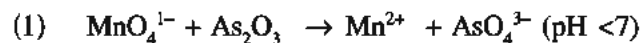
Give the following informations :

- (1) Which reactant is oxidized ?
- (2) Which reactant is reduced ?
- (3) Which reactant is an oxidizing agent ?
- (4) Which reactant is a reducing agent ?



**4. Write the answers of the following questions in detail :**

- (1) Explain any three oxidation-reduction (redox) reactions on the basis of electron exchange.
- (2) Balance the following reactions by both (oxidation number and half reaction equation) methods.



# HYDROGEN

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- 5.1 Introduction
- 5.2 Position of Hydrogen (H) in the Periodic Table
- 5.3 Isotopes of Hydrogen
- 5.4 Preparation of Dihydrogen and Its Physical Properties.
- 5.5 Hydrides
  - 5.5.1 Saline or Ionic hydrides
  - 5.5.2 Metallic or non-stoichiometric or interstitial hydrides
  - 5.5.3 Molecular or Covalent hydrides
- 5.6 Water :  $\text{H}_2\text{O}$ 
  - 5.6.1 Physical properties
  - 5.6.2 Structure of ice
  - 5.6.3 Chemical properties
  - 5.6.4 Hard Water and Soft water
- 5.7 Hydrogen Peroxide :  $\text{H}_2\text{O}_2$ 
  - 5.7.1 Preparation
  - 5.7.2 Physical properties
  - 5.7.3 Chemical properties
- 5.8 Heavy Water :  $\text{D}_2\text{O}$
- 5.9 Economic Utility of Dihydrogen

## 5.1 Introduction

The dihydrogen ( $\text{H}_2$ ) (hydrogen molecule) available in most abundance in the world and having number three in the order on the surface of the earth is seen as the biggest source of energy in future. Amongst all the elements, hydrogen has the simplest atomic structure. It is composed of one proton and one electron, even then it exists as a diatomic molecule or dihydrogen ( $\text{H}_2$ ). It forms many compounds as compared to other elements. Do you know that dihydrogen can be used as an energy related source so that the global problem can be solved ? Water is available in most abundance on the earth. If it can be made a source of energy, scientists can achieve much more about energy. In fact dihydrogen possesses great industrial importance which we will study in this unit.

## 5.2 Position of Hydrogen (H) in the Periodic Table

Hydrogen (H) is the first element of the first period of the periodic table. Even then its position in periodic table has remained a subject of discussion. As compared to all the elements its atomic structure is the simplest. The atomic number of hydrogen is  $Z = 1$  and atomic mass is 1.0054. Hence, it is considered as the first element in the periodic table. The physical properties of hydrogen are like those of nonmetal while some chemical properties are like those of metals and of nonmetals.

The electronic configuration of hydrogen is  $1s^1$  which is similar to the outermost electronic configuration of the alkali metals of group 1. On the other hand by accepting an electron it can attain the electron configuration of noble gas He ( $1s^2$ ).

Alkali metals form positively charged ions (cations) ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) by losing one electron. Similarly hydrogen can lose one electron and form positively charged ion or cation ( $\text{H}^+$ ). The valency of alkali metals is considered as 1+. Like alkali metals, 1+ forms stable oxide, peroxide, halide and sulphide ions e.g.  $\text{Na}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaCl}$ ,  $\text{HCl}$ ,  $\text{Na}_2\text{S}$ ,  $\text{H}_2\text{S}$ . Hydrogen, like alkali metals, is a strong reducing agent. Though alkali metals are obtained in solid form, hydrogen is a gaseous nonmetal. The ionization enthalpy of metals is very less while the ionization enthalpy of hydrogen is very high ( $\text{Li}\Delta_i\text{H} = 520\text{kJ mol}^{-1}$  and  $\text{H}\Delta_i\text{H} = 1312\text{kJ mol}^{-1}$ ). With reference to ionization enthalpy hydrogen has more similarity with halogens. ( $\text{F}\Delta_i\text{H} = 1680\text{ kJ mol}^{-1}$ ).

Hydrogen can be placed with halogens in group 17 (old - VII) because hydrogen possesses similarity with halogen elements of group 17.

Hydrogen forms hydride ion by accepting one electron whereas halogens form halide ions by receiving one electron. As halogen elements form stable diatomic molecule ( $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ ), hydrogen molecules form diatomic ( $\text{H}_2$ ) molecule. It combines with strongly electropositive elements like metals and form hydride compounds but, with reference to reactivity, it possesses very less reactivity in comparison to halogens. Halogen elements are coloured and strong oxidizing agents whereas hydrogen is a strong reducing agent.

Though hydrogen resembles alkali metals in many definite aspects, it also resembles non-metallic halogen elements, in fact it differs from them. Hence, the position of hydrogen is still uncertain that whether it can be considered in first group or seventeenth group. Hence, nowadays, instead of showing in first group or group 17, it is shown in the middle of the first period.

Hydrogen loses one electron and forms proton  $\text{H}^+$ , ionic radius  $1.5 \times 10^{-3}\text{pm}$  ( $\text{pm} = \text{picometer} = 10^{-12}\text{ meter}$ ) ion which is very small in comparison to atomic and ionic size (ionic radius 50 to 200 pm). Hence  $\text{H}^+$  can not have free existence and it combines with other atom or molecule. e.g.  $\text{H}^+_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})}$

Hence, hydrogen element is unique from behaviour point of view. Therefore, it is placed separately in the first period.

### 5.3 Isotopes of Hydrogen

There are three isotopes of hydrogen which are known as protium ( $^1_1\text{H}$ ), Deuterium or heavy hydrogen ( $^2_1\text{H}$  or D) and tritium ( $^3_1\text{H}$  or T). These isotopes differ from the point of view of the presence of neutrons. American scientist Harold C. Urey received the Nobel Prize in 1934 for separation of isotopes of hydrogen by physical method.

The nucleus of protium possesses only one proton, deuterium possesses one proton and one neutron and tritium possesses one proton and two neutrons. Thus their mass numbers are one, two and three respectively. Protium is in the highest proportion in dihydrogen available in nature. Its atoms are about 5000 times more than that of deuterium. The proportion of tritium atoms is very less. The relative proportion of atoms of tritium and protium is  $1:10^{17}$ . The property responsible for very low proportion of tritium is its radioactivity and emission of low energy  $\beta$  particles. Its half life is ( $t_{1/2} = 12.33$ ) years.

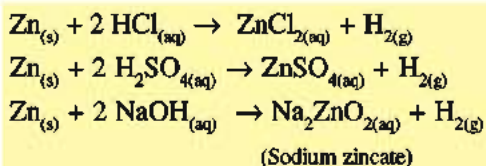
As the electronic configuration of these three isotopes is same, their chemical properties are similar but because of the difference in their binding energy, the change in reaction rate is observed. The physical properties of these isotopes are quite different because of their abundant quantity. This is shown in table 5.1

Table 5.1

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	$10^{-15}$
Relative atomic mass ( $\text{g mol}^{-1}$ )	1.008	2.014	3.016
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.39	23.67	25.0
Density ( $\text{g l}^{-1}$ )	0.09	0.18	0.27
Enthalpy of fusion ( $\text{kJ mol}^{-1}$ )	0.117	0.197	-
Enthalpy of vaporization ( $\text{kJ mol}^{-1}$ )	0.904	1.226	-
Enthalpy of bond dissociation ( $\text{kJ mol}^{-1}$ ) at 298 K	435.88	443.35	-
Internuclear distance (pm)	74.14	74.14	-
Ionization enthalpy ( $\text{kJ mol}^{-1}$ )	1312	-	-
Electron gain enthalpy ( $\text{kJ mol}^{-1}$ )	-73	-	-
Covalent radius (pm)	37	-	-
Ionic radius ( $\text{H}^-$ ) (pm)	208	-	-

#### 5.4 Preparation of Dihydrogen and Its Physical Properties

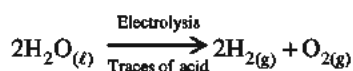
Hydrogen is available in abundance in the nature in the form of compound, the water. Generally dihydrogen can be obtained by reaction of zinc metal with dilute hydrochloric acid, dilute sulphuric acid or concentrated aqueous alkali.



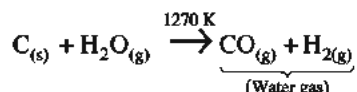
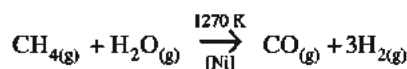
In laboratory, generally dihydrogen gas is prepared by using zinc and dilute  $\text{H}_2\text{SO}_4$ .

##### Industrial preparation of dihydrogen :

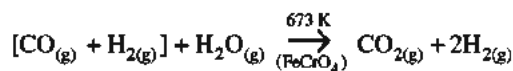
- (i) Dihydrogen can be obtained by electrolysis of water in which few drops of sulphuric acid are added, between platinum electrodes.



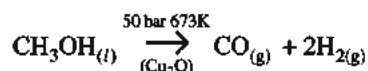
- (ii) To obtain pure dihydrogen (> 99.95 %) the hot aqueous solution of barium hydroxide is electrolysed between two nickel electrodes.
- (iii) Dihydrogen is obtained as a component of water gas by heating hydrocarbons or coal at 1270 K temperature using iron (Fe), nickel (Ni) catalyst.



This water gas is used in synthesis of methanol and hydrocarbons so that it is called syngas. Dihydrogen can be obtained by heating water gas at 673 K in presence of iron chromate ( $\text{FeCrO}_4$ ) catalyst. With water vapor, carbon dioxide is removed and dihydrogen can be obtained.



- (iv) Dihydrogen can be obtained by heating methanol at 50 bar pressure (SI Unit is bar instead of atmosphere) and 673K temperature in presence of cuprous oxide catalyst



In the present time it is obtained from synthetic gas, sewage, saw dust, newspaper etc.



77% of the industrial production of dihydrogen is from petrochemicals, 18% from coal, 4% by electrolysis and 1% from other sources.

### Physical Properties of Dihydrogen :

Dihydrogen ( $H_2$ ) is a colourless, odourless and tasteless gas. It is lighter than air and is insoluble in water. It is a combustible gas. Dihydrogen is diamagnetic. The value of its reduction potential is 0.0 volt (V). Other properties are shown in table 5.1

### Chemical properties of dihydrogen :

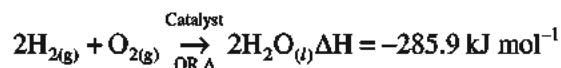
#### (i) Reactivity (reaction) with halogen :

Dihydrogen ( $H_2$ ) reacts with dihalogen ( $X_2$ ) and gives hydrogen halide (HX)



#### (ii) Reactivity with oxygen :

Dihydrogen ( $H_2$ ) gives hydrogen oxide-water ( $H_2O$ ) by reacting violently with dioxygen.



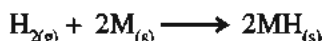
#### (iii) Reactivity with nitrogen :

Dihydrogen ( $H_2$ ) reacts with dinitrogen giving ammonia gas



#### (iv) Reactivity with metal

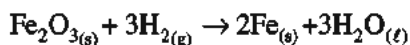
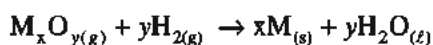
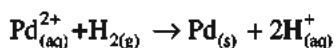
Dihydrogen reacts with many metals at high temperature and gives corresponding hydrides



(M = Alkali metal)

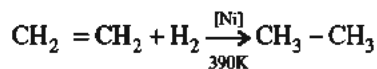
#### (v) Reactivity of metal ion and metal oxides :

Many metal ions in aqueous solutions and metal oxides (less reactive than Fe) react with dihydrogen and gives metal.



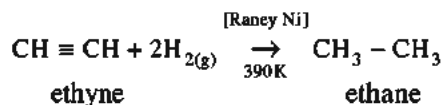
#### (vi) Reactivity with organic compounds :

Dihydrogen ( $H_2$ ) gives hydrogenated product which possesses industrial importance, by reacting as strong reducing agent with many organic compounds in presence of catalyst.



ethene

ethane



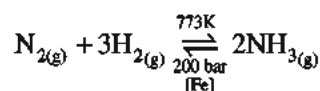
ethyne

ethane

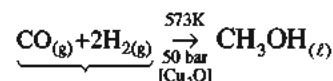
Edible fat (vegetable ghee) is formed by the hydrogenation of edible oil in presence of nickel catalyst.

### Uses of dihydrogen :

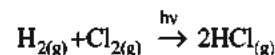
- (i) Dihydrogen is an important raw material for the industrial production of ammonia by Haber process



- (ii) Dihydrogen in synthetic gas is useful for industrial production of methanol.



- (iii) Dihydrogen is useful for industrial production of important chemical like hydrochloric acid



It is also useful in production of halogen acid like HBr and HI.

- (iv) It is useful for obtaining metal from oxides of heavy metal and preparation of metal hydrides.
- (v) Dihydrogen is useful as fuel in rockets used for space research and in fuel cells.
- (vi) It is used in cutting and in welding work of metals in the molecular hydrogen and oxy-hydrogen flame.

## 5.5 Hydrides

Dihydrogen forms hydrides of the type  $MH_x$  or  $M_mH_n$  by reaction with most of the metals. Certain elements like indium (In) and thallium (Tl) do not give hydrides. Hydride compounds can be divided in to three types :

- (1) Saline or ionic hydrides
- (2) Metallic or interstitial hydrides
- (3) Molecular or covalent hydrides

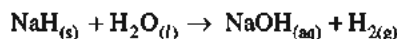
### 5.5.1 Saline or Ionic hydrides :

Metal elements of s-block (group-1 and group-2) possess more electropositive character so it forms light metallic hydride compounds e.g LiH, NaH, BeH<sub>2</sub>, and MgH<sub>2</sub>

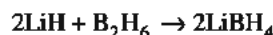
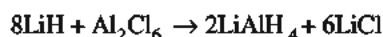
Hydrides of beryllium and magnesium possess polymeric structure like (BeH<sub>2</sub>)<sub>n</sub> and (MgH<sub>2</sub>)<sub>n</sub>. Ionic hydrides are crystalline solid, nonvolatile and nonconductor of electricity but in their molten states they ionise and H<sup>-</sup> liberates dihydrogen at the anode by oxidation during electrolysis.



Saline hydrides react violently with water and liberate dihydrogen (H<sub>2</sub>)



Lithium hydride does not react with O<sub>2</sub> and Cl<sub>2</sub> at normal temperature, so they are used in preparation of other hydrides.



**5.5.2 Metallic or non-stoichiometric or Interstitial hydrides :** Metallic elements of d-block as well as p-block combine with dihydrogen and give metallic hydrides which are non-stoichiometric,

e.g (VH, VH<sub>2</sub>, NbH, NbH<sub>2</sub>, TiH, TiH<sub>3</sub>, LaH<sub>2</sub>, LaH<sub>3</sub>, HfH<sub>2</sub>)

Metals of groups 7, 8, and 9 do not form hydrides. Cr of group VI forms CrH which is not good conductor for heat and electricity like original metal.

Metallic hydrides are mostly non-stoichiometric compounds e.g LaH<sub>2.87</sub>, YbH<sub>2.55</sub>, TiH<sub>1.5-1.8</sub>, ZrH<sub>1.3-1.75</sub>, VH<sub>0.56</sub>, NiH<sub>0.6-0.7</sub>, PdH<sub>0.6-0.8</sub> etc. In these metallic hydrides, hydrogen is absorbed in the interstitial places of the metals. During this there is no change in types of bonds in them and so they are called interstitial hydrides. Hydrides of metals like Ni, Pd, Ce and Ac possess different structures than their original metal. So the hydrides of these metals are used in more proportion in catalytic reaction like hydrogenation.

### 5.5.3 Molecular or Covalent hydrides :

Metallic and nonmetallic elements of p-block combine with hydrogen and give molecular hydrides e.g CH<sub>4</sub>, NH<sub>3</sub>, PH<sub>3</sub>, SbH<sub>3</sub>, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se, H<sub>2</sub>Te, HF etc. Molecular hydrides can be classified as following on the basis of their Lewis structure.

- (i) Electron deficient hydrides e.g. B<sub>2</sub>H<sub>6</sub>
- (ii) Electron precise hydrides e.g. CH<sub>4</sub>
- (iii) Electron rich hydrides e.g. H<sub>2</sub>O, HF

### 5.6 Water (H<sub>2</sub>O)

Water plays an important role for living entities. Water is about 65% in human body and as high as about 95% in some of the vegetation. It is an important compound for living beings and is essential for life. It is a universal solvent. Water is distributed unevenly on the earth which in percentage is as given in table 5.2

Table 5.2

Natural sources	Percentage
Oceans	97.33
Saline lakes and inland seas.	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Lakes or Ponds	0.009
Soil moisture	0.005
Atmospheric water vapour	0.001
Rivers	0.0001

**5.6.1 Physical properties :** Water is a colourless, tasteless and odourless liquid. Its melting point is 273 K and boiling point is 373 K. Its density at 298 K temperature is 1.00 gram cm<sup>-3</sup> (Density is expressed in kg/m<sup>3</sup> or kgm<sup>-3</sup> units in SI). It possesses polar properties and its molecule possesses angular structure which has sp<sup>3</sup> hybridisation. The H-O-H bond angle is about 104.5° instead of 109° 28'. It possesses anomalous volume expansion between 273 K to

277 K. At higher than this temperature it shows normal expansion like other liquids.

It possesses higher boiling and melting points than the hydrides  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  of the other elements S, Se, Te of oxygen group. This is due to the hydrogen bond present in it. It Possesses Proton donating solvent and proton accepting solvent characteristic. Thus, it acts as an amphoteric oxide.

**Structure of water :** The bonds, bond length and bond angles formed between two H and one O present in  $\text{H}_2\text{O}$  are shown in Fig 5.1

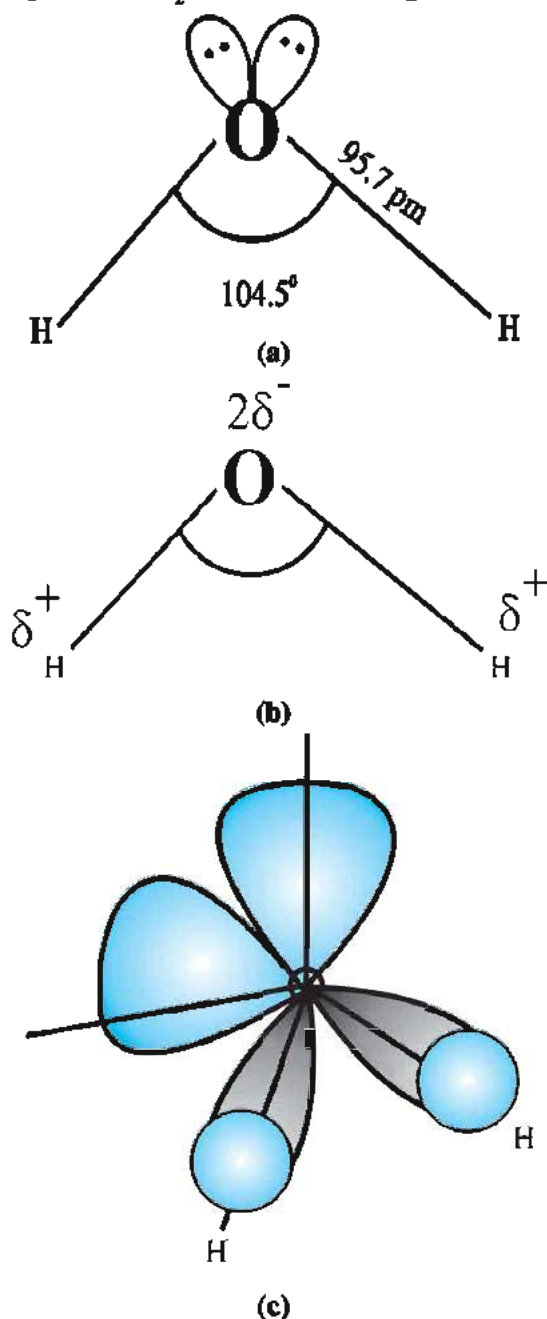


Figure 5.1

### 5.6.2 Structure of ice :

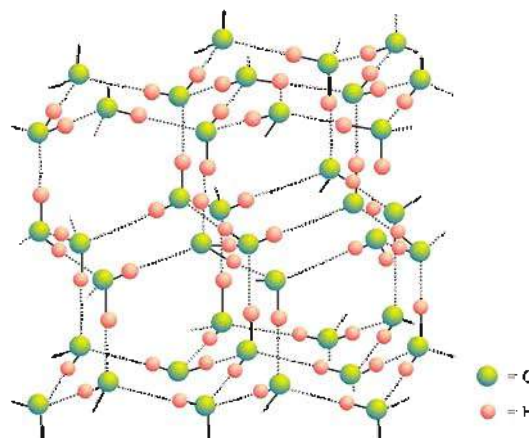


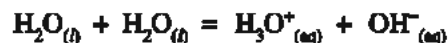
Figure 5.2

In ice, a definite three dimensional structure formed by hydrogen bonds. This is shown in figure 5.2. On examination of crystalline structure of ice with the help of X-rays, it is found that around each oxygen atom tetrahedral structure is formed and four oxygen atoms are arranged at 276 pm distance.

Because of hydrogen bond in ice, it forms an open structure with holes and forms spacious type structure. It contains internally the definite volume of big molecules.

### 5.6.3 Chemical properties :

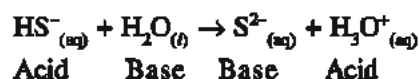
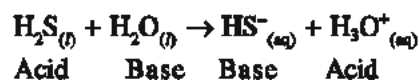
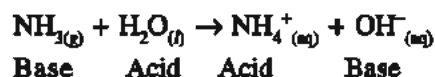
- The concentration of water is  $55.55 \text{ mol lit}^{-1}$  or  $\text{M}$  at 298 K. Because of its self ionization  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol lit}^{-1}$  is obtained at equilibrium condition.



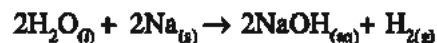
- Its  $\text{pH} = \text{pOH} = 7.0$ . Hence it is a neutral solvent.

- Water acts as amphoteric

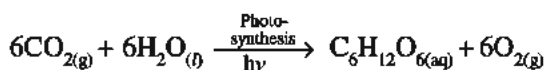
Ammonium hydroxide is obtained by reaction of ammonia gas with water.



- Redox (oxidation and reduction) reaction with more electropositive metal it reduces hydrogen ion in water as an oxidizing agent.



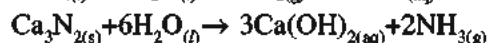
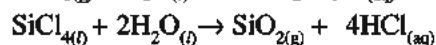
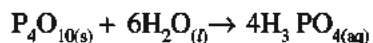
O<sub>2</sub> is liberated in the photochemical reaction.



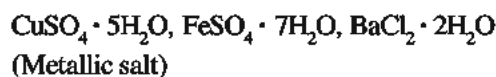
As a reducing agent it reduces fluorine to F<sup>-</sup>



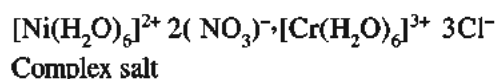
(v) Hydration reaction of water



(vi) Some compounds are hydrous. The number of molecules of water associated with it is called water of crystallization



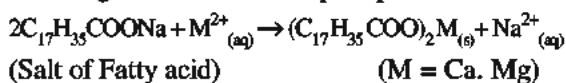
It also combines as ligand to form complex salt



**5.6.4 Hard water and Soft water :** Rain water is mostly pure but some atmospheric gases mix with it. They are available as solid, liquid and gas on the surface of the earth. Thus, in any kind of water, some type of impurities are present and as it can easily flow it flows on the surface of earth. while flowing it passes through minerals like magnesite, dolomite etc. Magnesium hydrogen carbonate (Magnesium bicarbonate) enters into water as impurity over and above, sodium hydrogen carbonate (Sodium bicarbonate) sodium chloride, calcium sulphate, calcium chloride, magnesium sulphate, magnesium chloride and different minerals undergo chemical reactions and are added as impurities due to their solubility. In this way, salts of calcium and magnesium become soluble in water and the hardness enters into water. The definition of such a hard water can be given as follows :

The water which does not form lather easily with soap and wastes soap is called hard water.

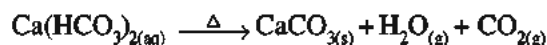
When hard water comes in contact with soap, the cations from the sodium salts formed from fatty acids react with calcium and magnesium ion in water and insoluble calcium and magnesium salts are precipitated



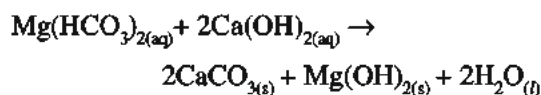
Thus, instead of removing dirt or cleansing reaction, majority of soap's amount is changed to calcium and magnesium salts. If hard water is used in boilers, salts deposit and hence, there are problems of bursting of boilers. Therefore, the water used in boilers must be soft, that is, the salt of Ca and Mg must be removed or minimized.

Hardness is of two types : (1) Temporary and (2) Permanent

**Temporary hardness :** In temporary hardness the salt of calcium and magnesium dissolved in water are calcium and magnesium hydrogen carbonates. This type of hardness can be removed by boiling the water. On boiling water, calcium and magnesium hydrogen carbonate soluble in water decompose by giving carbon dioxide and insoluble carbonates are formed.



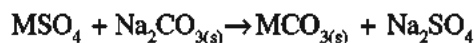
Insoluble carbonates can be removed by filtration process. Temporary hardness can be removed by addition of lime water (Ca(OH)<sub>2</sub>) to temporary hard water. In this reaction insoluble salts of calcium and magnesium are precipitated which can be removed by filtration process. This method is known as Clark's method.



**Permanent hardness :**

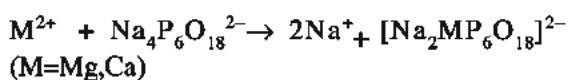
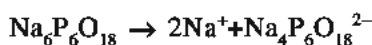
The permanent hardness enters into the water by bicarbonates dissolved in water and by chloride, and sulphate salts of calcium and magnesium. The permanent hardness can not be removed by boiling. The methods for removal of permanent hardness are as follows :

**(i) Chemical methods :** In this method amount of washing soda, determined by calculation is used. By this hardness (Ca<sup>2+</sup> and Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) is removed. By addition of washing soda carbonates of calcium and magnesium are formed.





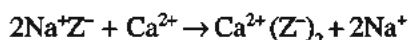
By use of sodium hexametaphosphate ( $\text{Na}_6\text{P}_6\text{O}_{18}$ ),  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions can be made ineffective. Sodium hexametaphosphate is known as 'Calgon' on commercial base.



Complex negative ion remains in solution.

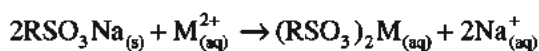
**(ii) Ion exchange method :** The method of displacing or exchanging  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  present in soluble form in permanent hard water by the  $\text{Na}^+$  ions is called ion exchange method. First of all, the mineral zeolite was used as positive ion exchanger. Zeolite is the calcium silicate having formula  $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ . The complex structure is formed by aluminium (Al), silicon (Si) and oxygen (O) atoms in it. In this structure, there is a void like that in honey comb in which sodium ions are present. When the hard water passes over the particles of zeolite, some of the sodium ions come out from the zeolite and mix with the solution and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions enter into their places; so they exchange their sites. So that they exchange there and  $\text{Na}^+$  is released. This way hardness of water can be removed. The used zeolite can be again made efficient for reuse because  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in them can also be exchanged.

If  $\text{Z}^-$  is considered as the small part of the structure of zeolite having one negative charge in water by  $\text{Na}^+$ , it can be shown by following reaction.



**(iii) Synthetic resin method :** In the present times synthetic cation exchangers are used to soften the hard water. This method is more effective than the Zeolite method.

Cation exchange resin is a solid organic molecule having  $-\text{SO}_3\text{H}$  group. The cation exchange resin ( $\text{RSO}_3\text{H}$ ) reacts with  $\text{NaCl}$  and converted into  $\text{RSO}_3\text{Na}$ . When hard water passes through  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  ions present in water are exchanged by  $\text{Na}^+$  ion that is  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are removed from hard water and the water becomes soft.



where,  $\text{M}^{2+} = \text{Ca}^{2+}, \text{Mg}^{2+}$

To make this resin efficient again  $\text{NaCl}$  is passed through it.

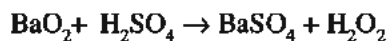
In the same water, to remove anions from the water, anion exchange resins are used.

## 5.7 Hydrogen Peroxide : $\text{H}_2\text{O}_2$

In everyday life hydrogen peroxide is an important chemical to control pollutants formed industrially.

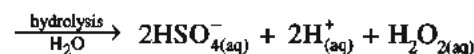
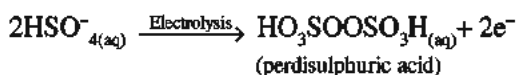
### 5.7.1 Preparation :

- (1) In 1818, J. L. Thenard obtained hydrogen peroxide by the reaction of barium peroxide and sulphuric acid.

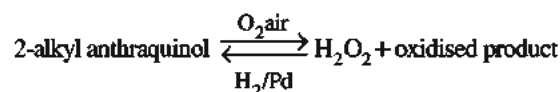


- (2) When bisulphate ( $\text{HSO}_4^-$ ) ion containing solution is electrolytically oxidized at high current density, perdisulphuric acid is obtained which on hydrolysis gives hydrogen peroxide.

#### Anode :



- (3) Industrially it can be prepared by self oxidation of 2-alkyl anthraquinol

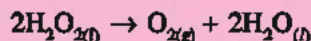


In hydrogen peroxide the amount of oxygen is two times more than the oxygen in water. The prefix 'per' means more. Hence the word peroxide is used. In hydrogen peroxide more oxygen is there as compared to that in hydrogen oxide (water) and it possesses peroxide bond structure.

**5.7.2 Physical Properties :** Hydrogen peroxide in the pure form is colourless but if it is in more proportion, it is a blue coloured dense liquid. Its density in solid form is  $1.64 \text{ g cm}^{-3}$  and in liquid form it is  $1.44 \text{ g cm}^{-3}$ . Its melting point is  $272.4 \text{ K}$  and boiling point is  $423 \text{ K}$ . It is a very strong oxidising agent. It carries out self oxidation of organic compounds. Its uses are due to its oxidising power. It completely mixes with water.  $\text{H}_2\text{O}_2$  sold in the market has  $\text{H}_2\text{O}_2$  30 % in 100 volume with water. At STP in one milliliter 30 %  $\text{H}_2\text{O}_2$  gives 100 ml of oxygen. On commercial bases the sample available in the market 3 %  $\text{H}_2\text{O}_2$  is there in the sample of 10 volume. Let us study this matter by following example :

**Example :** Calculate the strength of 10 volume solution of  $\text{H}_2\text{O}_2$ .

**Solution :** 10 volume of  $\text{H}_2\text{O}_2$  solution will give 10 litre  $\text{O}_2$  at STP



$$2 \times 34 = 68\text{g}$$

The volume of 1 mole gas is 22.4 litre at STP

68 g  $\text{H}_2\text{O}_2$  will be equivalent to 22.4 litre  $\text{O}_2$  gas

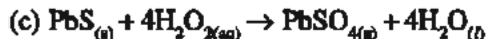
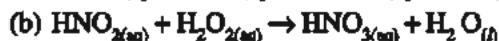
$\therefore$  How many gram of  $\text{H}_2\text{O}_2$  will be equivalent to 10 litre  $\text{O}_2$  gas

$$\therefore \frac{10 \times 68}{22.4} = 30.36\text{ g}$$

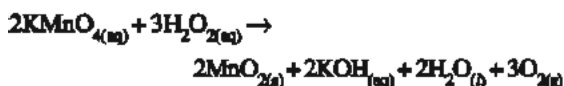
**5.7.3 Chemical properties :** Hydrogen peroxide is an aqueous solution. By adding small amount of stabilizer like phosphoric acid, its oxidation and decomposition in water can be reduced.



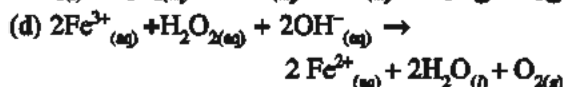
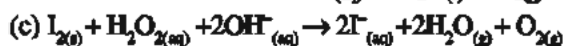
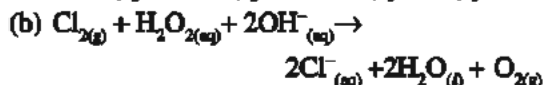
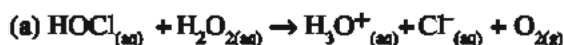
Hydrogen peroxide can function as oxidising agent and reducing agent in both acidic and basic media. When hydrogen peroxide functions as an oxidising agent, the oxidation number of each atom of oxygen becomes -2 from -1. The examples are given below.



When hydrogen peroxide functions as a reducing agent, the oxidation number of each oxygen atom becomes 0 (zero) from -1. In basic medium it decolourises potassium permanganate solution.

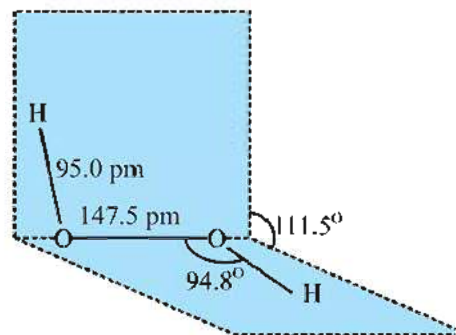


Some examples are given below :

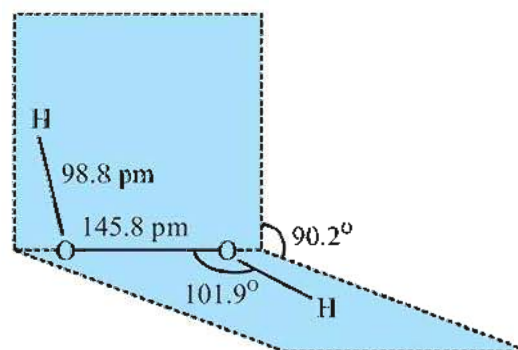


### Structure :

There are two bonds O-O and H-O in hydrogen peroxide. In peroxide  $(-\text{O}-\text{O}-)^{2-}$  ion is present. Its molecule is nonplanar. Its molecular structure is as follows :



Gaseous form



Solid form

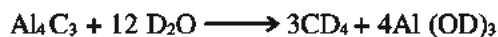
### Uses :

- (1) Hydrogen peroxide is used as bleaching agent in industrial units like textile, paper, leather, oil, fat etc.
- (2) In everyday life to bleach hair, and as mild disinfectant in dentistry which is sold in market as perhydrol.
- (3) Hydrogen peroxide is used in preparation of chemicals such as sodium percarbonate, sodium perborate etc. and used in preparation of good quality detergents.
- (4) It is used as the controller of pollutants in industrial field. Especially it is used in oxidation of cyanide and oxidation of excreted materials. In present days it is used to decrease industrial pollution (Green chemistry) in maintenance of environment.

### 5.8 Heavy Water : $\text{D}_2\text{O}$

Heavy water is the oxide of deuterium the isotope of hydrogen. As deuterium oxide is considered as heavy water, it is largely used as moderator in nuclear reactors to obtain compounds of deuterium, to understand

mechanism of a reaction exchange of ions etc. Heavy water ( $D_2O$ ) is obtained as the by product during electrolysis of water used in production of fertilisers.



### 5.9 Economic Utility of Dihydrogen

Because of the decrease in quantity of crude oil available from the earth, not possible to store electrical energy and limitations of obtaining nuclear energy, the utility of dihydrogen can be the source of energy in its place.

The main aim and advantage of economic utility of dihydrogen is that the transfer of available energy is carried out in the form of hydrogen which solves the problems of storage and transmission of energy.

### Use of liquid hydrogen as fuel :

By using liquid hydrogen as fuel the pollution of air can be decreased. It possesses very high efficiency in comparison to thermal power electric stations.

The scientists in America had used this type of fuel in the spaceshuttles in the Apollo programme. The use of this type of fuel in fuel cells, water vapours were obtained during cell reaction and it was cooled down whereby they got the drinking water.

It is a history for India that in October, 2005 only one pilot project was selected for use of dihydrogen as a fuel. Thereby new researches were taken up in the automobile age. Generally use of 5% dihydrogen in CNG is mixed for a vehicle like car, similarly simple and cheaper machines are manufactured for the use of dihydrogen as fuel. Scientists should give their contribution in solving the global problem of energy.

### SUMMARY

Hydrogen atom is the lightest which possesses only one proton and one electron. It becomes positively charged by loss of the electron and is changed to proton. There are three isotopes of dihydrogen whose information we have studied in detail. In this unit preparation of hydrogen, its physical properties, chemical properties and its utility have been studied. Economic utility of dihydrogen, in fuel cell, rocket CNG etc. have been studied. Preparation of dihydrogen, its structure and properties have been discussed. We studied in this unit the methods of softening hard water. Heavy water and its uses as well as structure of ice, hydrogen economy etc. have also been discussed in this unit. Hydrogen peroxide is interesting non polar configuration possessing, compound used on a large scale in industrial field, for bleaching preparation of medicines in methods of control of pollutants and removal of industrial pollutants.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) Which of the following statements is true for dihydrogen ?
  - (A) It is a stable oxide and gives a peroxide
  - (B) It is an unstable oxide and gives a stable peroxide
  - (C) It violently reacts with dioxygen at normal temperature.
  - (D) It gives unstable peroxide.
- (2) In which of the following dihydrogen is useful ?
  - (A) in fuel cell
  - (B) in preparation of ammonia
  - (C) in preparation of vegetable ghee
  - (D) in all the given

- (3) Which method is useful to remove temporary hardness ?  
(A) Heating the water and then cooling  
(B) Resin method  
(C) Ion exchange method  
(D) None from the given
- (4) Which scientist had obtained hydrogen peroxide from barium peroxide ?  
(A) J. L. Leonard (B) J.J. Thomson  
(C) J.L. Thenard (D) Goldstein
- (5) What is correct about reactivity ?  
(A) Protium = Tritium (B) Protium < Deuterium  
(C) Protium > Deuterium (D) Protium = Deuterium
- (6)  $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$  which reaction occurs in  $\text{H}_2\text{O}_2$  in the given reaction ?  
(A) Oxidation (B) Reduction  
(C) Neutralisation (D) Redox
- (7) Which substance is called “calgon” on commercial base ?  
(A) Sodium pyrometaphosphate (B) Sodium metaphosphate  
(C) Sodium hexametaphosphate (D) Sodium polyphosphate
- (8) What is used as exchanger in ion exchange method ?  
(A) alum (B) zeolite  
(C) lime (D) all the given
- (9) What is the correct formula of sodium hexametaphosphate ?  
(A)  $\text{Na}_4\text{P}_4\text{O}_{16}$  (B)  $\text{Na}_6\text{P}_6\text{O}_{16}$   
(C)  $\text{Na}_6\text{P}_4\text{O}_{18}$  (D)  $\text{Na}_6\text{P}_6\text{O}_{18}$
- (10) What is the proportion of tritium relative to protium ?  
(A)  $10^{16}$  (B)  $10^{17}$   
(C)  $10^{-16}$  (D)  $10^{-16}$

**2. Write answers of following questions in short :**

- (1) What is isotope ?  
(2) Where in the modern periodic table hydrogen is placed ?  
(3) Write names of isotopes of hydrogen.  
(4) Mention the types of hydrides giving examples.  
(5) Impurities of which metal ions are present in hard water ?  
(6) Write molecular formula of heavy water.




- (7) Write bond angle and type of hybridization in water.
- (8) Write about Clark's method.
- (9) Discuss structure of hydrogen peroxide.
- (10) Hydrogen peroxide acts as oxidising agent. Write reaction equation for it.
- (11) Write molecular formulas of two metallic hydrides.

**3. Write answers of the following questions :**

- (1) Give explanation of isotopes of hydrogen in brief.
- (2) Explain hard water and soft water.
- (3) Write economic utility of dihydrogen.
- (4) Explain the structure of  $H_2O$ .
- (5) Write chemical methods for removal of permanent hardness.
- (6) Write the ion exchange method for removal of permanent hardness.
- (7) Write uses of hydrogen peroxide

**4. Write answers of following questions in detail :**

- (1) Discuss the position of hydrogen in the modern periodic table.
  - (2) Write the preparation of dihydrogen and explain its physical and chemical properties.
  - (3) Write uses of dihydrogen.
  - (4) Write preparation of hydrogen peroxide and explain the physical and chemical properties.
  - (5) What are hydride compounds ? Explain them by giving types.
- 

## THE s-BLOCK ELEMENTS (ALKALI AND ALKALINE EARTH ELEMENTS)

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- 6.1 Introduction
- 6.2 Alkali Metals-Occurrence, Atomic and Physical Properties.
- 6.3 Atomic size and Ionic size
- 6.4 Reaction Enthalpy of Elements
  - 6.4.1 Ionisation enthalpy (energy)
  - 6.4.2 Hydration enthalpy (energy)
- 6.5 Chemical Reactivity (reactions) of Alkali Metals
- 6.6 Oxide and Hydroxide Compounds and Reactivity (reactions) towards dihydrogen, dihalogen, water, ammonia
- 6.7 Diagonal Relationship and Irregularity (Lithium and Magnesium)
  - 6.7.1 Diagonal relationship of lithium with magnesium
  - 6.7.2 Anomalous behaviour of lithium from other elements of the group
- 6.8 Diagonal Relationship and Irregularity (Beryllium and Aluminium)
  - 6.8.1 Diagonal relationship of beryllium with aluminium
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- 6.9 Lithium (Occurrence, Properties and Uses)
- 6.10 Sodium (Occurrence, Properties and Uses)
- 6.11 Alkaline Earth Metals (Occurrence, Physical Properties and Electronic Structure)
- 6.12 Related trend between Physical Properties.
- 6.13 Chemical Properties-Reactivity (reactions) of Dioxygen and Water with Metals
- 6.14 Oxide and Hydroxide Compounds
- 6.15 Halide Compounds
- 6.16 Solubility and Thermal Stability of Oxosalts
- 6.17 Production, Properties and Uses of some Compounds of Sodium :  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaHCO}_3$
- 6.18 Biological Importance of  $\text{Na}^+$  and  $\text{K}^+$  ions
- 6.19 Production, Properties and Uses of some Compounds of Calcium :  $\text{CaO}$ ,  $\text{CaCO}_3$ , Plaster of Paris and Cement
- 6.20 Biological Importance of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions

### 6.1 Introduction

The elements are divided into four blocks namely s, p, d and f in the modern periodic table. We shall study s-block elements of the periodic table in this unit. s-block elements are those elements in which the last electron, enters into the outermost s-orbital. Only two electrons can be accommodated in s-orbital, so there are two groups (1 and 2) ( Old I-A and II-A) in s-block.

The elements of first group-1 (group I-A) of periodic table are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Cesium (Cs) and Francium (Fr). These elements are collectively known as alkali metals. This word is derived from arabic word 'Al-quaily' which means ash of shrubs, because sodium and potassium carbonate salts are in larger proportions in the ash of shrubs or plants. The other reason is that they react with water and form the hydroxides which are alkaline in nature (property).

In the elements of Group-2 (II-A) are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

These elements, except beryllium, are generally known as alkaline earth metals because their oxides and hydroxides are alkaline in nature (property) and the oxides of these metals are available in the \*crust.

### 6.2 Alkali Metals : Occurrence, Atomic and Physical Properties

Amongst alkali metals, sodium and potassium are in greater abundance. The proportion of sodium and potassium in the composition of the soil is about 4%. The proportion of lithium, rubidium and cesium is very less. Even then they are available in many minerals. (Table 6.1) Francium is highly radioactive. The half life period of its isotope  $^{223}\text{Fr}$  is having longest life of only 21 minutes.

\* The thin outer sphere of earth is called crust of the earth.

Calcium and magnesium amongst the alkaline earth metals have their abundance order as fifth and sixth in the crust of the earth. The abundance of strontium and barium is much less. Beryllium is rare and radium is the rarest. Its proportion is only  $10^{-10}$  percent in igneous rocks.

The electronic configurations of s-block elements are [noble gas]  $ns^1$  for alkali metals and [noble gas]  $ns^2$  for alkaline earth metals. The first elements of group-1 and group-2 lithium and beryllium show some properties which are different from those of other elements in that group. These elements having anomalous properties show similarities with elements in the second group following them. Thus lithium (group-1) and beryllium (group-2) show similarity in many of their properties and magnesium (group-2) with aluminium (group-3) respectively. This type of diagonal similarity is generally expressed as "Diagonal relationship" in the periodic table.

This diagonal relationship is due to ionic size and/or charge/radius ratio of the elements. The monovalent sodium and potassium ions and divalent magnesium and calcium ions are available in large proportion in biological fluid. These ions perform important biological functions like maintenance of equilibrium of ions and nerve impulse conductions.

The chief minerals and the compositions of elements of group-1 elements are as follows:

- (i) **Lithium** : Spodumene-  $\text{Li}(\text{AlSiO}_3)_2$   
Lepidotele-  
 $(\text{Li, Na, K})_2\text{Al}_2(\text{SiO}_3)_3[\text{F}(\text{OH})]_6$
- (ii) **Sodium** : Rock salt-  $\text{NaCl}$ ,  
Carnite-  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ,  
Borax-  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  
Chilie Saltpetre-  $\text{NaNO}_3$
- (iii) **Potassium** : Sylvine-  $\text{KCl}$ ,  
Carnalite-  $\text{KCl, MgCl}_2, 6\text{H}_2\text{O}$ .

The atomic and physical properties of alkali metal elements are given in table 6.1

Table 6.1

Properties	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Cesium Cs	Francium Fr
Atomic number	3	11	19	37	55	87
Atomic mass ( $\text{gmol}^{-1}$ )	6.94	22.99	39.10	85.47	132.91	223
Electronic Configuration	$[\text{He}]2s^1$	$[\text{Ne}]3s^1$	$[\text{Ar}]4s^1$	$[\text{Kr}]5s^1$	$[\text{Xe}]6s^1$	$[\text{Rn}]7s^1$
Ionization enthalpy ( $\text{kJmol}^{-1}$ )	520	496	419	403	373	–375
Hydration enthalpy ( $\text{kJmol}^{-1}$ )	–506	–406	–330	–310	–270	–
Metallic radius (pm)*	152	186	227	248	265	–
Ionic radius (pm)*	76	102	138	152	167	(180)
m. p. (K)	454	371	336	312	302	–
b. p. (K)	1615	1156	1032	961	944	–
♦ Density ( $\text{gcm}^{-3}$ )	0.53	0.97	0.86	1.53	1.90	–
Standard potentials $E^0$ (V) for ( $\text{M}^+/\text{M}$ )	–3.04	–2.714	–2.925	–2.930	–2.927	–
Occurrence in lithosphere	18*	2.27**	1.84**	78.12**	2.6*	$10^{-18}$ *

\* ppm (parts per million or parts per ten lacs. \*\* percentage by weight, \*pm = picometer =  $10^{-12}$  meter

(\*) Lithosphere - outlayer of earth : Its crust and upper mantle portion. ♦ SI unit of density is  $\text{kgm}^{-3}$

\*\* A type of rock formed from magma (Molten rock) that has cooled and has become hard.



It will be seen from table 6.1 that alkali metal elements possess one electron in their outermost orbit that is  $ns^1$ . As this electron possesses weak attraction, it can be easily removed and positive ions can be formed. Their ionization enthalpy is low and form easily monovalent ions. Hence, they are called highly electropositive metals. As they lose the electron easily, they are not available in free state in nature but are available in large abundance in the salts having monovalent ions. All the elements are silvery white but their surface becomes dull in air having moisture because a layer of oxide (hydroxide) is formed on their surface. These metals are light. Their low melting points and high electrical conductivity indicate weak bond in solid state.

These metals give different colour flames in oxidising (blue) flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue violet
$\lambda$ (nm)	670.8	589.2	766.5	780.0	455.5

(nm =  $10^{-9}$  meter)

**Activity :** Light a match stick. After some time blow it out. Dip its upper black part in water and wet it. Keep it in salt (sodium chloride) so that salt will stick. Now, start your cooking gas in the house and put it in oxidising (blue) flame. Note what you observe. You will see yellow colour flame which tests the presence of  $Na^+$  in the salt. This is known as flame test in qualitative analysis.

Because of low ionization enthalpy, the outermost electron in s-orbital absorbs energy and gets excited, and goes to higher energy level. Afterwards, in instantaneous time the excited electron returns to its original orbital (ground state) and the absorbed energy is emitted through radiation having specific wave lengths. As the radiations are of different wavelengths, they give different colour flames. Due to this the flame test is carried out in qualitative analysis.

The amounts of Na and K can be determined with the help of instruments like flame photometer or atomic absorption spectrophotometer. Cesium and potassium are used in photoelectric cells because of this property.

Their densities are low because of their larger sizes. The density increases as we move from Li to Cs. Their melting and boiling points

are low which indicate that they possess weak metallic bonds which is due to only one valence electron.

### 6.3 Atomic Size and Ionic Size

The sizes of atoms of alkali metals are highest compared to atomic sizes of other elements in any period of the periodic table. With the increase in atomic number the atom becomes bigger. Monovalent ions ( $M^+$ ) are smaller in size as compared to their parent atoms. The atomic and molecular radii of alkali metals increase as we go down in the group, i.e. as we move from Li to Cs, their sizes and radii increase.

### 6.4. Reaction Enthalpy of Elements

**6.4.1 Ionization enthalpy (energy) :** The ionization enthalpy is lowest for alkali metals as compared to elements of any other group of the periodic table. It decreases as we move from Li to Cs because the nuclear attraction of electron in valence orbit decreases because of their bigger atomic sizes and the electron is easily removed.

Because of high electropositive nature of alkali metals, they can easily form ionic bonds with elements having higher electronegativity e.g. NaCl. As these elements are good conductors of heat, some of them are used as coolants in atomic reactor.

**6.4.2 Hydration enthalpy (energy) :** The hydration enthalpy of alkali metals decreases with increase in their ionic sizes.



The degree of hydration of Li is the highest due to which lithium salts are mainly hydrated, e.g.  $LiCl \cdot 2H_2O$ .

### 6.5 Chemical Reactivity (reactions) of Alkali Metals

Alkali metals are very reactive because of their large size and low ionization enthalpy. The reactivity of these elements increases as we go down in the group.

#### Chemical reactions :

##### (i) Reactivity towards air or oxygen :

The alkali metals get tarnished in dry air because of the formation of their oxides which further react with moisture and form hydroxides. They burn vigorously in air and form oxides. Lithium forms monoxide.





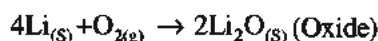
Lithium oxide

Sodium forms peroxide.



(Sodium peroxide)

The other metals form superoxides. Superoxide ions ( $\text{O}_2^{1-}$  ion) are stable only in presence of big cations like K, Rb, Cs.



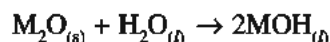
(M = K, Rb, Cs)

The oxidation state of alkali metal in all these oxides is +1.

Lithium, as an exception, also forms lithium nitride ( $\text{Li}_3\text{N}$ ) by direct reaction with nitrogen of air. Alkali metals are kept in kerosene because of their high reactivity.

## 6.6 Oxide and Hydroxide Compounds and Reactivity (reactions) towards dihydrogen, dihalogen, water, ammonia

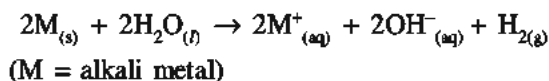
(i)  $\text{M}_2\text{O}$  type oxides of alkali metals react with water and gives strong basic solutions :



The peroxides of these metals give basic solution with water. MOH type basic hydroxides being very strong bases are called alkalies. Sodium hydroxide is called caustic soda and potassium hydroxide is called caustic potash. It burns the skin. LiOH is sparingly soluble in water while the hydroxides of Na, K, Rb and Cs are soluble in water.

(ii) **Reactivity towards water :**

Alkali metals react with water and form hydroxides and dihydrogen (hydrogen molecule) -  $\text{H}_2$ .

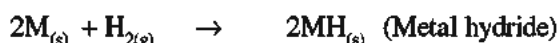


Here, it is necessary to note that the value of reduction potential, Lithium ( $E^0$ ) is negative (Table 6.1) but it reacts less vigorously than sodium which has the lowest value of reduction potential. This behaviour of lithium is

considered due to its small size and high hydration enthalpy. The other metals of the group react violently with water. They also react with proton donors like alcohol, gaseous ammonia and alkyne.

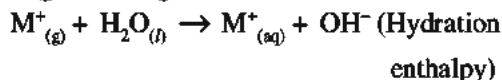
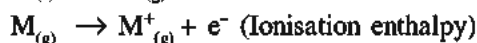
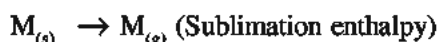
(iii) **Reactivity towards dihydrogen :**

Alkali metals, when heated with dihydrogen, form their hydrides which on reaction with water release dihydrogen gas.



**Reduction nature :**

Alkali metals are strong reducing agents (table 6.1). Lithium is the strongest and sodium is the least strong reducing agent. The standard electrode potential ( $E^0$ ) determines the strength as reducing agent.



With the lowest size of its own ion, lithium, with its highest hydration enthalpy and high negative value of  $E^0$  possesses high reducing strength.

(iv) **Reactivity towards halogens :**

Alkali metals react instantaneously and violently with halogens and form ionic halides  $\text{M}^+\text{X}^-$ . Lithium halide is somewhat covalent. The reason for this is the high polarization capability of lithium ions. The distortion in electron cloud of electron produced by cation is called polarization.  $\text{Li}^+$  ion is very small in size and distorts the electron cloud around halide ion. The anions with large size easily get destroyed and so lithium iodide amongst halides is more covalent. Halogens act as oxidising agent in formation of halides.

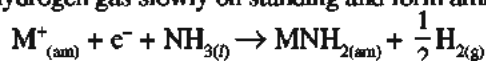
The halide compounds of alkali metals are colourless, crystalline, solids having high melting point and are stable ionic compounds. The melting points and boiling points of any alkali metal is in order fluoride > chloride > bromide > iodide. All halide compounds except lithium fluoride are soluble in water.

(v) **Reactivity towards liquid ammonia :**

The alkali metals dissolve in liquid ammonia and give deep blue coloured solutions which are electric conductor in nature.

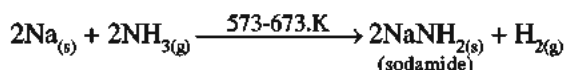


The blue colour of the solution is due to ammoniated electron, which absorbs light from visible spectrum and gives blue colour to solution. These solutions are paramagnetic and liberate dihydrogen gas slowly on standing and form amide.



where 'am' indicates solution which is in ammonia. The blue colour in strong solutions changes to bronze colour and becomes diamagnetic.

When dry ammonia gas is passed over sodium metal at 573-673K temperature sodamide is formed and dihydrogen gas is liberated.



#### (vi) Salts of oxo acids :

Oxo-acids are such acids in which acidic proton is in hydroxyl group and the oxo group is combined with the same atom. e.g. Carbonic acid  $H_2CO_3$  ( $OC(OH)_2$ ), Sulphuric acid  $H_2SO_4$  ( $O_2S(OH)_2$ ). Alkali metals form salts with all oxo acids. They are generally soluble in water and are thermally stable. Their carbonates ( $M_2CO_3$ ) and most of the hydrogen carbonates (bicarbonates) are more stable towards heat. As we go down in the group the stability of carbonates and hydrogen carbonates increases. Lithium carbonate is not so stable towards heat. Lithium, being small in size, decomposes into  $Li_2O$  and  $CO_2$ . Its hydrogen carbonate does not exist as solid.

### 6.7 Diagonal Relationship and Irregularity (Lithium and Magnesium)

**6.7.1 Diagonal relationship of lithium with magnesium :** The similarities between lithium (group-1) and magnesium (group-2) is surprising. The reason for its existence is their similar sizes.

Atomic radii	Li = 152 pm	Mg = 160 pm
Ionic radii	$Li^+ = 76$ pm	$Mg^{2+} = 72$ pm

The main points of the similarity are as follows :

- (i) Lithium and magnesium elements are harder but softer than the other elements of the corresponding groups.
- (ii) Lithium and magnesium react slowly with water. Their oxides and hydroxides are very less soluble in water. Their hydroxides decompose on heating.

- (iii) Lithium and magnesium both combine with nitrogen directly and form nitrides ( $Li_3N$  and  $Mg_3N_2$ )
- (iv) The oxides  $Li_2O$  and  $MgO$  do not give superoxides by combining with more oxygen.
- (v) On heating carbonates of lithium and magnesium, decompose easily and give oxides and carbon dioxide. Solid hydrogen carbonates are not formed by lithium and magnesium.
- (vi) Both  $LiCl$  and  $MgCl_2$  are soluble in ether.
- (vii) Both  $LiCl$  and  $MgCl_2$  are hygroscopic and crystallise, as  $LiCl \cdot 2H_2O$  and  $MgCl_2 \cdot 8H_2O$  from their aqueous solutions.

#### 6.7.2 Anomalous behavior of lithium from other elements of the group :

- (i) Lithium is very hard. Its melting point and boiling point are higher than those of other alkali metals.
- (ii) Lithium is least reactive amongst alkali metals. Monoxide  $Li_2O$  and nitride  $Li_3N$  are formed. This does not happen in other alkali metals.
- (iii)  $LiCl$  is deliquescent and crystallises as hydrate  $LiCl \cdot 2H_2O$  while other alkali metals do not form hydrates.
- (iv) Lithium hydrogen carbonate (lithium bicarbonate) is not obtained in solid form while all other elements form solid hydrogen carbonates (bicarbonates.)
- (v) Lithium unlike other alkali metals does not form ethynide by reaction with ethyne.
- (vi) Lithium nitrate when heated gives lithium oxide ( $Li_2O$ ) while other alkali metal nitrates decompose into their corresponding nitrites.
 
$$4LiNO_{3(s)} \rightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$2NaNO_{3(s)} \rightarrow 2NaNO_{2(s)} + O_{2(g)}$$
- (vii)  $LiF$  and  $Li_2O$  are very less soluble in water compared to the corresponding compounds of their metals.

### 6.8 Diagonal Relationship and Irregularity (Beryllium and aluminium)

**6.8.1 Diagonal relationship of beryllium with aluminium :** The ionic radius of  $Be^{2+}$  is about 31 pm. The ratio of charge/radius of  $Be^{2+}$  ion is almost nearer to that of  $Al^{3+}$  ion. Hence, beryllium possesses similarities in certain cases. Some of such similarities are as under :

- (i) Beryllium like aluminium does not react very fast with acid because of the oxide layer on the surface of metal.

- (ii) Beryllium hydroxide becomes soluble in excess alkali forming beryllate ion.  $[\text{Be}(\text{OH})_4]^{2-}$  which is similar to aluminate ion.  $[\text{Al}(\text{OH})_4]^-$  is formed by aluminium hydroxide with excess alkali.
- (iii) The chlorides of both beryllium and aluminium possess -Cl bridge in their vapour state. Chlorides of both are soluble in organic solvents and are strong Lewis acids.  $\text{AlCl}_3$  is used as Friedel-Crafts catalyst.
- (iv) Beryllium and aluminium ions have greater tendency to form complexes. e.g.  $[\text{BeF}_4]^{2-}$ ,  $[\text{AlF}_6]^{3-}$
- (v) Beryllium like aluminium is passive towards nitric acid.
- (vi) Aluminium carbide  $\text{Al}_4\text{C}_3$  and beryllium carbide  $\text{Be}_2\text{C}$  with water gives methane gas.

**6.8.2 Anomalous behavior of beryllium from other elements of the group :** Beryllium, the first element of second group elements, shows anomalous behaviour as compared to other members of the group.

- (i) Beryllium as an exception has small atomic and ionic sizes and so it can not be compared with other elements of the group. Its compound that it forms are mostly covalent because of their high ionization enthalpy and small size and consequently hydrolyse easily.
- (ii) Beryllium has four electrons in its orbital and so there are four orbitals and therefore it can not exhibit coordination numbers more than four. Other elements of the group can utilize d-orbitals and obtain co-ordination number six.
- (iii) Oxide and hydroxide of beryllium are amphoteric compared to other members of the group. Oxides and hydroxides of other members are basic in nature.

### 6.9 Lithium (Occurrence, Properties and Uses)

The chief minerals of lithium and their compositions are as follows :

- (i) Spodumene -  $\text{LiAl}(\text{SiO}_3)_2$ ,
- (ii) Lepidolite  $(\text{Li}, \text{Na}, \text{K})_2\text{Al}_2(\text{SiO}_3)_3(\text{F}, \text{OH})_2$ ,
- (iii) Amblygonite -  $\text{Li}_2\text{Al}(\text{PO}_4)\text{F}(\text{OH})$ .

**Extraction :** The extraction of lithium from its minerals is carried out by the following two steps :

- (i) To obtain LiCl from mineral and (2) electrolysis of LiCl. In the first step, the mineral is heated at 1373 K and then it reacts with sulphuric acid at 573 K temperature and then mixed with water it converts in to  $\text{Li}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . Then reacts with sodium carbonate and finally reacting with hydrochloric acid LiCl is formed.
- (ii) In the second step, the molten mixture of 55% LiCl and 45% KCl is electrolysed giving lithium containing 1% impurity of K.

### Properties :

- (i) Lithium is silvery white and softer metal than lead, but harder than sodium.
- (ii) Being smallest in the size of the elements of group-1 the values of its melting point, boiling point and ionization enthalpy are the highest.

### Uses :

It is used

- (i) As reducing agent.
- (ii) In formation of alloys.
- (iii) In aeronautic industry.
- (iv) In formation of Armeour plate.
- (v) In formation of very strong and corrosion resistant alloy (1% Mg + 14% Li)

### 6.10 Sodium (Occurrence, Properties and Uses)

Sodium metal, being very reactive, is not available free in nature but it can lose one electron easily and form stable monovalent ion. So it is available in large abundance in combined form in the crust of earth, sea water etc. Its chief minerals and their compositions are as follows :

- (i) Rock Salt ( $\text{NaCl}$ ) (ii) Chile salt petre ( $\text{NaNO}_3$ ) (iii) Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )

**Extraction :** On electrolysis of aqueous solutions of sodium salts, dihydrogen gas instead of sodium metal is obtained at the cathode, because the reduction potential of sodium metal is more negative than that of dihydrogen. Hence, the salts of sodium are melted and then electrolysed, so that sodium metal is obtained at the cathode. The industrial production of sodium is carried out via Down cell by electrolysis of sodium chloride melted at 1123 K. In the Down cell, anode is inert graphite and steel or iron is cathode. Sodium metal



is obtained at cathode. Chlorine gas is liberated at anode. In the Down cell, a protective membrane is kept between the two electrodes so that there is no reaction between sodium and chlorine. Sodium is kept in kerosene so as to keep it away from the reaction with air and water.

#### Cell reaction :

Anode :  $2\text{Cl}^-_{(l)} \rightarrow \text{Cl}_{2(g)} + 2e^-$  (Oxidation)

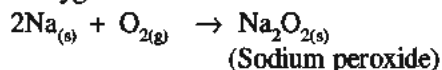
Cathode :  $\text{Na}^+_{(l)} + e^- \rightarrow \text{Na}_{(s)}$  (Reduction)

#### Properties :

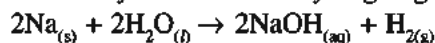
**Physical :** Sodium is a silvery shining and soft metal. It gets tarnished when kept in open air because it is very reactive. (If it is cut with a knife, its inner part will shine). It is kept in kerosene because it is very reactive.

#### Chemical :

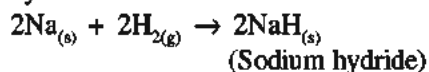
- (i) **Reactivity towards dioxygen :** Sodium metal reacts very fast with dioxygen and gives peroxide in presence of excess of dioxygen.



- (ii) **Reactivity towards water :** Sodium metal reacts very fast and vigorously with water and sometimes there is explosion and it gives sodium hydroxide and dihydrogen gas.



- (iii) **Reactivity towards dihydrogen :** Sodium reacts with dihydrogen and forms sodium hydride.



- (iv) **Reactivity towards halogen :** Sodium reacts very fast with halogens and forms halides.



**Uses :** Sodium is used

- (i) as reducing agent
- (ii) as liquid coolant in atomic reactor
- (iii) in dye industry
- (iv) as vapour in sodium light (yellow colour street lights)
- (v) in the test of elements in organic compounds Lassaigne test.

### 6.11 Alkaline Earth Metals (Occurrence, Physical Properties and Electronic Structure)

Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra) are the elements of group-2 (II-A). They follow alkali metals in the periodic table. These elements, except beryllium, are called alkaline earth metals. The first element beryllium differs from other elements of the group but possesses diagonal relationship with second element of the next group. The chief minerals of these elements are mentioned in table 6.2. These metals are not available free in nature. Calcium and magnesium are available in greater abundance and strontium and barium in very small proportion, radium is radioactive and is obtained in very less proportion in the combined form.

Table 6.2

Element	Chief minerals and composition
Beryllium	Oxide Beryl : $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ , $6\text{SiO}_2$ (15% BeO) Oxide crenaside : $\text{BeO} \cdot \text{Al}_2\text{O}_3$ (7% BeO) Oxide bromalite : BeO (45% BeO)
Magnesium	Magnesite : $\text{MgCO}_3$ , Epsom salt : $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ Criserite : $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , Carnalite : $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ Crinite : $\text{K}_2\text{SO}_4$ , $\text{MgSO}_4$ , $\text{MgCl}_2$ Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$
Calcium	Lime stone, Chalk, Marble : $\text{CaCO}_3$ Gypsum : $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Flourspar : $\text{CaF}_2$ Flourapatite : $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ , Chlorapatite : $[\text{Ca}_5(\text{PO}_4)_3\text{Cl}]$
Strontium	Strontianide : $\text{SrCO}_3$ , Silastine : $\text{SrSO}_4$
Barium	Witherite : $\text{BaCO}_3$ , Baryte : $\text{BaSO}_4$
Radium	In combined salt form in minerals like Pitchblende, Carnalite



Table 6.3

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic number	4	12	20	38	56	88
Atomic mass (g mol <sup>-1</sup> )	9.01	24.31	40.08	87.62	137.33	226.03
Electronic configuration	[He]2s <sup>2</sup>	[Ne]3s <sup>2</sup>	[Ar]4s <sup>2</sup>	[Kr]5s <sup>2</sup>	[Xe]6s <sup>2</sup>	[Rn]7s <sup>2</sup>
First ionization enthalpy (kJmol <sup>-1</sup> )	899	737	590	549	503	509
Second ionization enthalpy (kJmol <sup>-1</sup> )	1157	1450	1145	1064	965	979
Hydration enthalpy (kJmol <sup>-1</sup> )	-2494	-1921	-1577	-1443	-1305	—
Metallic radius (pm)	111	160	197	215	222	—
Ionic radius (pm) (M <sup>2+</sup> ion)	31	72	100	118	135	148
Melting point (K)	1560	924	1124	1062	1002	973
Boiling point (K)	274	1363	1767	1655	2078	(1973)
Density (g cm <sup>-3</sup> )	1.84	1.74	1.55	2.63	3.59	(5.5)
Standard potential (E <sup>(0)</sup> for M <sup>2+</sup> /M)V	-1.97	-2.36	-2.84	-2.89	-2.92	-2.02
Lithosphere	2*	2.76**	4.6**	3.84*	3.90*	10 <sup>-6</sup> *

\* ppm (Parts per million) \*\* Percentage by weight

**Electronic configuration :** It is clear from table 6.3 that the general electronic configuration of these elements can be shown as [noble gas] ns<sup>2</sup> and have two electrons in their outermost orbital. As these electrons can be easily lost, they are mainly ionic.

**Ionization enthalpy :** The reason for low ionization enthalpy of alkaline earth metals is to some extent due to their large size. The first ionization enthalpy ( $M \rightarrow M^{1+} + e^{-}$ ) of alkaline earth metals is more than that of corresponding group-1 metals. The reason for this is that their size is smaller in comparison to corresponding alkali metals. It is interesting to note that the second ionization enthalpy of alkaline earth metals ( $M^{1+} \rightarrow M^{2+} + e^{-}$ ) is less than that of their corresponding alkali metals.

**Hydration enthalpy :** Like alkali metal ions, the hydration enthalpy of alkaline earth metal ions is more than alkali metal ions. Hence the compounds of alkaline earth metals get hydrated extensively as compared to alkali metal compounds. e.g. MgCl<sub>2</sub> and CaCl<sub>2</sub> exist as MgCl<sub>2</sub>·6H<sub>2</sub>O and CaCl<sub>2</sub>·2H<sub>2</sub>O respectively while NaCl and KCl do not form hydrates.

### 6.12 Related trend between Physical Properties

Alkaline earth metals are generally white, shiny and soft but hard in comparison to alkali metals. Beryllium and magnesium appear somewhat like ash colour. They are ductile and malleable. The melting points and boiling points of these metals are higher than the corresponding alkali metals. Because they are small in size, this trend is not systematic. Due to low ionization

enthalpy they are strongly electropositive in nature. This characteristic increases as we move from Be to Ba. Calcium, barium and strontium give characteristic flames. Calcium-Brick red, Barium-Light green and Strontium-Crimson red. The electron in the outermost orbit gets excited to higher energy level when kept in flame and on returning of electron the emitted energy absorbs colour from the visible spectrum. The electrons of beryllium and magnesium are so strongly bonded that they do not get excited in flame. Ca, Sr and Ba are detected by flame test in qualitative analysis. The quantitative analysis of calcium can be done with flame photometer or atomic absorption spectrophotometer. The alkaline earth metals are good conductors of heat and electricity because of the higher electrical and thermal conductivity. This is a specific characteristic of these metals.

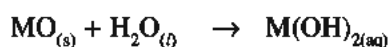
### 6.13 Chemical Properties : Reactivity (reactions) of Dioxigen and Water with Metals

The alkaline earth metals are less reactive as compared to alkali metals. The reactivity increases as we go down in the group.

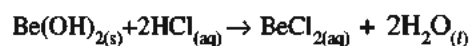
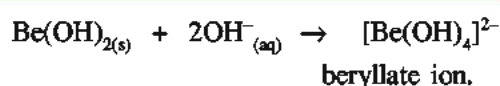
Beryllium and magnesium are inert from reactivity point of view because there is an oxide layer on their surfaces, but powdered beryllium burns brightly in air and gives BeO and Be<sub>3</sub>N<sub>2</sub>. Magnesium being more electropositive burns in air brightly giving shining light and gives MgO and Mg<sub>3</sub>N<sub>2</sub>. Calcium, strontium and barium quickly get attacked by air and give oxides and nitrides. They react quickly with water and form hydroxides.

### 6.14 Oxide and Hydroxide Compounds

Alkaline earth metals form oxides of the type MO which are white coloured compounds. The oxides of beryllium and magnesium are sparingly soluble in water, while solubility of oxides of remaining metals increases gradually. Beryllium oxide is amphoteric while other oxides are strongly basic and absorb moisture and carbon dioxide of air.



Be(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> can be obtained by reaction of NaOH with their water soluble salts. They are less basic than oxides of alkali metals. As we go down in the group there is gradual increase in the solubility of the hydroxides. Beryllium hydroxide is amphoteric, so it reacts with base and acid respectively.



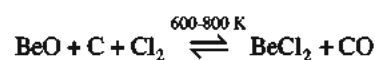
### 6.15 Halide Compounds

#### Reactivity towards halogens :

All the alkaline earth metals at high temperature combine with halogens and form their halides.

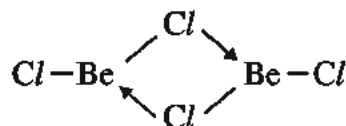


The best reaction of formation of BeF<sub>2</sub> is the decomposition of (NH<sub>4</sub>)<sub>2</sub> BeF<sub>4</sub> BeCl<sub>2</sub>. It can be prepared easily from its oxide.



All the halides of alkaline earth metals with exception of beryllium halide are ionic in nature. Beryllium halide is chiefly covalent and soluble in organic solvents. The form of beryllium chloride in solid state is chain-like.

BeCl<sub>2</sub> in vapour state forms a dimer having chloro-chloro (Cl-Cl) bridge.

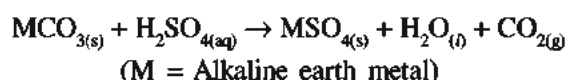


It dissociates into monomer at about 1200 K. The tendency of formation of halide hydrates decreases gradually as we go down in the group. e.g. MgCl<sub>2</sub>·8H<sub>2</sub>O, CaCl<sub>2</sub>·6H<sub>2</sub>O, CrCl<sub>2</sub>·6H<sub>2</sub>O, BaCl<sub>2</sub>·2H<sub>2</sub>O. The dehydration of hydrated chloride, bromide and iodide of barium, calcium and strontium can be carried out by heating, but the corresponding hydrated halides of Be and Mg undergo hydrolysis. Fluorides are relatively less soluble than chlorides. The reason for this is their higher lattice energy.

### 6.16 Solubility and Thermal Stability of Oxosalts

Alkaline earth metals form salts of oxo acids. Some of them are as follows :

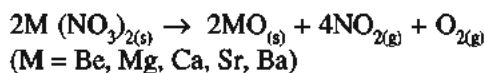
**Sulphates :** Sulphates of alkaline earth metals can be obtained by reaction of sulphuric acid with carbonates of metals.



It is a white solid substance and thermally stable. BeSO<sub>4</sub> and MgSO<sub>4</sub> dissolve readily in water. The solubility decreases as we move from

CaSO<sub>4</sub> to BaSO<sub>4</sub>. The hydration enthalpy of Be<sup>2+</sup> and Mg<sup>2+</sup> ions is more than the lattice enthalpy and so they are soluble in water.

**Nitrates :** Nitrates can be obtained by reaction of dilute nitric acid with metal carbonates. Magnesium nitrate crystallizes as magnesium nitrate with molecules of water, while barium nitrate crystallizes as anhydrous salt. This also shows that with increase in ionic size and with decreasing hydration enthalpy, there is a decrease in tendency of formation of hydrates. All of them, when heated, decompose into oxides like lithium nitrate.



**Carbonates :** The carbonates of alkaline earth metals are insoluble in water. They can be precipitated by adding sodium carbonate or ammonium carbonate to aqueous solutions of their soluble salts. With the increase in atomic number, the solubility of carbonate salts gradually decreases.

#### Reduction nature of metals :

The alkaline earth metals like alkali metals are strong reducing agents. This is indicated by their more negative reduction potentials (Table 6.3). Their power as reducing agent is less than that of their corresponding alkali metals. In comparison to other alkaline earth metals, the value of beryllium is less negative. Its reducing nature is associated with its higher hydration enthalpy which is in accordance with its (Be<sup>2+</sup>) small size and higher value of metal atomic enthalpy.

**Solutions in liquid ammonia :** Alkaline earth metals like alkali metals dissolve in liquid ammonia and give dark blue coloured solutions by forming ammoniated ion.



The ammoniated ion  $[\text{M}(\text{NH}_3)_x]^{2+}_{(am)}$  can be obtained from solution.

**Uses :** Beryllium is used in production of alloys. Copper-beryllium alloy is used in the formation of springs having more strength. Beryllium metal is used in windows of X-ray tubes. Magnesium and aluminium form alloys with zinc, manganese and tin. Magnesium-aluminium alloy being light in weight is used in making aeroplanes. Magnesium powder and ribbons are used in flash powder, bulbs incendiary bombs and signals. Mg metal is used in preparation of Grignard reagent. The suspension

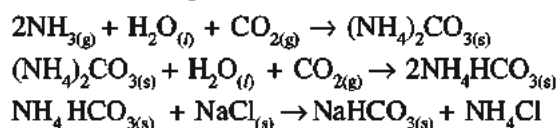
of magnesium hydroxide in water is known as milk of magnesia. It is used as antacid in medicines. Magnesium carbonate is one of the components in tooth paste. The use of calcium is made in the reduction of oxides which cannot be reduced by carbon to obtain metals. Calcium and barium metals, having reactivity with oxygen and nitrogen at higher temperatures, are used to remove air from vacuum tubes. Salts of radium are used in radiotherapy. e.g. in treatment of cancer.

### 6.17 Production, Properties and Uses of Some Compounds of Sodium : Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaHCO<sub>3</sub>

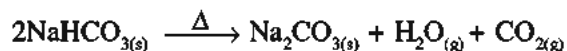
The useful compounds of sodium are NaOH, Na<sub>2</sub>CO<sub>3</sub>, 10H<sub>2</sub>O and NaHCO<sub>3</sub>. Their production, properties and uses will be studied here.

**Production of Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O) :** Sodium carbonate is also known as washing soda and soda ash. Generally, its industrial production is carried out by Solvay method (Solvay ammonia soda method) or process.

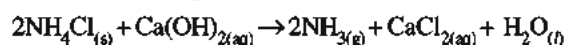
In this process advantage of less solubility of sodium hydrogen carbonate (Sodium bicarbonate) -NaHCO<sub>3</sub> is taken. It is precipitated by reaction of ammonium hydrogen carbonate (ammonium bicarbonate) with sodium chloride. Ammonium hydrogen carbonate is prepared by passing carbon dioxide from a solution of sodium chloride saturated with ammonia. Ammonium carbonate obtained is later on converted to ammonium bicarbonate. The reaction equations for the whole process are as follows :



Sodium hydrogen carbonate being sparingly soluble, its crystals are formed. They are separated and then heated so that sodium carbonate is formed.



Ammonia can be obtained back in this process. By reaction of Ca(OH)<sub>2</sub> with the solution containing NH<sub>4</sub>Cl, ammonia can be obtained as by product.



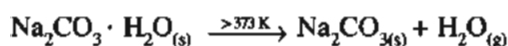
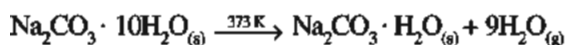
It is necessary here to remember that Solvay process cannot be used for production of potassium carbonate. The reason for this is that potassium hydrogen carbonate (bicarbonate)



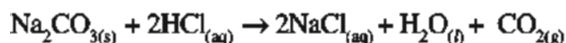
is very highly soluble that by addition of ammonium hydrogen carbonate to potassium chloride, does not get precipitated.

### Properties :

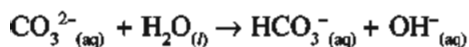
Sodium carbonate is a crystalline white solid substance which possesses existence as decahydrate (ten molecules of water of crystallisation  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). It is known as washing soda. When decahydrate is heated, it loses water of crystallisation and forms monohydrate (One molecule of water of crystallisation and forms monohydrate). On heating at temperature higher than 373K, it becomes completely anhydrous and changes to white powder form which is known as soda ash  $\text{Na}_2\text{CO}_3$ .



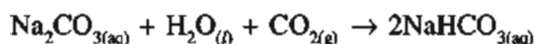
It produces carbon dioxide by reacting with acid.



The carbonate ion of sodium carbonate reacts with water and forms alkaline solution by hydrolysis.



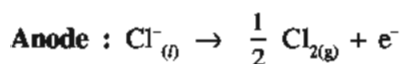
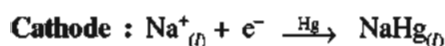
Sodium hydrogen carbonate is formed when carbon dioxide gas is passed through a solution of sodium carbonate.



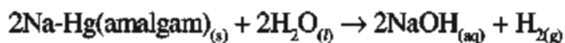
**Uses :** It is used in (i) softening hard water (ii) washing and cleansing (iii) manufacturing of compounds like glass, soap, borax and caustic soda (iv) paper, dye and textile industries and (v) as laboratory reagent in chemical analysis.

### Sodium hydroxide (Caustic soda) (NaOH) :

**production :** The industrial production of sodium hydroxide is carried out by electrolysis of a solution of sodium chloride in Castner Kellner cell. Electrolysis of brine solution (Solution containing sodium chloride) is carried out using mercury cathode and carbon anode. Sodium metal that is liberated at the cathode combines with mercury and forms sodium amalgam (Na-Hg) and chlorine is produced at the anode



Sodium hydroxide and dihydrogen gas are produced by reacting amalgam with water.



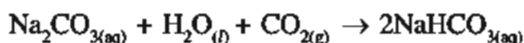
**Properties :** Sodium hydroxide is white translucent solid substance. It melts at 591 K temperature. It reacts with water and dissolves in it and produces heat because of its exothermic reaction and gives strong alkaline solution. Its crystals are highly hygroscopic. The solution of sodium hydroxide absorbs  $\text{CO}_2$  from the atmosphere above its surface and reacts, so that  $\text{Na}_2\text{CO}_3$  is formed.

**Uses :** Sodium hydroxide is used in (i) preparation of soap, paper, artificial silk and number of chemicals (ii) refining of petroleum (iii) purification of bauxite the mineral of aluminium (iv) textile industry for mercerization of cotton cloth (v) to prepare pure fat and oil and (vi) as reagent in laboratory.

### Sodium hydrogen carbonate (Sodium bicarbonate) ( $\text{NaHCO}_3$ ) :

Sodium bicarbonate is called sodium hydrogen carbonate in modern nomenclature. It is also known as baking soda (baking powder). On heating it decomposes and produces bubbles of liberated carbon dioxide. Because of this holes are produced fluffy in edible substance like pastry etc. Due to this they become soft.

Sodium carbonate solution is saturated with carbon dioxide to prepare sodium hydrogen carbonate. It can also be obtained by Solvay ammonia soda process.



It separates out as it is less soluble in water.

**Properties :** Sodium hydrogencarbonate is a white crystalline solid substance. It is less soluble than  $\text{Na}_2\text{CO}_3$ . It gives alkaline solution on reaction with water.

**Uses :** Sodium hydrogencarbonate is a mild antiseptic for the infection of skin diseases. Hence, (1) used as antiseptic, (2) it is used as fire extinguisher in extinguisher - cylinders, in the cylinder the acid kept with it reacts and produces carbon dioxide gas (3) As an antacid for the acid in the stomach and (4) as reagent in laboratory.

### 6.18 Biological Importance of $\text{Na}^+$ and $\text{K}^+$ Ions

Anybody having weight of 70 kg possesses 90 gram Na and 170 gram K. In its comparison only 5 gram Fe and 0.06 gram Cu are possessed.



Primarily sodium ions are present on the cells being located in blood plasma and the interstitial fluid which surrounds the cells. These ions play an important role in nerve signal transmission control of flow of water between cell membrane, for transport of sugar and amino acids. It seems that sodium and potassium possess many similarities from chemistry point of view but differentiate quantitatively in penetration through cell wall, their flow mechanism and efficiency in activating the enzyme. Thus potassium ions are cation in abundance where they activate the enzyme and become responsible for producing ATP by oxidation of glucose and transport of nerve signal with sodium. On the opposite sides of the cell membrane there is a noticeable variation in the concentration of sodium and potassium ions.

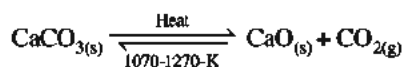
If we take a typical example, the level of sodium in the red blood cells in blood plasma is about  $143 \text{ mmol lit}^{-1}$  while that of potassium is only  $5 \text{ mmol lit}^{-1}$ . These concentrations change to  $10 \text{ mmol lit}^{-1} (\text{Na}^+)$  and  $105 \text{ mmol lit}^{-1} (\text{K}^+)$ . This concentration degradation is the indication of a discriminative mechanism which is called sodium potassium pump. This pump utilises more than one third part of ATP when the animal is taking rest and in human being 15 kg per 24 hours. If this sodium-potassium pump does not work properly it creates many problems regarding blood pressure in human beings. For example, if concentration of  $\text{Na}^+$  increases doctors advise to stop taking more sodium chloride. The high concentration of sodium ion increases blood pressure.

### 6.19 Production, Properties and Uses of Some Compounds of Calcium : $\text{CaO}$ , $\text{CaCO}_3$ , Plaster of Paris and Cement

Amongst the important compounds of calcium are quick lime (calcium oxide), slaked lime (calcium hydroxide), lime stone (calcium carbonate) and cement. These are important compounds from industrial point of view. We shall study production on large scale, properties and uses of these compounds

#### (1) Quick lime (Calcium oxide) ( $\text{CaO}$ ) :

Calcium oxide is obtained on commercial scales by heating lime stone ( $\text{CaCO}_3$ ) at  $1070\text{--}1270 \text{ K}$  temperature in rotary kiln

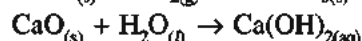
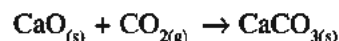


As soon as carbon dioxide is produced it is removed, so that the reaction goes towards

completion (Forward direction) and reverse reaction is stopped.

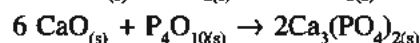
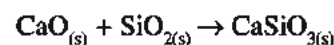
#### Properties :

- (i) It is a pure white solid substance whose melting point is  $2870 \text{ K}$ .
- (ii) When heated in oxyhydrogen flame it emits bright white luminous flame.
- (iii) It absorbs carbon dioxide and moisture when kept open in air.



On adding limited amount of water, lumps of limestone break into pieces. This process is known as slaking of lime.

- (iv) Quick lime gives soda lime on mixing with caustic soda.
- (v) Being basic it combines with acidic oxides at high temperature.



- (vi) It forms calcium carbide with carbon at  $2273 \text{ K}$ .

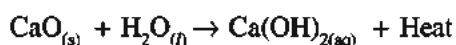


#### Uses : Calcium oxide is used in

- (1) preparation of slaked lime (2) preparation of bleaching powder, dyes and distemper, (3) in preparation of calcium carbide, cement, mortar etc. (4) in purification of sugar, coal gas and softening of hard water (5) as layers on the inner sides of electric furnaces (6) preparation of ammonia gas in the laboratory.

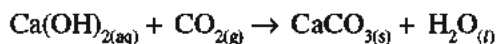
#### (2) Calcium hydroxide (Slaked lime

$(\text{Ca(OH)}_2)$  -Preparation : When water is added to lumps of quick lime, large amount of heat is produced and the lumps break to give powder which makes the solution containing calcium hydroxide.

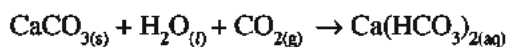


#### Properties :

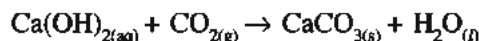
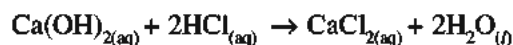
- (i) Calcium hydroxide is a white powder form solid.
- (ii) It is sparingly soluble in water.
- (iii) Its aqueous solution is called lime water which is alkaline.
- (iv) The suspension of slaked lime is known as milk of lime which is alkaline.
- (v) When carbon dioxide is passed through its solution it becomes turbid because sparingly soluble  $\text{CaCO}_3$  is formed.



If carbon dioxide gas is passed for a longer time from this solution, the precipitates of calcium carbonate dissolve in water and the solution of calcium hydrogen carbonate (calcium bicarbonate)  $\text{Ca(HCO}_3)_2$  is obtained.



- (vi) Milk of lime forms hypochloride by reaction with chlorine which is component of bleaching powder.
- (vii) Being alkaline it reacts with acid or acidic oxide to give salt and water

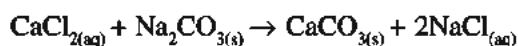
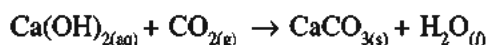


**Uses :** Calcium hydroxide is used in (i) preparation of mortar which is one of the components of building materials (ii) white washing of walls because of its insecticide nature (iii) absorption of acidic gases and to get ammonia from ammonium chloride (iv) glass and leather industry, purification of sugar, preparation of bleaching powder (v) as antiseptic and in softening of hard water as well as in the laboratory for the test of carbon dioxide.

### Calcium carbonate (lime stone) ( $\text{CaCO}_3$ ):

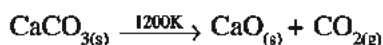
**Preparation :** The chemical name of lime stone is calcium carbonate. It is obtained from nature in different forms such as chalk, marble, corals, shells. It is obtained in two crystalline forms Calcite and Aegonite.

It can be prepared by passing carbon dioxide through slaked lime or adding sodium carbonate to a solution of calcium chloride.

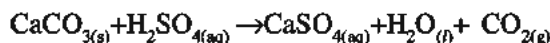


Large amount of carbon dioxide should not be passed, otherwise calcium hydrogen carbonate will be obtained which is soluble in water

**Properties :** Calcium carbonate is (i) white fluffy powder (ii) It is almost insoluble in water (iii) On heating at 1200 K temperature it decomposes to give calcium oxide and carbon dioxide gas.



(iv) On reaction with dilute acids it forms the corresponding calcium salts and carbon dioxide.

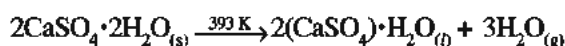


**Uses :** (i) In the form of marble as construction material (ii) It is used in production of quick lime (iii) The mixture of calcium carbonate and magnesium carbonate is used as flux in the extraction of metal like iron (iv) Specially precipitated calcium carbonate is used for manufacture of high quality paper (v) It is used as antacid in medicines as abrasive in tooth paste as one component in chewing gum and as filler in cosmetic materials.

### Plaster of Paris : ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) OR ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) :

Plaster of Paris is hemihydrate or semihydrate of calcium sulphate.

When gypsum is heated at 393K plaster of Paris is obtained



There is no water of crystallisation. When heated at temperature more than 393 K it becomes anhydrous  $\text{CaSO}_4$ . This is known as dead burnt plaster. With every two  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions one molecule of water is combined.

### Properties :

(i) Plaster of Paris is white powder form solid substance. (ii) When it is soaked in water by one third portion of its weight, it becomes hard expanded substance by intercombination of gypsum crystals. This property of its setting with water is noticeable. It becomes very hard solid substance by setting in 5 to 15 minutes. (iii) Its setting velocity can be increased by addition of common salt. The setting velocity can be decreased by addition of borax or alum. (iv) When heated at temperature higher than 473K anhydrous  $\text{CaSO}_4$  is formed and is unable to set. (v) The mixture of alum and plaster of Paris which becomes very hard on setting is called keem cement.

**Uses :** The maximum use of plaster of Paris is in (i) construction industry and in plastering (ii) plastering of fractured bones after operation, in muscles having sprain, in dentistry

for preparation of casts for dentures, casts for ornaments, preparation of statues (iii) in laboratory its plaster is applied on the vessels to make them airtight (iv) in chalks for writing on board.

**Cement :** Cement is one of the important substances for construction. It was first introduced by Joseph Aspidin in England in 1824. It is also called Portland because it is similar to natural lime stone available in the mines of stone in the 'Isle of Portland'.

Cement is such a product which can be obtained by reaction of quick lime rich in CaO with silica ( $\text{SiO}_2$ ). It is reacted with oxides of aluminium, magnesium and iron. The average composition of cement is CaO : 50-60%,  $\text{SiO}_2$  : 20-25%,  $\text{Al}_2\text{O}_3$  : 5-10%, MgO : 2-3%,  $\text{Fe}_2\text{O}_3$  : 1-2% and  $\text{SO}_3$  : 1.3%

For a good quality of cement, the ratio of silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) must be between 2.5 to 4 and the ratio of lime (CaO) and total oxide [oxide of silicon ( $\text{SiO}_2$ ) to oxide of aluminium ( $\text{Al}_2\text{O}_3$ ) + oxide of iron ( $\text{Fe}_2\text{O}_3$ )] should be as near as possible to 2.

The raw materials for production of cement are lime stone and clay. When clay and lime are heated very strongly, they melt and give a hard brick like substance which is known as cement clinker. To this cement clinker, 2-3% by weight gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is added and heated at 1773 K temperature in rotary furnace. The substance obtained is passed through 325 mesh (measure of pores of sieve) sieve and 2-5% gypsum is added.

The important ingredients of portland cement are dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ) 26%, tricalcium silicate ( $\text{Ca}_3\text{SiO}_5$ ) 51% and tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) 11%

#### Properties :

- (i) The quality of portland cement is known by

$$(A) \text{ Silica module : } \eta = \frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3}$$

$$(B) \text{ Alumina module } P = \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3}$$

- (ii) If brought in contact with water it starts gaining strength and becomes hard.

- (iii) It appears like ash colour due to presence of iron.

- (iv) The constructions with this cement get affected by acid.

- (v) The water containing dissolved carbon dioxide and water containing calcium and magnesium salts have effect on its strength.

**Setting of cement :** When cement is mixed with water, it sets down and a hard substance is formed. This is called setting of cement. The reason for this is the hydration of component molecules and their rearrangement. The reason for addition of gypsum is to slow down the time of setting of cement so that it can become sufficiently hard. Its primary strength is seven days. The setting times of dicalcium and tricalcium silicates are 28 days and one year respectively.

**Uses :** After iron and steel, the selection of national requirement of any country is cement. It is used in

- Construction of roads and buildings.
- Around the iron bars the concrete containing portland cement is allowed to set so that very hard reinforce cement concrete is formed and it is used in construction of slabs, bridges, dams etc.

#### 6.20 Biological Importance of $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ Ions

The body of an adult contains about 25 gram Mg and 1200 gram Ca as well as 5 gram Fe and 0.06 gram Cu. Its daily requirement in human body is estimated to be 200-300 milligram.

All the enzymes which use ATP in the transfer of phosphate; they require magnesium as a cofactor. The chief pigment of absorption of light in the plants is chlorophyll which contains magnesium (It is a complex of magnesium). About 99% of calcium present in the body is in bones and teeth.

In addition, it also plays an important role in neuromuscular function, interneuronal transmission cell membrane integrity and coagulation of blood. About 100 milligram liter<sup>-1</sup> concentration of calcium is regulated in plasma. It is carried out by two hormones calcitonin and dissolving and redepositing substance. Its proportion in human being is 400 milligram per day. All this calcium passes across the plasma.



### SUMMARY

Group-1 (alkali metals) and group-2 (alkaline earth metals) are included in the s-block elements of the periodic table. They are known like this because their oxides and hydroxides are alkaline in nature. Alkali metals possess one and alkaline earth metals possess two s-electrons. They are highly electropositive metals and form monovalent cations ( $M^+$ ) and divalent cations ( $M^{2+}$ ) respectively.

With the increase in atomic number, the physical and chemical properties of alkali metals show regular trend. The atomic and ionic sizes increase on going down in the group and ionization enthalpies decrease in alkali metals. The same type of trend is observed in alkaline earth metals.

The first element of each of these two groups, namely, lithium in group-1 and beryllium in group-2 show similarities with the element of the next group viz. Li-Mg and Be-Al. This is called diagonal relationship. In fact, the first element of each group shows difference with other elements in the same group i.e their behaviour is anomalous.

Alkali elements are bright white, soft metals melting at low temperatures. Li and Na are obtained by electrolysis. They are very active and their compounds are ionic. Their oxides and hydroxides are soluble in water and give strong alkaline solution.

Amongst important compounds of sodium are sodium carbonate, sodium hydrogen-carbonate, sodium hydroxide, NaOH is produced by Castner Kellner process and sodium carbonate by Solvay ammonia soda process.

The chemistry of alkaline earth metals is similar to that of alkali metals. Even then some differences are there, because the atomic and ionic sizes of alkaline earth metals decrease and the charge of the cation increases. Their oxides are less basic than those of alkali metals.

Amongst the industrially important compounds of sodium are caustic soda, washing soda and those of calcium are calcium oxide, calcium hydroxide, plaster of Paris, calcium carbonate and Portland cement. The production of cement can be carried out by grinding the mixture of lime stone and clay and heating it in rotary kiln. The clinker obtained is mixed with gypsum (2-3%) which gives fine powder of cement. All these substances have many uses.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in larger proportion in biological fluid in a human being. These ions carry out important biological functions like maintenance of ionic equilibrium and nerve impulse conduction which is known as sodium-potassium pump.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) Sodium metal is kept in
 

(A) Water	(B) Kerosene
(C) Alcohol	(D) Open in air
- (2) The formula of washing soda is
 

(A) $Na_2CO_3$	(B) $Na_2CO_3 \cdot H_2O$
(C) $Na_2CO_3 \cdot 10H_2O$	(D) $NaHCO_3$
- (3) The formula of baking powder is
 

(A) $Na_2CO_3$	(B) $NaHCO_3$
(C) NaOH	(D) NaCl



- (4) Which of the following pairs of elements possess diagonal relationship ?  
(A) Li and Mg (B) Li and Al  
(C) Na and Mg (D) Cs and Ba
- (5) In which of the following solvents, the alkali metal gives coloured solutions ?  
(A) Water (B) Alcohol  
(C) Acetone (D) Liquid ammonia
- (6) Alkali metals can be obtained from  
(A) Aqueous solutions (B) Ammoniated solutions  
(C) Melted salts (D) Nature
- (7) Which metal from the following alkali metals has the lowest melting point ?  
(A) Na (B) K  
(C) Rb (D) Cs
- (8) Which of the following alkali metals gives hydrated salts ?  
(A) Li (B) Na  
(C) K (D) Cs.
- (9) Which of the following alkaline earth carbonates is thermally stable ?  
(A)  $\text{MgCO}_3$  (B)  $\text{CaCO}_3$   
(C)  $\text{SrCO}_3$  (D)  $\text{BaCO}_3$
- (10) Which of the following alkali metals is used in the street lights on the road ?  
(A) Li (B) Na  
(C) K (D) Cs
- (11) Which of the following elements give light green colour in flame test ?  
(A) K (B) Rb  
(C) Ca (D) Ba
- (12) Which metal is used in photoelectric cell ?  
(A) Na (B) K  
(C) Rb (D) Cs
- (13) Which salt cannot be obtained by Solvay ammonia soda process ?  
(A)  $\text{Na}_2\text{CO}_3$  (B)  $\text{NaHCO}_3$   
(C)  $\text{KHCO}_3$  (D)  $\text{NH}_4\text{HCO}_3$
- (14) Which pump is important in biological reaction in human body ?  
(A) Ca-Mg pump (B) Na - K pump  
(C) Fe - Ca pump (D) Ca- Fe pump
- (15) Which is more basic -  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  ?  
(A)  $\text{Na}_2\text{CO}_3$  (B)  $\text{NaHCO}_3$   
(C) Both (D) Neither of the two

**2. Write balanced chemical equations for the following reactions :**

- (1) Sodium metal and liquid ammonia
- (2) Calcium hydroxide and ammonium chloride
- (3) Sodium peroxide and water
- (4) Beryllium hydroxide and sodium hydroxide
- (5) Lithium nitride and water
- (6) Heating calcium oxide with phosphorus pentoxide at high temperature
- (7) Passing more carbon dioxide from a solution of calcium carbonate
- (8) Passing chlorine gas from calcium hydroxide solution
- (9) Reaction of aluminium oxide with con. NaOH

**3. Write answers of the following questions :**

- (1) Explain the diagonal relationship of Li of first group and Mg of second group.
- (2) How beryllium differs from other elements of its group ?
- (3) Describe Castner–Kellner process of obtaining sodium hydroxide.
- (4) Describe Solvay ammonia soda method (process) for obtaining sodium carbonate.
- (5) Describe biological importance of  $\text{Na}^+$  and  $\text{K}^+$  ions.
- (6) Write preparation and uses of cement.
- (7) Describe biological importance of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions.
- (8) Explain the solubility and stability of oxo salts of alkaline earth metals.

**4. Give scientific reasons for the following :**

- (1) Sodium gives yellow colour in flame test.
  - (2) Potassium hydrogen carbonate can not be obtained by Solvay soda process.
  - (3) Alkali and alkaline earth metals are not available free in nature.
  - (4) Discuss the oxidation number of oxygen in oxide, dioxide and superoxide.
  - (5) Sodium is found to be more useful than potassium.
-

## BASIC PRINCIPLES OF ORGANIC CHEMISTRY

7.1	Introduction
7.2	Tetravalency of Carbon
7.3	Hybridisation and Hybrid Orbitals
7.4	Hybridisation in Carbon Atom and Shapes of Organic Molecules.
7.4.1	Shape of $sp^3$ hybrid orbitals and $\sigma$ bond
7.4.1.1	Shape of methane molecule
7.4.1.2	Shape of ethane molecule
7.4.2	Shape of $sp^2$ hybrid orbitals and $\pi$ bond.
7.4.2.1	Shape of ethene molecule
7.4.3	Shape of $sp$ hybrid orbitals and $\pi$ bond
7.4.3.1	shape of ethyne molecule
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7.6	Homologous Series
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7.10.4	Hyperconjugation
7.11	Fission of Covalent Bond
7.12	Electrophile, Nucleophile, Carbocation or Carbonium Ion, Carbanion
7.13	Main Types of Organic Reactions

### 7.1 Introduction

From the ancient times, the minerals, plants and animals constitute the major important sources of naturally occurring substances. The compounds obtained from minerals i.e. from nonliving sources are called inorganic compounds. The compounds obtained from animals and plants i.e. from living sources are called organic compounds. Organic compounds are essential (vital) for sustaining the life on earth. During the ancient time it was believed that there was some vital force within the living beings which was needed for the formation of organic compound. In 1828, Friedrich Wohler a German scientist prepared organic compound urea from inorganic compound ammonium cyanate. So the ancient belief was rejected. Now 95% organic substances are synthesised by human beings.

The basic constituent of organic compounds is carbon. The basic organic compounds in organic chemistry are hydrocarbon. Hydrocarbon compounds comprise of carbon and hydrogen. Variety of organic compounds are obtained by substitution of one or more hydrogen atoms of hydrocarbon by elements like nitrogen, oxygen, sulphur and halogen or by functional groups. So, in real sense, the organic chemistry consists of hydrocarbon and large variety of compounds obtained from the substitution of their hydrogens.

### 7.2 Tetravalency of Carbon

The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of an organic compound. Therefore, it is necessary to have the knowledge and information of the tetravalency of carbon. The atomic number of carbon is 6 and hence, the number of electrons in carbon is 6, so the electronic configuration is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ . Here, the number of electrons in its outermost orbit are four. In order to attain a stable electronic configuration like inert gas, carbon atom should either lose four electrons or

gain four electrons. To achieve this, a very large amount of energy (ionisation enthalpy  $\Delta_i H$  and electron gain enthalpy  $\Delta_{eg} H$ ) is required. Consequently it cannot form  $C^{4+}$  or  $C^{4-}$  ion. However, the carbon atom shares four electrons with some elements and forms four covalent bonds.

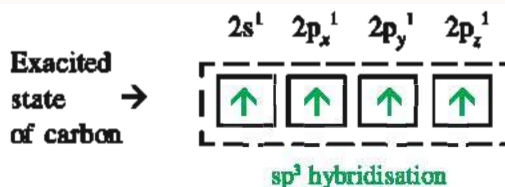
So generally the characteristic of carbon to form four covalent bonds is called tetravalency of carbon. To explain tetravalency of carbon, in its electronic configuration having two electrons in 2s orbital, one of its electron from 2s orbital gets excited and enters in empty  $2p_x$  orbital. Hence, the electronic configuration of carbon in excited state is  $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ . In the excited state electronic configuration of carbon outermost orbit has all four electrons unpaired. These four electrons are in two different types of orbitals like s and p orbitals. If these unpaired electrons are to form four covalent bonds then four bonds which are formed cannot be considered equivalent. However, it has been experimentally established that the four bonds formed by carbon in the molecules like methane and carbon tetrachloride are equivalent. The equivalent character of these four bonds can be explained by the hybridisation of orbitals of these four unpaired electrons.

### 7.3 Hybridisation and Hybrid Orbitals

When in an atom there are different types of orbitals having very less energy difference, then such type of two or more than two orbitals combine and form same number of orbitals having similar shapes and energies which are known as hybrid orbitals and the process is known as hybridisation.

### 7.4 Hybridisation in Carbon Atom and Shapes of Organic Molecules

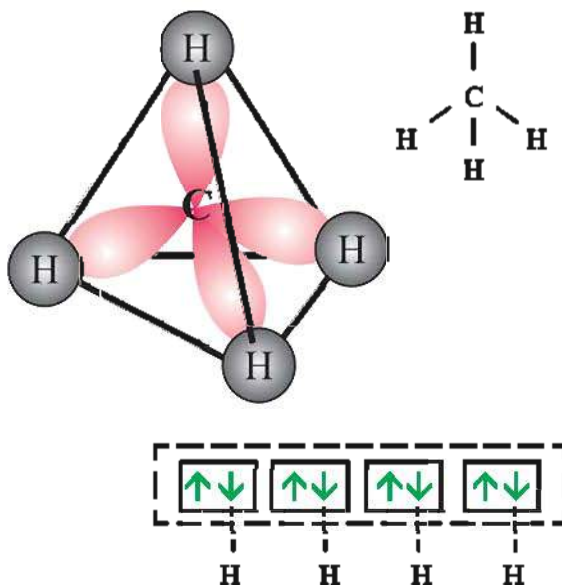
**7.4.1 Shape of  $sp^3$  hybrid orbitals and  $\sigma$  bond :** As there is C-C single bond in compounds of alkane series, the  $sp^3$  hybridisation taking place in them can be explained as follows: In the excited state of carbon having electronic arrangement in outermost orbital from which one 2s type and three 2p type of orbitals containing unpaired electrons combine and form four hybrid orbitals having equal energies and similar shape, it is known as  $sp^3$  hybridisation.



The four hybrid orbitals having unpaired electrons of equal energy are arranged in tetrahedral shape having bond angle  $109^\circ 28'$

#### 7.4.1.1 Shape of methane molecule :

In methane ( $CH_4$ ) molecule the carbon atom having four unpaired equivalent orbitals, obtained by  $sp^3$  hybridisation are arranged in a tetrahedral shape. Here, the angle between any two adjacent hybrid orbital is  $109^\circ 28'$ . The four orbitals formed by  $sp^3$  hybridisation of carbon atom which axially overlap with each of the four 1s orbital of four hydrogen atoms containing unpaired electrons with opposite spin to form four covalent bonds of equal energy strength. Thus, an axially overlapping bond formation by sharing of the electrons of two valence orbitals containing unpaired electrons with opposite spin is called  $\sigma$  bond. Hence, the shape of methane molecule is tetrahedral and the four C-H  $\sigma$  bonds have equal energy, the four C-H bonds have equal bond length of 112 pm and H - C - H bond angle is  $109^\circ 28'$

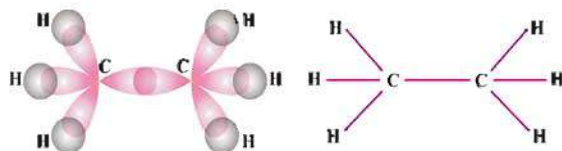


#### 7.4.1.2 Shape of ethane molecule :

The molecular formula of ethane is  $C_2H_6$  and its molecular structure is  $CH_3-CH_3$ . One of the  $sp^3$  hybrid orbital on each of two carbon

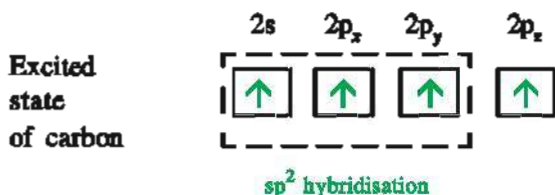


atoms overlap each other axially by sharing of the unpaired electrons to form  $\sigma$  bond. Remaining three  $sp^3$  hybrid orbitals of both the carbon overlap with each of the three  $1s$  orbital of three hydrogen atoms having unpaired electrons with opposite spin which results in total six C-H  $\sigma$  bonds. In ethane molecule the C-C and C - H bond lengths are 154 pm and 112 pm respectively and the bond angle is  $109^\circ 28'$ .



#### 7.4.2 Shape of $sp^2$ hybrid orbitals and $\pi$ bond :

The compounds of alkene series contain carbon-carbon double bond  $>C=C<$  involving  $sp^2$  hybridisation which can be explained as follows : The carbon atom in excited state electronic configuration of outermost orbitals from which one orbital is of  $2s$  type and two orbitals of  $2p$  type i.e. total three orbitals combine and three orbitals having same shape and equal energy formed is known as  $sp^2$  hybridisation. The unpaired electrons in three  $sp^2$  hybrid orbitals have same energy but the  $2p_z$  orbital having unpaired electron of carbon atom which has not participated in the formation of  $sp^2$  hybridisation, whose energy is not same as those of the unpaired electrons of the  $sp^2$  hybrid orbitals.

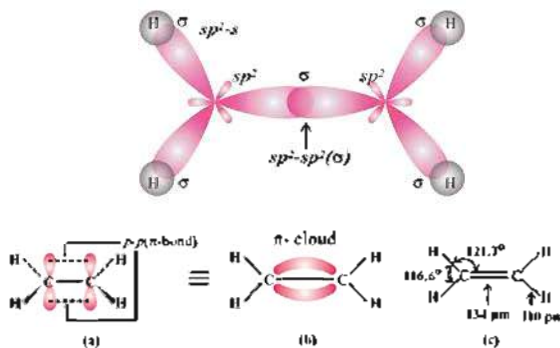


Three orbitals formed due to  $sp^2$  hybridisation are arranged in a planar triangular shape. The angle between any two adjacent orbitals is  $120^\circ$ .

**7.4.2.1 Shape of ethene molecule :** The molecular formula of ethene is  $C_2H_4$  and its molecular structure is  $CH_2=CH_2$ . In each carbon atom one orbital which is obtained by  $sp^2$  hybridisation having unpaired electron with opposite spin overlap each other axially and form  $\sigma$  bond between two carbon atoms. Now, both the carbons have remaining two  $sp^2$  hybrid orbitals on each carbon atom which overlap with each

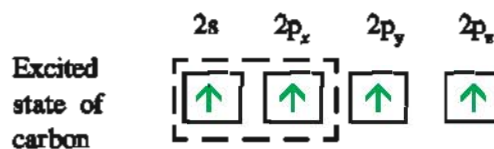
of the two  $1s$  orbital of two hydrogen atoms having unpaired electron with opposite spin result in formation of total four C - H  $\sigma$  bond having equal energy. The four C - H bonds have equal bond length of 110 pm.

Further, both the carbon atoms have  $2p_z$  orbital containing unpaired electron which had not participated in hybridisation. Now, due to sharing of these electrons with opposite spin a  $\pi$  bond is formed. Thus, in ethene molecule between two carbon atoms, one  $\sigma$  bond and another  $\pi$  bond i.e. double bond is formed. In ethene molecule C = C bond length is 134 pm which is less than C-C bond length in ethane. The shape of ethene molecule is planar triangular and bond angle H-C-H is  $116.6^\circ$  and C-C-H is  $121.7^\circ$ .



#### 7.4.3 Shape of $sp$ -hybrid orbitals and $\pi$ bond :

The compound of alkyne series contains carbon-carbon triple bond  $-C\equiv C-$  involving  $sp$  hybridisation which can be explained as follows : A carbon atom in an excited state electronic configuration of outer most orbitals from which one orbital is of  $s$  type and one orbital is of  $2p$  type. Hence, total two orbitals combine and form two orbitals having same shape and equal energy, these are known as  $sp$  hybrid orbitals and this phenomenon is known as  $sp$  hybridisation. The unpaired electrons in these two hybrid orbitals have same energy. Now, remaining  $2p_y$  and  $2p_z$  orbitals of carbon atom which have not participated in formation of  $sp$  hybridisation containing unpaired electrons whose energies are not the same as those of the unpaired electrons of the  $sp$  hybrid orbitals.

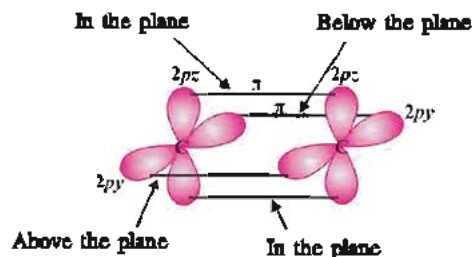
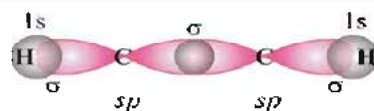


The two orbitals formed due to  $sp$  hybridisation are arranged linearly and bond angle between them is  $180^\circ$ .

### 7.4.3.1 Shape of ethyne molecule :

The molecular formula of ethyne molecule is  $C_2H_2$  and its molecular structure is  $HC\equiv CH$ . In each carbon atom orbital which is obtained by  $sp$  hybridisation having unpaired electron overlap axially with opposite spin and form  $\sigma$  bond between two carbon atoms. Now both the carbon atoms have remaining one  $sp$  hybrid orbital on each carbon atom overlap with  $1s$  orbital of hydrogen atom having unpaired electron with opposite spins result in formation of two  $C-H$   $\sigma$  bond having equal energy and equal bond length.

Further, both the carbon atoms have  $2p_y$  and  $2p_z$  orbitals containing unpaired electron which have not participated in hybridisation. These unpaired electron orbitals when spin becomes opposite to each other sharing of electrons results in two  $\pi$  bond formation. Thus in ethyne molecule between two carbon atoms one  $\sigma$  bond and two  $\pi$  bonds i.e triple bond is formed having bond length 120 pm which is less than  $>C=C<$  bond length in ethene. The shape of ethyne molecule is linear and bond angle is  $180^\circ$ .



Shape of ethyne molecule

### 7.5 Functional Groups

An atom or group of atoms that determines the characteristic reaction of an organic compound is known as functional group. In alkane hydrocarbons due to their saturation they do not contain functional group for their characteristic reaction. The different compounds have the same functional group under similar reactions. Some of the functional groups responsible for their chemical reactions are given in table 7.1.

Table 7.1 Classification of some functional groups

Class of compound	Functional group	IUPAC group prefix/suffix	Structural Formula	IUPAC Name
Alkane	R-H	-/ ane	$CH_3 - CH_3$ $CH_3 - CH_2 - CH_3$ $CH_3 - CH_2 - CH_2 - CH_3$	Ethane Propane Butane
Alkene	$\begin{array}{c} \diagup \\ C=C \\ \diagdown \end{array}$	-/ ene	$CH_2 = CH_2$ $CH_3 - CH = CH_2$ $CH_3 - CH_2 - CH = CH_2$ $CH_3 - CH = CH - CH_3$	Ethene Propene But-1-ene But-2-ene
Alkyne	$-C \equiv C-$	-/ yne	$HC \equiv CH$ $CH_3 - C \equiv CH$ $CH_3 - CH_2 - C \equiv CH$ $CH_3 - C \equiv C - CH_3$	Ethyne Propyne But-1-yne But-2-yne
Halide	-X (-F, -Cl, -Br, -I)	halo/-	$CH_3 - CH_2 - CH_2 - Cl$ $CH_3 - \underset{\substack{  \\ Cl}}{CH} - CH_3$ $CH_3 - \underset{\substack{  \\ Cl}}{CH} - CH_2 - CH_2 - CH_3$	1-Chloropropane 2-Chloropropane 1-Chloropentane

Alcohol	-OH	-/ ol	$\text{CH}_3\text{OH}$ $\text{CH}_3\text{CH}_2\text{OH}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ $\text{CH}_3\text{CHCH}_3$ $\quad  $ $\quad \text{OH}$	Methanol Ethanol Propan-1-ol  Propan-2-ol
Ether	-O-	alkoxy / -	$\text{CH}_3 - \text{O} - \text{CH}_3$ $\text{CH}_3 - \text{O} - \text{CH}_2 \text{CH}_3$ $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$	Methoxy methane Methoxy ethane Ethoxy ethane
Aldehyde	-CHO	-/ al	$\text{HCHO}$ $\text{CH}_3\text{CHO}$ $\text{CH}_3\text{CH}_2\text{CHO}$	Methanal Ethanal Propanal
Ketone	-CO-	-/ one	$\text{CH}_3\text{COCH}_3$ $\text{CH}_3\text{COCH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	Propanone Butan-2-one Pentan-3-one
Carboxylic acid	-COOH	-/ oic Acid	$\text{HCOOH}$ $\text{CH}_3\text{COOH}$ $\text{CH}_3\text{CH}_2\text{COOH}$	Methanoic acid Ethanoic acid Propanoic acid
Ester	-COOR	-/ oate	$\text{HCOOCH}_3$ $\text{CH}_3\text{COOCH}_3$ $\text{CH}_3\text{COOCH}_2\text{CH}_3$	Methyl methanoate Methyl ethanoate Ethyl ethanoate
Amide	-CONH <sub>2</sub>	-/ amide	$\text{CH}_3\text{CONH}_2$ $\text{CH}_3\text{CH}_2\text{CONH}_2$	Ethanamide Propanamide
Amine	-NH <sub>2</sub>	(1 <sup>o</sup> )-/ amine (Primary)	$\text{CH}_3\text{NH}_2$ $\text{CH}_3\text{CH}_2\text{NH}_2$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  $\text{CH}_3 \quad \text{CH} \quad \text{CH}_3$ $\quad  $ $\quad \text{NH}_2$	Methanamine Ethanamine Propan-1-amine  Propan-2-amine
	-NH-	(2 <sup>o</sup> )-/ amine (Secondary)	$\text{CH}_3 \text{NHCH}_3$ $\text{CH}_3 \text{CH}_2 \text{NHCH}_3$	N-methyl methanamine N-methyl ethanamine

	$\begin{array}{c}   \\ -\text{N}- \\   \end{array}$	(3°)-/ amine (Tertiary)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{N} - \text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{NCH}_3 \end{array}$	N-N dimethyl ethanamine  N-N dimethyl methanamine
Nitro	$\text{NO}_2$	nitro/-	$\text{CH}_3\text{CH}_2\text{NO}_2$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$ $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\   \\ \text{NO}_2 \end{array}$	Nitroethane  1-Nitropropane  2-Nitropropane
Cynide OR Nitrile	$-\text{C} \equiv \text{N}$	-/ nitrile	$\text{CH}_3\text{CN}$ $\text{CH}_3\text{CH}_2\text{CN}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	Ethane nitrile  Propane nitrile  Butane nitrile

## 7.6 Homologous Series

A series of organic compounds having same functional group in which two successive members differ from each other by fixed number of carbon and hydrogen ( $\text{CH}_2$ ). Such series of organic compounds is known as homologous series. Almost all types of organic compounds form homologous series and they have similar chemical characteristics e.g.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  etc.

### 7.6.1 Characteristics of Homologous series :

- (1) The elements and functional group present in compound of a homologous series are same.
- (2) Each member of the series can be expressed by common molecular formula. For example, each member of alkane series can be indicated by a common formula  $\text{C}_n\text{H}_{2n+2}$ .
- (3) The difference between the molecular formula of two successive members of the series will be of  $\text{CH}_2$ .
- (4) The difference between the molecular weights of two successive members of a series will be of 14 amu (u).
- (5) The name of each member of a series begins either with a common prefix or suffix.
- (6) The chemical reactions of each member of series are same if the functional group present in them is same and their methods of preparation are also the same.
- (7) As the number of carbon and hydrogen atoms increase with member of a given series the molecular mass of the members increases. Hence there will be gradual change in the properties of the members which depend upon their molecular mass which include

boiling point, melting point, density, solubility etc. The characteristics of homologous series of alkane compounds are given in table 7.2.

**Table 7.2 Characteristics of homologous series of alkanes**

Name of Alkane	Molecular formula	Molecular mass gram mol <sup>-1</sup>	Melting point K	Boiling point K	State
Methane	$\text{CH}_4$	16	91	109	gas
Ethane	$\text{C}_2\text{H}_6$	30	87	184	gas
Propane	$\text{C}_3\text{H}_8$	44	83	231	gas
Butane	$\text{C}_4\text{H}_{10}$	58	135	272.5	gas
Pentane	$\text{C}_5\text{H}_{12}$	72	143	309	gas, liquid

## 7.7 Isomerism

The organic compounds having the same molecular formula but different structural formula are called isomers. This phenomenon is called isomerism. The isomerism has been classified mainly in two types depending upon their differences in structural aspects :

- (1) structural isomerism
- (2) stereo isomerism.

**7.7.1 Structural Isomerism :** Structural isomerism is a result of different arrangements of atoms or groups of atoms in molecules of organic compounds having same molecular formula. Hence, the organic compounds having same molecular formula but different structures are called structural isomers and the phenomenon as structural isomerism. There are five different types of structural isomerism :



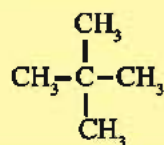
(1) Skeletal or chain isomerism (2) Position isomerism (3) Functional group isomerism (4) Metamerism (5) Tautomerism.

**(1) Skeletal or chain isomerism :** The organic compounds having same molecular formula but arrangement of carbon atoms in a linear or branch are different; such type of isomerism is called chain isomerism. Methane, ethane and propane do not exhibit chain isomerism but butane has two isomers. Pentane has three isomers, hexane has five isomers. For example three isomers of pentane are given below.

(i) n- pentane  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

(ii) 2- methyl butane  $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

(iii) 2,2-dimethyl propane



**(2) Position isomerism :** Organic compounds have same molecular formula and similar carbon chain but differ in the position of functional group. This type of isomerism is called position isomerism. For example

(i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  Propan-1-amine

$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{NH}_2 \end{array}$  Propan-2-amine

(ii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  Pentan-1-ol

$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \\ | \\ \text{OH} \end{array}$  Pentan-2-ol

$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$  Pentan-3-ol

**(3) Functional group isomerism :** The organic compounds having the same molecular formula but different functional groups are called functional group isomers and this phenomenon is called functional group isomerism; for example.

(i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  propan-1-ol  $\text{CH}_3\text{-O-CH}_2\text{CH}_3$  methoxy ethane

(ii)  $\text{CH}_3\text{CH}_2\text{CHO}$  propanal  $\text{CH}_3\text{-CO-CH}_3$  propanone

(iii)  $\text{CH}_3\text{CH}_2\text{COOH}$  propanoic acid  $\text{CH}_3\text{-COO-CH}_3$  methyl ethanoate

**(4) Metamerism :** The organic compounds having same molecular formula and same functional group but different number of carbon in alkyl group on either side of the functional group are called metamers and such isomerism is called metamerism. This type of isomerism is shown by ethers, ketones and amines. For example.

(i)  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$  Pentan-3-one

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$  Pentan-2-one

(ii)  $\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$  Methoxy propane

$\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_3$  Ethoxy ethane

(iii)  $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{CH}_3$  N-Methyl propan-1-amine

$\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$  N-Ethyl ethenamine

**(5) Tautomerism :** The organic compounds having same molecular formula but isomers differ in the arrangement of atoms and are in dynamic equilibrium with each other are called tautomers and this phenomenon is called tautomerism. For example

(i)  $\begin{array}{ccc} \text{H} & \text{O} & \text{H} \\ | & || & | \\ \text{H}-\text{C}-\text{C}-\text{H} & \rightleftharpoons & \text{H}-\text{C}=\text{C}-\text{H} \\ | & & | \\ \text{H} & & \text{OH} \\ \text{ethanal} & & \text{vinyl alcohol} \end{array}$

(ii)  $\begin{array}{ccc} \text{CH}_3-\text{C}-\text{CH}_3 & \rightleftharpoons & \text{CH}_2=\text{C}-\text{CH}_3 \\ || & & | \\ \text{O} & & \text{OH} \\ \text{propanone} & & \text{prop-1-en-2-ol} \end{array}$

(iii)  $\begin{array}{ccc} \text{O} & & \text{O} \\ || & & || \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 & \rightleftharpoons & \\ \text{keto form} & & \\ & & \begin{array}{c} \text{O} \quad \text{OH} \\ || \quad | \\ \text{CH}_3-\text{C}-\text{CH}=\text{C}-\text{CH}_3 \\ \text{enol form} \end{array} \end{array}$

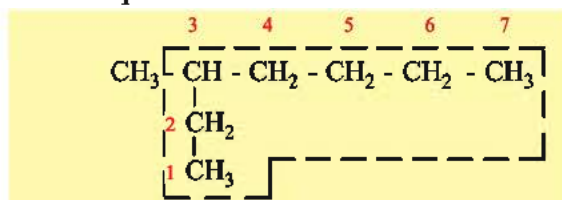
In structure of organic compounds having keto form and enol form in dynamic equilibrium with each other is known as keto-enol tautomerism.

## 7.8 Nomenclature of Organic Compounds

About a century ago a few number of organic compounds were known. At that time the naming of compounds was done as per their properties, structures or their origin. During the first half of the 20<sup>th</sup> century many types of

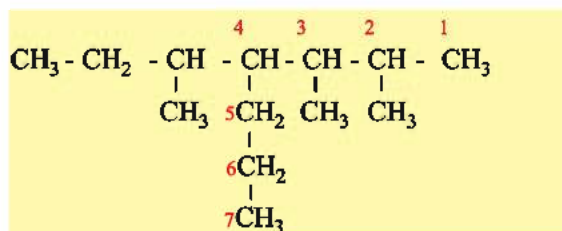
organic compounds were synthesised, hence, the nomenclature by old pattern became impossible. Besides that the nomenclature of an organic compound should be such that the structure of a newly synthesised compound can be understood by all the chemists. So, in 1889, a committee was formed by International Chemical Congress for laying down definite rules for nomenclature. The report of this committee submitted, in 1892, at Geneva was inadequate. So based on that, in 1930, International Union of Pure and Applied Chemistry presented a more meaningful account. After the naming of organic compounds was over, a committee formed in 1947, recommended various types of rules. The nomenclature done by these rules is known today as IUPAC (International Union of Pure and Applied Chemistry) system. The changes in rules take place from time to time. The IUPAC nomenclature rules in order are given below :

**(1) To determine the longest carbon chain.** Select the longest continuous chain of carbon atoms in given structure of organic compound. For example,

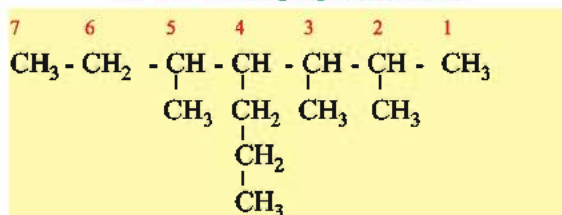


In this structure, the longest chain of carbons is seven and so original hydrocarbon will be heptane.

If in a given organic compound, the two different chains but of equal length are possible, the chain with maximum number of side branch or alkyl groups is selected. For example



Longest chain at 7-carbon total branch - 3  
So this is not proper selection

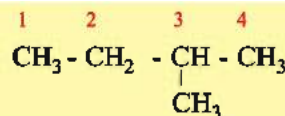


longest chain at 7 carbon total branch 4  
so this is proper selection.

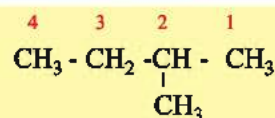
## (2) To determine the position of substituted group :

### (i) Position of mono substituted group :

The carbon atoms of longest chain, the number given from the end which gives lower number to the carbon atoms carrying the substituent i.e branch starts as early as possible. For example

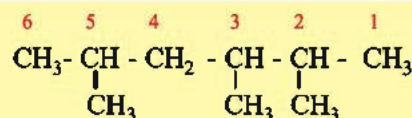


If carbon numbering of chain starts from left side end then branched carbon gets 3 number  
(incorrect method)

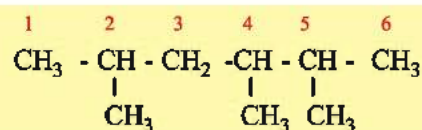


If numbering at carbon chain starts from right side end then branched carbon gets 2 number (correct method)

**(ii) Lowest set of locants :** When two or more substituents are present in a given carbon chain, then number is given to the chain in such a way so that substituent gets the lowest set of locants which is known as the lowest set of locants. For example

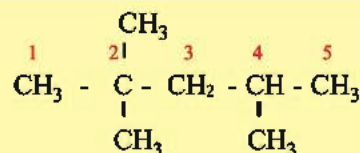


sets of locant 2,3,5 (correct method)

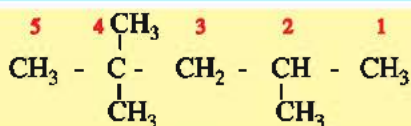


sets of locant 2,4,5 (incorrect method)

Here, the first locant number is 2-2 in both; hence comparing second locant 3-4, 3 is lower number of locant so the the first structure having locant 2, 3, 5, is the correct method of numbering while 2, 4, 5 numbering is incorrect method.



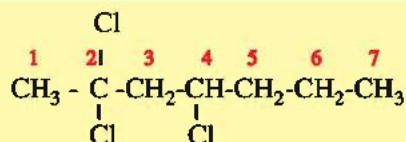
(set of locant 2,2,4) (correct method)



set of locant 2,4,4 (incorrect method)

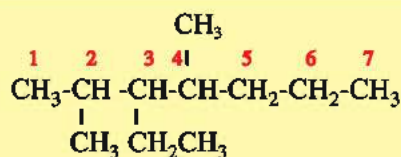
Here in the number of chain from both the ends, the first locant numbering of chain is from both the ends, the first locant number is 2-2 which is same but second locant number is 2, 4 in which 2 is lower than 4 so the first structure having sets of locant 2, 2, 4 is the correct method of numbering while 2, 4, 4, numbering is the incorrect method.

(3) If the same substituent (or side chain) occurs more than once i.e. 2,3,4,5,6,... the prefix di, tri, tetra, penta, hexa... are added respectively before the name of substituents. For example



Here the functional groups substituted on carbon number 2,2,4 are all same substituents i.e. functional groups -Cl and hence that substituent is indicated as 2,2,4 "trichloro" in nomenclature.

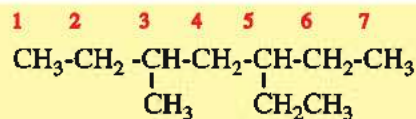
(4) If in a given structure of organic compound having different types of branches are substituted then their IUPAC nomenclature is followed in the Alphabetical Order. By comparing alphabetical order the prefix di, tri, tetra used are to be ignored. For example.



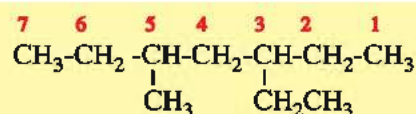
3-Ethyl-2,4-dimethyl heptane (correct method)-  
2,4-dimethyl-3-ethyl heptane (incorrect method)

Here the two different types of branches like methyl and ethyl when arranged in alphabetical order the ethyl comes first and then the second is methyl. The word dimethyl is taken as only methyl because prefix di is ignored and hence correct method of nomenclature is 3-ethyl-2,4-dimethyl heptane whereas-2,4-dimethyl 3-ethyl heptane is incorrect method.

(5) If two different substituents are in equivalent position from the two ends of chain (equal number) then the numbering of the chain is done in such a way that the group which comes first in the alphabetical order gets the lowest number. For example.



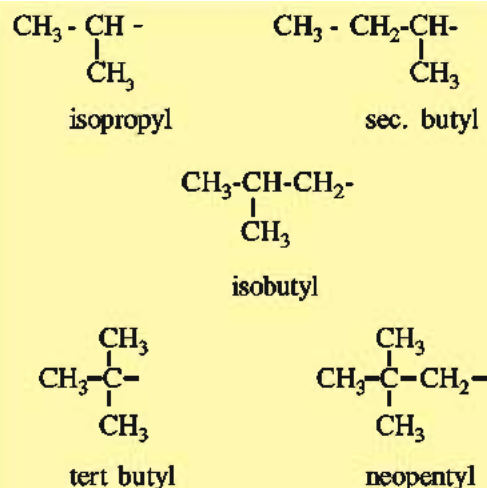
3-methyl -5-ethyl heptane  
(incorrect method)



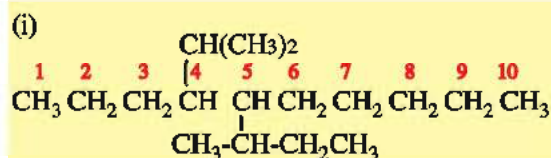
3-ethyl -5- methyl heptane  
(correct method)

If ethyl comes first then methyl, the ethyl substituent gets less number, is the right method of nomenclature and hence 3-ethyl-5-methyl heptane is correct method.

(6) If some alkyl functional groups like



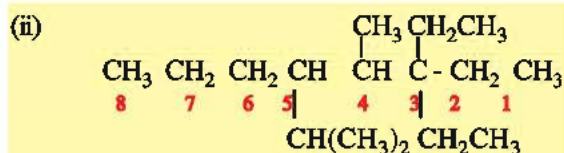
are substituents then during nomenclature the substituents are arranged in alphabetical order, the prefixes 'iso'-and 'neo'- are the parts of the names of substituents. So they are taken into consideration by prefix 'sec' and 'tert' is not taken into consideration. For example :



5- sec-butyl-4-isopropyl decane



Here, the prefix 'sec' is not taken into consideration so butyl comes first and written first with its position on carbon and then isopropyl substituent is written with its position on carbon.

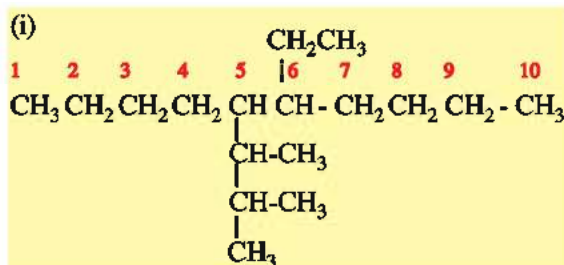


### 3,3 diethyl -5- isopropyl-4-methyl octane

Here, in the alphabetical order ethyl substituent comes first then isopropyl and at last comes methyl substituent and so they are written in that order.

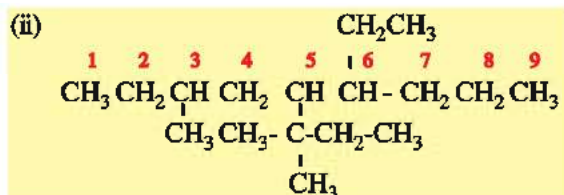
(7) If the carbon chain having alkyl branch and the alkyl branch is also having sub branch alkyl group then during the nomenclature some points given below are taken into consideration :

- The name of subbranch is always written in bracket.
- During numbering of alkyl branch having subbranch the carbon which is attached to the carbon chain acquires number 1(one) and then continuous number is given to carbon of subbranch.
- During nomenclature of subbranch the prefix which indicates the number of subbranch is taken into consideration in the alphabetical order. For example.



### 5(1,2 dimethyl propyl)-6- ethyl decane

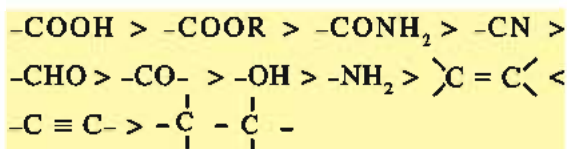
Here the branch contains ethyl and subbranch dimethyl, so in alphabetical order dimethyl comes first and then comes ethyl so the subbranch is indicated first.



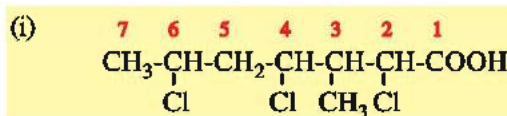
### 5(1,1 dimethyl propyl) -6-ethyl 3-methyl nonane

The alphabetical arrangement order is dimethyl propyl and then ethyl and at last methyl, so the nomenclature is written in that order with its position on carbon chain.

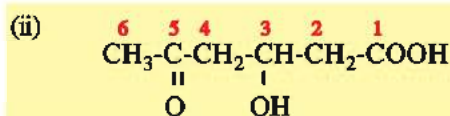
(8) When structure of organic compound is containing more than one functional groups as a substituent at that time during the nomenclature one group having highest order of preference becomes principal functional group and other remaining groups are treated as substituted groups. This is the order of preference.



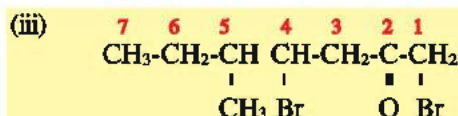
For example,



### 2,4,6-trichloro -3- methyl - heptanoic acid



### 3-hydroxy -5-oxo- hexanoic acid

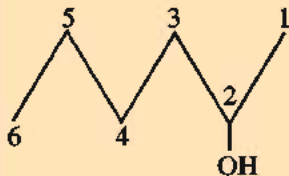

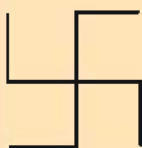
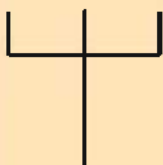
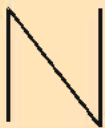

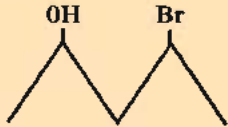


### 1,4- dibromo -5- methyl - heptan-2-one

Bond-line structure is a method in which the structure of organic compounds can easily be expressed. For the IUPAC nomenclature of such structures is first converted into complete structure by using points given below and then to apply to the points of IUPAC nomenclature rules.

- Alkyl groups or carbon and hydrogen atoms in a chain are not shown but the remaining atom or group of atoms present in functional groups are shown.
- Line at both the ends without any functional group is considered as  $-\text{CH}_3$  group.
- Every junction indicates carbon atom and to satisfy the tetravalency of carbon the required number of hydrogen atoms are taken.
- Double bond and triple bond are represented by two and three parallel lines respectively.



Bond-line structure	Complete structural formula
	$\overset{6}{\text{CH}_3} - \overset{5}{\text{CH}_2} - \overset{4}{\text{CH}_2} - \overset{3}{\text{CH}_2} - \overset{2}{\underset{\text{OH}}{\text{CH}}} - \overset{1}{\text{CH}_3}$ Hexan-2-ol
	$\overset{8}{\text{CH}_3} \overset{7}{\text{CH}_2} \overset{6}{\text{CH}_2} - \overset{5}{\text{CH}_2} - \overset{4}{\text{CH}} = \overset{3}{\text{CH}} - \overset{2}{\underset{\text{Br}}{\text{CH}}} - \overset{1}{\text{CH}_3}$ 2-bromo oct -3 - ene
	$\overset{1}{\text{CH}_3} - \overset{2}{\text{CH}_2} - \overset{3}{\underset{\text{CH}_2\text{-CH}_3}{\overset{\text{CH}_2\text{-CH}_3}{\text{C}}}} - \overset{4}{\text{CH}_2} - \overset{5}{\text{CH}_3}$ 3, 3-diethyl pentane
	$\overset{1}{\text{CH}_3} - \overset{2}{\text{CH}_2} - \overset{3}{\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}} - \overset{4}{\text{CH}_2} - \overset{5}{\text{CH}_3}$ 3,3-dimethyl pentane
	$\text{CH}_3 \text{ CH}_2 \text{ CH}_2 - \text{CH}_3$ Butane
	$\overset{1}{\text{CH}_3} - \overset{2}{\underset{\text{CH}_3}{\text{CH}}} - \overset{3}{\text{CH}_2} - \overset{4}{\underset{\text{CH}_3}{\text{CH}}} - \overset{5}{\text{CH}_3}$ 2,4-dimethyl pentane
	$\overset{1}{\text{CH}_3} - \overset{2}{\underset{\text{OH}}{\text{CH}}} - \overset{3}{\text{CH}_2} - \overset{4}{\underset{\text{Br}}{\text{CH}}} - \overset{5}{\text{CH}_3}$ 4-bromopentan-2-ol

## IUPAC names of some structural formula

Structural formula	IUPAC Name
$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CHO}$	3, 4-dimethyl pentanal
$\text{CH}_2 = \text{CHCH}_2 \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$	4-methyl pent-1-ene
$\text{CH}_2 = \text{CHCH}_2 \underset{\text{NH}_2}{\text{CH}} \text{CH}_3$	pent-4-en-2-amine

$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH} = \text{CCHCH}_2\text{C}(\text{O})\text{CH}_3 \end{array}$	4- methyl hex-5-yn-2-one
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_2\text{COOH} \\   \quad   \quad   \\ \text{Br} \quad \text{Br} \quad \text{CH}_2\text{CH}_3 \end{array}$	4,5-dibromo-3-ethyl hexanoic acid
	5- bromo-1-nitrononan-2-one

### 7.9 Common and IUPAC Nomenclature of Organic Compounds

The common and IUPAC nomenclature of organic compounds based on functional groups are given in table 7.3.

**Table 7.3 Common and IUPAC names based on functional group**

Type of compound	Functional group	Structure	Common name	IUPAC name
Alkene	$-\text{C}=\text{C}-$	$\text{CH}_2=\text{CH}_2$	ethylene	ethene
		$\text{CH}_3\text{CH}=\text{CH}_2$	propylene	propene
		$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	Butylene	but-1-ene
		$\text{CH}_3\text{CH}=\text{CHCH}_3$	2-butylene	but -2-ene
Halide	-X	$\text{CH}_3\text{CH}_2\text{Cl}$	ethyl chloride	chloro ethane
		$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	propyl chloride	1-chloro propane
Alcohol	-OH	$\text{CH}_3\text{CH}_2\text{OH}$	ethyl alcohol	ethanol
		$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	propyl alcohol	propan-1-ol
Ether	-O-	$\text{CH}_3-\text{O}-\text{CH}_3$	dimethyl ether	methoxy methane
		$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$	ethyl methyl ether	methoxy ethane
		$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$	diethyl ether	ethoxy ethane
Aldehyde	-CHO	HCHO	formaldehyde	methanal
		$\text{CH}_3\text{CHO}$	acetaldehyde	ethanal
Ketone	$-\text{C}(=\text{O})-$	$\text{CH}_3\text{COCH}_3$	acetone or dimethyl ketone	propanone
		$\text{CH}_3\text{COCH}_2\text{CH}_3$	ethyl methyl ketone	butan -2-one
Carboxylic acid	-COOH	HCOOH	formic acid	methanoic acid
		$\text{CH}_3\text{COOH}$	acetic acid	ethanoic acid

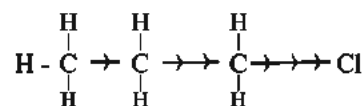
Amide	-CONH <sub>2</sub>	HCONH <sub>2</sub> CH <sub>3</sub> CONH <sub>2</sub>	formamide acetamide	methanamide ethanamide
Amine	-NH <sub>2</sub> (1°)	CH <sub>3</sub> NH <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> -CH(NH <sub>2</sub> )-CH <sub>3</sub>	methyl amine ethyl amine 2-butyl amine	methanamine ethanamine butan -2- amine
	-NH- (2°)	CH <sub>3</sub> NH CH <sub>3</sub> CH <sub>3</sub> NH CH <sub>2</sub> CH <sub>3</sub>	dimethyl amine ethyl methyl amine	N-methyl methanamine N-methyl ethanamine
	$\begin{array}{c}   \\ -N- \\   \end{array}$ (3°)	(CH <sub>3</sub> ) <sub>3</sub> N (CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>3</sub> $\begin{array}{c} \text{CH}_2\text{CH}_3 \\   \\ \text{CH}_3 - \text{N} - \text{CH}_2\text{CH}_3 \end{array}$	trimethylamine ethyl dimethyl amine diethyl methyl amine	N, N-dimethyl methamine N, N-dimethyl ethanamine N- methyl-N-ethyl ethanamine
Nitro	-NO <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NO <sub>2</sub> $\begin{array}{c} \text{CH}_3 \quad \text{CH} \quad \text{CH}_3 \\   \\ \text{NO}_2 \end{array}$	nitromethane nitroethane nitropropane 2- nitropropane	nitromethane nitroethane 1- nitropropane 2- nitropropane
Cynide/ Nitrile	-CN	CH <sub>3</sub> CN CH <sub>3</sub> CH <sub>2</sub> CN CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN	methyl cynide ethyl cynide propyl cyanide	ethane nitrile propane nitrile butane nitrile
Ester	-COOR	HCOOCH <sub>3</sub> CH <sub>3</sub> COOCH <sub>3</sub> CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	methyl formate methyl acetate ethyl acetate	methyl methanoate methyl ethanoate ethyl ethanoate
Acid anhydride	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{O} \quad \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{CH}_3 - \text{C} - \text{O} - \text{C} - \text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{H} - \text{C} - \text{O} - \text{C} - \text{H} \end{array}$	acetic anhydride formic anyhydride	ethanoic anhydride methanoic anhydride

### 7.10 Electronic Displacement (Substitution) in Covalent Bond

Organic compounds contain mostly covalent bond. Hence the substitution of hydrogen atom or of functional group with or without electron pair takes place in different ways. Four types of electronic displacement are generally noticed in the mechanism of organic reactions.

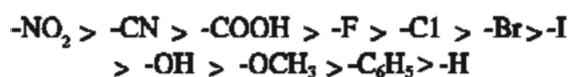
**7.10.1 (1) Inductive effect :** In organic compound if a carbon atom is covalently bonded to an atom of higher electronegativity (like halogen)

the bond becomes polar due to large difference in electronegativities and the polar effect of this spreads over the carbon atoms arranged in the chain. This effect is called an inductive effect (I- effect). It is shown by  $\rightarrow$  sign. For example, in propyl chloride (1-chloropropane) this effect is shown as under: Inductive effect is the permanent effect.



We know that chlorine is more electronegative than carbon. Due to large electronegativity of chlorine atom the electron pair which is shared between C-Cl, is displaced towards chlorine atom. As a result of this, chlorine atom acquires a partial negative charge ( $\delta^-$ ) and carbon atom acquires a partial positive charge ( $\delta^+$ ). This displacement is however not limited to C-Cl bond but is transmitted to other carbon atom along the chain. This effect goes on decreasing on moving from near carbon to farther carbon from chlorine atom generally after three carbon. From fourth carbon this effect becomes negligible. For comparing the relative effect hydrogen atom is taken as a standard and the atoms or groups can be classified into two categories.

**(i) Negative I effect (-I effect) :** Atoms or group of atoms having electron attraction capacity more than that of hydrogen are referred to as (electron attracting) atoms or electron negative (-I) effect. For example :



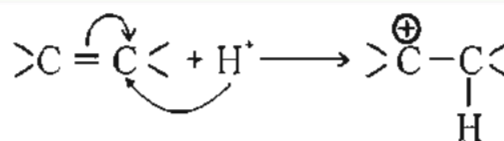
**(ii) Positive I effect (+I effect) :** Atoms or group of atoms having less electron attracting power than that of hydrogen are referred to as a (electron repelling) atom or positive I effect (+I effect). For example



**7.10.2 Electromeric effect :** An electron pair bonded between two atoms with more than one bond shifts to a more electronegative atom in presence of a reagent depending upon its characteristics. This effect is termed as electromeric (E-effect) effect. For example, electron pair of double bond between carbonyl group  $\text{>C=O}$  present in aldehydes and ketone shift to the original atom which is more electronegative when comes in contact with a reagent having higher electronegative charge. This effect is termed as an electromeric effect. This effect is due to the presence of reagent so it is a temporary effect.

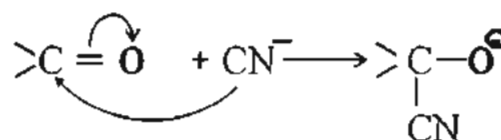
Electromeric effect can be classified into two categories :

**(i) Positive electromeric effect (+E effect) :** When the transfer of electrons takes place towards the attacking reagent, it is called positive electromeric effect. For example,



**(ii) Negative electromeric effect (-E effect) :**

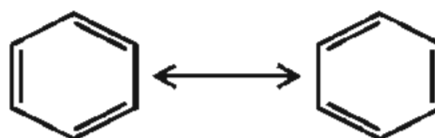
When the transfer of electron takes place away from the attacking reagent, it is called negative electromeric effect (-E effect). For example



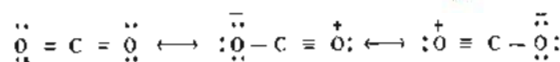
### 7.10.3 Resonance or Mesomeric effect :

A molecule of some organic compound can be represented by two or more electronic structures, however, all of its properties cannot be explained by a single structure. The actual structure is represented by an intermediate stage between two or among more electronic structures. These structures are called resonance or mesomeric structures and the resulting characteristic is known as resonance or mesomeric effect. Resonance effect is shown by a symbol  $\longleftrightarrow$ . For example

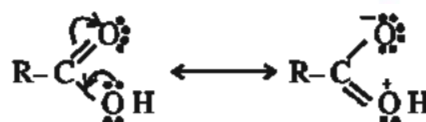
**Two resonance structures of benzene :**



**Three resonance structures of  $\text{CO}_2$  :**



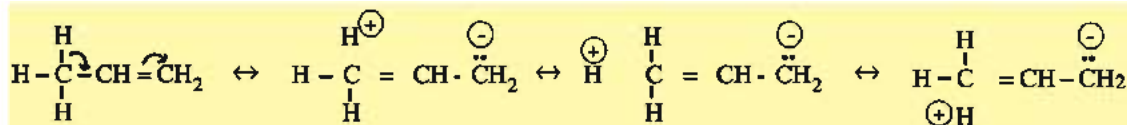
**Two resonance structures of carboxylic acid :**



**7.10.4 Hyperconjugation :** In some organic compounds when a C-C single bond is aligned with C=C double bond or attached to a benzene ring, the electron pair of the  $\sigma$  bond between C-H single bond is attracted towards the double bond. This effect is termed as hyperconjugation. If an alkyl group carrying at least one hydrogen atom is attached to an unsaturated carbon atom, it releases electrons of carbon hydrogen single bond ( $\sigma$  bond) toward the double bond. For example, hyperconjugation in propene is shown below :

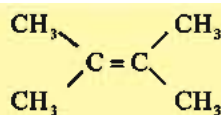


## Hyperconjugation in propene



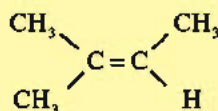
The hyperconjugation is very useful in explaining stabilities of some organic molecules. For example

(i) The order of stability for  $-\text{CH}_3$  substituted alkene as given below :



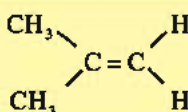
2,3-dimethyl but-2-ene

Structure - I



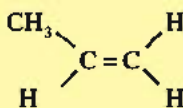
2-methyl but-2-ene

Structure - II



2-methyl propene

Structure - III



Propene

Structure - IV

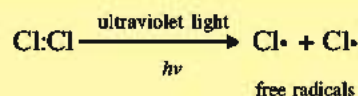
Hence, the structure I has 12 hyperconjugation C-H bond in structure II 9 C-H  $\sigma$  bond and hence structure I has more C-H  $\sigma$  bond so the hyperconjugation effect being more which makes it more stable. Same way structure III has 6 C-H  $\sigma$  bond and structure IV has only 3 C-H  $\sigma$  bonds, hence the descending order of stability can be explained.

- (ii) The stability of carbocation and free radicals can be explained by hyperconjugation.
- (iii) Shortening of carbon-carbon single bond adjacent to carbon having  $\text{C}=\text{C}$  double bond or  $\text{C}\equiv\text{C}$  triple bond is also explained by hyperconjugation.

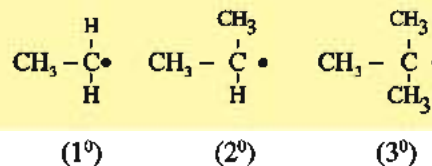
## 7.11 Fission of Covalent Bond

The fission of covalent bond can occur in two ways.

**(1) Homolytic fission :** A covalent bond is formed by sharing of two electrons between same two electronegative atoms then during fission of that covalent bond both atoms separated by gaining one-one electron each is called homolytic fission. The atoms separated in this way possessing unpaired electron are called free radicals. These free radicals have unpaired electrons so they have strong tendency to pair the electrons. Hence, they are very reactive and have a very short life.

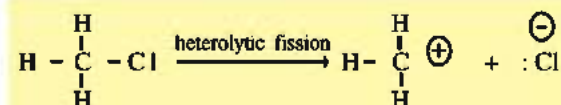


Alkyl free radicals are classified into three categories : primary ( $1^\circ$ ) secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ). For example



The order of stability for free radical is  $\text{CH}_3$ ,  $1^\circ < 2^\circ < 3^\circ$  which can be explained by hyperconjugation

**(2) Heterolytic fission :** A covalent bond is formed by sharing of two electrons between two different electronegative atoms then during fission of that covalent bond more electronegative atom acquires shared electrons paired and less electronegative atom has shortage of electron and such fission is known as heterolytic fission. The atoms get two electrons resulting into negative (-ve) ion and atoms having shortage of electron results into positive (+ve) ion; so heterolytic fission results into +ve and -ve ions. For example,



Hence, the breaking of C-Cl covalent bond in which chlorine atom is more electronegative compared to carbon atom results into shared electron pair with chlorine atom as ( $\text{Cl}^-$ ) ion while carbon atom has shortage of electron which results into  $\text{CH}_3^+$  positive ion.

### 7.12 Electrophile, Nucleophile, Carbocation or Carbonium Ion, Carbanion

**Electrophile :** The part of positive charge (positive ion) obtained during a heterolytic fission or some neutral molecules having capacity to accept pair of electrons are called electrophiles. Electrophiles are also called Lewis acid. For example

**+ve ions :**  $^+\text{NO}_2$ ,  $\text{Cl}^+$ ,  $^+\text{SO}_3\text{H}$ ,  $^+\text{CH}_3$ ,  $\text{CH}_3^+\text{CO}$ ,  $\text{H}^+$ ,  $\text{H}_3\text{O}^+$  etc.

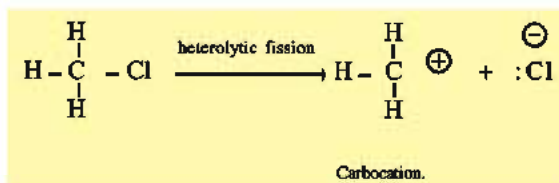
**Neutral molecules :**  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SO}_3$  etc.

**Nucleophile :** The part of negative charge (negative ions) obtained during heterolytic fission or some neutral molecules having capacity to donate electron pair are called nucleophiles. Nucleophiles are also called Lewis base. For example

**-ve ions :**  $^-\text{X}$ ,  $^-\text{OH}$ ,  $^-\text{CN}$ ,  $^-\text{NH}_2$  etc.

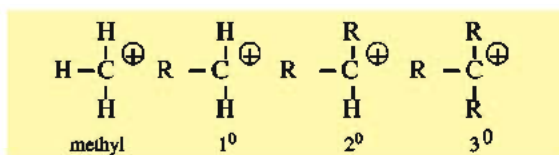
**Neutral molecules :**  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{ROH}$ ,  $\text{R-O-R}$ ,  $\text{R}_3\text{N}$ ,  $\text{R}_2\text{NH}$  etc.

**Carbocation or carbonium ion :** A group having several atoms in which a carbon atom has six electrons and consequently has positive charge is called a carbocation or carbonium ion. It is highly reactive and is very short lived. For example.



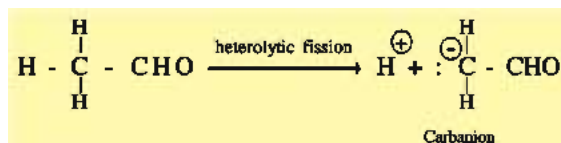
Carbocations are classified into three categories: primary ( $1^\circ$ ), secondary ( $2^\circ$ ) tertiary ( $3^\circ$ )

When a positively charged carbon atom is directly attached to one, two or three carbons such carbocation is called Primary ( $1^\circ$ ), Secondary ( $2^\circ$ ) and Tertiary ( $3^\circ$ ) respectively for example,



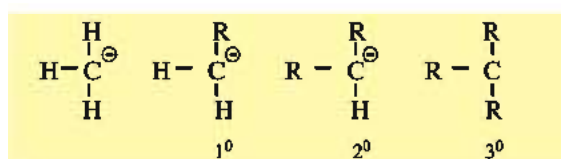
Now methyl (alkyl) group has (+I-effect) positive inductive effect. So alkyl group attached to positively charged carbon atom tends to release electrons towards carbon. As a result it decreases the +ve charge on the carbon atom but itself becomes positively charged so the positive charge on carbon atom gets dispersed. Therefore, more the number of alkyl groups, the greater will be the dispersion of charges decreasing the positive charge of carbon and stability of carbon (carbocation) increases. Thus the order of stability for carbocation is  $^+\text{CH}_3 < 1^\circ < 2^\circ < 3^\circ$ .

**Carbanion :** A group of atoms in which a carbon atom has eight electrons and hence has a negative charge, such a group is called carbanion. It is highly active and is very short lived. For example



Carbanions are classified into three categories as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ )

When a negatively charged carbon atom is directly attached to one, two or three alkyl groups are called primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) respectively. For example



Now alkyl group has positive inductive effect (+I effect); alkyl group has electron releasing tendency, and therefore, increases the electron density on the negatively charged carbon atom and hence stability decreases; more the number of alkyl groups attached to the negatively charged carbon atom greater will be the electron density on the carbon atom and lower will be its stability. So the order of stability for carbanion is  $^-\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$ .

### 7.13 Main Types of Organic Reactions


There are four main types of organic reactions :

**(1) Substitution reaction :** An atom or group of atom in an organic compound is substituted by different atoms or group of atoms in a reaction is called substitution reaction. For example,



## EXERCISE

## 1. Select the proper choice from the given multiple choices :

- (1) But-1-ene molecule carbon has which type of hybridisation ?  
 (A)  $sp^3$  (B)  $sp^2$   
 (C)  $sp^3$  and  $sp^2$  (D)  $sp$
- (2) Pent-2-yne has how many  $\sigma$  and  $\pi$  bonds ?  
 (A) 10  $\sigma$ , 2 $\pi$  (B) 12  $\sigma$ , 2 $\pi$   
 (C) 15  $\sigma$ , 2 $\pi$  (D) 13  $\sigma$ , 3 $\pi$
- (3) Which molecule has longest carbon chain ?  
 (A) Neopentane (B) Isopentene  
 (C) Neohexane (D) N-pentane
- (4) The IUPAC nomenclature of  is  
 (A) 2,3-dimethyl 7-bromo octane (B) 2-bromo-5,6-dimethyl octane  
 (C) 2-bromo-6,7-dimethyl octane (D) 1-bromo-5,6-dimethyl heptane
- (5) How many structural isomers of hexane are there ?  
 (A) 6 (B) 5  
 (C) 4 (D) 9
- (6) Which type of product is obtained by heterolytic fission?  
 (A) Electrophile (B) Nucleophile  
 (C) Carbonium ion (D) All
- (7) Which of the following is a nucleophile ?  
 (A) ROH (B)  $CH_3CN$   
 (C)  $CH_3NH_2$  (D) all
- (8) Which free radical is the most stable ?  
 (A)  $RCH_2^{\cdot}$  (B)  $R_2CH^{\cdot}$   
 (C)  $R_3C^{\cdot}$  (D)  $CH_3^{\cdot}$
- (9) Which molecule has the least C-C distance ?  
 (A)  $C_2H_6$  (B)  $C_2H_4$   
 (C)  $C_2H_2$  (D)  $C_4H_8$
- (10) In which molecule all the carbon atoms have same type of hybridisation ?  
 (A) ethyne (B) propene  
 (C) prop-1-yne (D) but-2-ene
- (11) During the addition reaction of ethene which type of change in hybridisation of carbon atom takes place ?  
 (A)  $sp^2$  to  $sp^3$  (B)  $sp^3$  to  $sp^2$   
 (C)  $sp$  to  $sp^3$  (D)  $sp^3$  to  $sp$
- (12)  $CH_3CONH_2 \xrightarrow{P_2O_5} CH_3CN$ ; during this reaction which type of change occurs in hybridisation of carbonyl carbon ?  
 (A)  $sp^3$  to  $sp^2$  (B)  $sp^2$  to  $sp^3$   
 (C)  $sp^2$  to  $sp$  (D)  $sp$  to  $sp^2$



- (13) Ethanal and vinyl alcohol are examples of which isomerism ?  
(A) Metamerism (B) Tautomerism  
(C) Position isomerism (D) Functional group isomerism
- (14) In which type of reaction a new  $\pi$  bond is added between two carbon atoms ?  
(A) Substitution (B) Addition  
(C) Elimination (D) Rearrangement

**2. Write the answers of the following questions in short :**

- (1) What is hybridisation ?
- (2) Mention bond angle and shape of methane molecule.
- (3) Mention bond length and hybridisation of ethane molecule.
- (4) Write examples of functional group isomerism.
- (5) Draw structures for isomers of butane.
- (6) Draw isomers of compound having formula  $C_3H_6O$ .
- (7) Draw isomers of compound having formula  $C_4H_{10}O$
- (8) Write two examples having -I effect.
- (9) Draw resonance structure of  $CO_2$ .
- (10) What is free radical ?

**3. Write answers of the following questions :**

- (1) Which belief was rejected by Wohler ? Give example.
- (2) What is an inductive effect ? Explain.
- (3) What is an electromeric effect ? Explain.
- (4) Explain hyperconjugation in propene.
- (5) What is homolytic fission ? Explain.
- (6) Explain carbonium ion and carbanion.

**4. Write the answers of the following questions :**

- (1) Explain with proper example shapes of  $sp^2$  hybridised orbitals and  $\pi$ -bonds.
- (2) What is homologous series ? Mention its characteristics.
- (3) Mention the types of structural isomerism and explain in brief.
- (4) Explain the methods of fission of electron in covalent bonds.
- (5) Explain types of organic reactions.
- (6) Write IUPAC names :
  - (1)  $CH_3CH_2CH_2CONH_2$
  - (2)  $CH_3CH_2OCH_2CH_3$
  - (3)  $CH_3CH_2CH_2COOCH_3$
  - (4)  $CH_3CH_2CH_2CH_2CN$
  - (5)  $CH_3CH=CH-C\equiv C-CH_2OH$

### APPENDIX -1

## Atomic Number and Molar Mass of Elements

Element	Symbol	Atomic Number	Molar mass(g mol <sup>-1</sup> )
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50

Element	Symbol	Atomic Number	Molar mass(g mol <sup>-1</sup> )
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94

Element	Symbol	Atomic Number	Molar mass(g mol <sup>-1</sup> )
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)

Element	Symbol	Atomic Number	Molar mass(g mol <sup>-1</sup> )
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of highest known half life

## APPENDIX -2

### Electronic Configuration of Elements

Element	Atomic Number	Electronic Configuration
H	1	1s <sup>1</sup>
He	2	1s <sup>2</sup>
Li	3	[He] 2s <sup>1</sup>
Be	4	[He] 2s <sup>2</sup>
B	5	[He] 2s <sup>2</sup> 2p <sup>1</sup>
C	6	[He] 2s <sup>2</sup> 2p <sup>2</sup>
N	7	[He] 2s <sup>2</sup> 2p <sup>3</sup>
O	8	[He] 2s <sup>2</sup> 2p <sup>4</sup>
F	9	[He] 2s <sup>2</sup> 2p <sup>5</sup>
Ne	10	[He] 2s <sup>2</sup> 2p <sup>6</sup>
Na	11	[Ne] 3s <sup>1</sup>
Mg	12	[Ne] 3s <sup>2</sup>
Al	13	[Ne] 3s <sup>2</sup> 3p <sup>1</sup>
Si	14	[Ne] 3s <sup>2</sup> 3p <sup>2</sup>
P	15	[Ne] 3s <sup>2</sup> 3p <sup>3</sup>
S	16	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
Cl	17	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>
Ar	18	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>
K	19	[Ar] 4s <sup>1</sup>
Ca	20	[Ar] 4s <sup>2</sup>
Sc	21	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>
Ti	22	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>
V	23	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>
*Cr	24	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>
Mn	25	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>
Fe	26	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>

Element	Atomic Number	Electronic Configuration
Co	27	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>
Ni	28	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>
*Cu	29	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
Zn	30	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>
Ga	31	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>
Ge	32	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>
As	33	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>
Se	34	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>
Br	35	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>
Kr	36	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>
Rb	37	[Kr] 5s <sup>1</sup>
Sr	38	[Kr] 5s <sup>2</sup>
Y	39	[Kr] 4d <sup>1</sup> 5s <sup>2</sup>
Zr	40	[Kr] 4d <sup>2</sup> 5s <sup>2</sup>
Nb	41	[Kr] 4d <sup>3</sup> 5s <sup>2</sup>
*Mo	42	[Kr] 4d <sup>5</sup> 5s <sup>1</sup>
Tc	43	[Kr] 4d <sup>5</sup> 5s <sup>2</sup>
Ru	44	[Kr] 4d <sup>6</sup> 5s <sup>2</sup>
Rh	45	[Kr] 4d <sup>7</sup> 5s <sup>2</sup>
Pd	46	[Kr] 4d <sup>8</sup> 5s <sup>2</sup>
*Ag	47	[Kr] 4d <sup>10</sup> 5s <sup>1</sup>
Cd	48	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>
In	49	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>
Sn	50	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>
Sb	51	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>
Te	52	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>



Element	Atomic Number	Electronic Configuration
I	53	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>
Xe	54	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>
Cs	55	[Xe] 6s <sup>1</sup>
Ba	56	[Xe] 6s <sup>2</sup>
*La	57	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>
*Ce	58	[Xe] 4f <sup>2</sup> 6s <sup>2</sup>
Pr	59	[Xe] 4f <sup>3</sup> 6s <sup>2</sup>
Nd	60	[Xe] 4f <sup>4</sup> 6s <sup>2</sup>
Pm	61	[Xe] 4f <sup>5</sup> 6s <sup>2</sup>
Sm	62	[Xe] 4f <sup>6</sup> 6s <sup>2</sup>
Eu	63	[Xe] 4f <sup>7</sup> 6s <sup>2</sup>
*Gd	64	[Xe] 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>
Tb	65	[Xe] 4f <sup>9</sup> 6s <sup>2</sup>
Dy	66	[Xe] 4f <sup>10</sup> 6s <sup>2</sup>
Ho	67	[Xe] 4f <sup>11</sup> 6s <sup>2</sup>
Er	68	[Xe] 4f <sup>12</sup> 6s <sup>2</sup>
Tm	69	[Xe] 4f <sup>13</sup> 6s <sup>2</sup>
Yb	70	[Xe] 4f <sup>14</sup> 6s <sup>2</sup>
Lu	71	[Xe] 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>
Hf	72	[Xe] 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>
Ta	73	[Xe] 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>
*W	74	[Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>1</sup>
Re	75	[Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>
Os	76	[Xe] 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>
Ir	77	[Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>
*Pt	78	[Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>
*Au	79	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
Hg	80	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup>
Tl	81	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>

Element	Atomic Number	Electronic Configuration
Pb	82	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Bi	83	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>
Po	84	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>
At	85	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>
Rn	86	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup>
Fr	87	[Rn] 7s <sup>1</sup>
Ra	88	[Rn] 7s <sup>2</sup>
Ac	89	[Rn] 6d <sup>1</sup> 7s <sup>2</sup>
Th	90	[Rn] 6d <sup>2</sup> 7s <sup>2</sup>
Pa	91	[Rn] 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>
U	92	[Rn] 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>
Np	93	[Rn] 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>
Pu	94	[Rn] 5f <sup>6</sup> 7s <sup>2</sup>
Am	95	[Rn] 5f <sup>7</sup> 7s <sup>2</sup>
Cm	96	[Rn] 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>
Bk	97	[Rn] 5f <sup>8</sup> 6d <sup>1</sup> 7s <sup>2</sup>
Cf	98	[Rn] 5f <sup>10</sup> 7s <sup>2</sup>
Es	99	[Rn] 5f <sup>11</sup> 7s <sup>2</sup>
Fm	100	[Rn] 5f <sup>12</sup> 7s <sup>2</sup>
Md	101	[Rn] 5f <sup>13</sup> 7s <sup>2</sup>
No	102	[Rn] 5f <sup>14</sup> 7s <sup>2</sup>
Lr	103	[Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>
Rf	104	[Rn] 5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>
Db	105	[Rn] 5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>
Sg	106	[Rn] 5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>
Bh	107	[Rn] 5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>
Hs	108	[Rn] 5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>
Mt	109	[Rn] 5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>

\* Elements having exceptional electronic configuration

### APPENDIX -3

## Physical Constants

Quantity	Symbol	Traditional Units	SI Units
Acceleration of gravity	$g$	$980.6 \text{ cm s}^{-1}$	$9.806 \text{ m s}^{-1}$
Atomic mass unit (1/12 <sup>th</sup> of the mass of $^{12}\text{C}$ atom)	amu or u	$1.6606 \times 10^{-24} \text{ g}$	$1.6606 \times 10^{-27} \text{ kg}$
Avogadro constant	$N_A$	$6.022 \times 10^{23}$ particles $\text{mol}^{-1}$	$6.022 \times 10^{23}$ particles $\text{mol}^{-1}$
Bohr radius	$a_0$	$0.52918 \text{ \AA}$	$5.2918 \times 10^{-11} \text{ m}$ $5.2918 \times 10^{-9} \text{ cm}$
Boltzmann constant	$k$	$1.3807 \times 10^{-16} \text{ erg K}^{-1}$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Charge-to-mass ratio of electron	$e / m$	$1.7588 \times 10^8 \text{ coulomb g}^{-1}$	$1.7588 \times 10^{11} \text{ C kg}^{-1}$
Electronic charge	$e$	$1.60219 \times 10^{-19} \text{ coulomb}$ $4.8033 \times 10^{-19} \text{ esu}$	$1.60219 \times 10^{-19} \text{ C}$
Electron rest mass	$m_e$	$9.10952 \times 10^{-28} \text{ g}$ $0.00054859 \text{ u}$	$9.10952 \times 10^{-31} \text{ kg}$
Faraday constant	$F$	$36,487 \text{ coulombs eq}^{-1}$ $23.06 \text{ kcalvolt}^{-1} \text{ eq}^{-1}$	$96,487 \text{ C (mol e}^{-})^{-1}$ $36,487 \text{ J V}^{-1} \text{ (mol e}^{-})^{-1}$
Gas constant	$R$	$0.8206 \text{ Latmmol}^{-1} \text{ K}^{-1}$ $1.987 \text{ calmol}^{-1} \text{ K}^{-1}$	$8.3145 \text{ kPa dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$
Molar volume (STP)	$V_m$	$22.710981 \text{ L mol}^{-1}$	$22.710981 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ $22.710981 \text{ dm}^3 \text{ mol}^{-1}$
Neutron rest mass	$m_n$	$1.67495 \times 10^{-24} \text{ g}$ $1.008665 \text{ u}$	$1.67495 \times 10^{-27} \text{ kg}$
Planck constant	$h$	$6.6262 \times 10^{-27} \text{ ergs}$	$6.6262 \times 10^{-34} \text{ J s}$
Proton rest mass	$m_p$	$1.6726 \times 10^{-24} \text{ g}$ $1.007277 \text{ u}$	$1.6726 \times 10^{-27} \text{ kg}$
Rydberg constant	$R$	$3.089 \times 10^{15} \text{ cycles s}^{-1}$ $2.1799 \times 10^{-11} \text{ erg}$	$1.0974 \times 10^7 \text{ m}^{-1}$ $2.1799 \times 10^{-18} \text{ J}$
Speed of light (in vacuum)	$c$	$2.9979 \times 10^{10} \text{ cm s}^{-1}$ (186,281 mile second <sup>-1</sup> )	$2.9979 \times 10^8 \text{ m s}^{-1}$

$$\pi = 3.1416 \quad 2.303 R = 4.576 \text{ calmol}^{-1} \quad K = 19.15 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$e = 2.71828 \quad 2.303 RT \text{ (at } 25^\circ\text{C)} - 1364 \text{ cal mol}^{-1} = 5709 \text{ J mol}^{-1}$$

$$\ln X = 2.303 \log X$$

## APPENDIX - 4

### Some Useful Conversion Factors

#### Common Units of Mass and Weight

**1 pound = 453.59 grams**  
 1 pound = 453.59 grams = 0.45359 kilogram  
 1 kilogram = 1000 grams = 2.205 pounds  
 1 gram = 10 decigrams = 100 centigrams  
           = 1000 milligrams  
 1 gram =  $6.022 \times 10^{23}$  atomic mass units or u  
 1 atomic mass units =  $1.6606 \times 10^{-24}$  gram  
 1 metric ton = 1000 kilograms  
                   = 2205 pounds

#### Common Unit of Volume

**1 quart = 0.9463 litre**  
**1 litre = 1.056 quarts**  
  
 1 litre = 1 cubic decimetre = 1000 cubic  
 centimetres = 0.001 cubic metre  
 1 millilitre = 1 cubic centimetre = 0.001 litre  
                   =  $1.056 \times 10^{-3}$  quart  
 1 cubic foot = 28.316 litres = 29.902 quarts  
                   = 7.475 gallons

#### Common Units of Energy

**1 joule =  $1 \times 10^7$  ergs**  
 1 thermochemical calorie  
                                   = 4.184 joules  
                                   =  $4.184 \times 10^7$  ergs  
 =  $4.129 \times 10^{-2}$  litre-atmosphere  
 =  $2.612 \times 10^{-19}$  electron volts  
 1 erg =  $1 \times 10^{-7}$  joule =  $2.3901 \times 10^{-8}$  calorie  
 1 electron volt =  $1.6022 \times 10^{-19}$  joule  
                       =  $1.6022 \times 10^{-12}$  erg  
                       = 96.487 kJ/mol

1 litre-atmosphere = 24.217 calories  
                           = 101.32 joules  
                           =  $1.0132 \times 10^9$  ergs  
 1 British Thermal Unit = 1055.06 joules  
                                   =  $1.05506 \times 10^{10}$  ergs  
                                   = 252.2 calories

#### Common Units of Length

**1 inch = 2.54 centimetres (exactly)**  
 1 mile = 5280 feet = 1.609 kilometres  
 1 yard = 36 inches = 0.9144 metre  
 1 metre = 100 centimetres = 39.37 inches  
                   = 3.281 feet  
                   = 1.094 yards  
 1 kilometre = 1000 metres = 1094 yards  
                   = 0.6215 mile  
 1 angstrom =  $1.0 \times 10^{-8}$  centimetre  
                   = 0.10 nanometre  
                   =  $1.0 \times 10^{-10}$  metre  
                   =  $3.937 \times 10^{-9}$  inch

#### Common Units of Force\* and Pressure

1 atmosphere = 760 millimetres of mercury  
                   =  $1.013 \times 10^5$  pascal  
                   = 14.70 pounds per square inch  
 1 bar =  $10^5$  pascals  
 1 torr = 1 millimetre of mercury  
 1 pascal =  $1 \text{ kg/ms}^2 = 1 \text{ N/m}^2$

#### Temperature SI Base Unit: Kelvin (K)

K =  $-273.15^\circ\text{C}$   
 K =  $^\circ\text{C} + 273.15$   
 $^\circ\text{F} = 1.8(^\circ\text{C}) + 32$

### APPENDIX - 5

#### Nobel Prize Winners of 21<sup>st</sup> century (chemistry)

Year	Scientist	Birth place (Birth date)	Place of work	Research work
2001	K. Barry Sharpless Ryoji Noyori William S. Knowles	USA (28-04-1941) Japan (03-09-1938) USA (01-06-1917)	USA Japan USA	Study on chirality Catalysed hydrohination reactions
2002	John B. Fenn Koichi Tanaka Kurt Wuthrich	USA (15-6-1917) Japan (3-8-1959) Switzerland (4-10-1938)	USA Japan USA	Development of Nuclear Magnetic Resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution
2003	Peter Agre Roderick Mackinnon	USA (30-1-1949) USA (19-2-1956)	USA	Discovery of Water channels (transport of water and ions from cell membrane)
2004	Aaron Ciechanover Avram Hershko Irwin Rose	Israel (1-10-1947) Hungary (31-12-1937) USA (16-7-1926)	Israel Israel USA	Discovery of degradation of Ubiquitin Mediated protein
2005	Yves Chauvin Robert H. Grubbs Richard R. Schrock	France (10-10-1930) USA (27-2-1942) USA (4-1-1945)	France USA USA	Development of the metathesis method in organic synthesis
2006	Roger D. Kornberg	USA (26-4-1947)	USA	Studies of mechanism and control of the eukaryotic transcription
2007	Gerhard Ertl	Germany (10-10-1936)	Germany	Studies of the chemical processes on solid surfaces
2008	Osamu Shimomura Martin Chalfie Roger Y. Tsien	Japan (1928) USA (1947) USA (1-2-1952)	USA USA USA	Discovery and development of the Green Fluorescent Protein
2009	Venkatraman Rama krishnan Thomas A. Steitz Ada E. Yonath	India(Tamilnadu)(1952) USA (23-8-1940) Isreal (22-6-1939)	UK USA Israel	Studies of the Structure and Function of the Ribosome