

BUREAU'S

HIGHER SECONDARY (+2)

CHEMISTRY

VOL. - I

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FOREWORD

(New Edition - 2016)

The Council of Higher Secondary Education, Odisha has revised the Courses of Studies in Chemistry for its examination, 2017 and onwards. It is really heartening to know that the Chemistry - Vol-I is an exclusive textbook of CHSE and its new edition is being published by the Odisha State Bureau of Text Book Preparation and Production, Bhubaneswar.

I acknowledge with thanks to the Board of Writers and Reviewers who have worked hard in writing the chapters of the book and setting new pattern of questions as per the requirement of the new syllabus of CHSE.

My special thanks due to Dr. Akhil Krishna Panigrahi, Dr. Gobinda Chandra Dash, Dr. Hrushikesh Mohanty, Dr. Panchanan Goud, Dr Santosini Patra & Dr. Sakuntala Jena for taking pain and strain of doing arduous work in preparing the book within the frame work of the new syllabus of CHSE. I also take this opportunity to convey my heartfelt thanks to Dr. Jibanananda Kar who have gone through the proofs of the entire book before final printing. The new edition of the book could see the light of the day in record time due to sincere effort of Sri Biraja Bhushan Mohanty, Deputy Director of the Bureau.

My earnest gratitude is also due to the Commissioner Cum Secretary, Department of Higher Education, Odisha and Chairman, Council of Higher Secondary Education, Odisha in entrusting the Bureau the task of publishing the book for Higher Secondary students of the state.

Improvement has no limit specially when one aims at excellence. The Bureau is always alive to any constructive suggestions from the students as well as the teachers to make the book more purposeful.

11.3.2016

Dr. Geetika Patnaik

Director

Odisha State Bureau of Text Book
Preparation and Production, Pustak Bhavan,
Bhubaneswar, Odisha

PREFACE

India is on the verge of a great leap into the global scientific and technological advancement in the New Millennium. Our Universities and Council of Higher Secondary Education have taken up the upgrading of science curriculum as a challenge. Society is becoming largely knowledge based. To prepare our young students to achieve the goal, Council of Higher Secondary Education, Odisha has revised the syllabus of all science subjects and has taken up the challenge to arm our students with advanced scientific education.

The biggest challenge in the present times in the field of scientific education is the preparation of textbooks suited to the needs of the students. Some of the most experienced, learned and brilliant teachers of the State have made attempts towards fulfilling the national need of providing a good textbook in Chemistry for +2 students. As a result the book titled **+2 Chemistry** has been prepared in accordance with the new syllabus of C.H.S.E. Odisha which will be effective for the students who will be admitted in 2016 and onwards. This book has many special features, the salient ones of which may be enumerated as follows :

- (i) The text book has been prepared keeping in view the type of questions set in the +2 as well as entrance examinations.
- (ii) The subject matter has been put in a lucid manner and in a simple language to be easily followed by the students.
- (iii) Large numbers of numerical problems have been worked out.
- (iv) Neat diagrams are given to provide suitable explanation of the texts.
- (v) Large number of questions of very short answer type, short answer type, multiple choice type and long answer type including questions of H. S. Examinations are given in each chapter.
- (vi) At the end of every chapter, summary of the topics dealt in the chapter is given under **Chapter at a glance**.

The authors express their gratitude to the authorities of C.H.S.E. for accepting them as the members of Board of Editors and to the **ODISHA STATE BUREAU OF TEXTBOOK PREPARATION AND PRODUCTION** for publishing the book. The authors sincerely hope that their endeavour would fulfil the need of students. There may be minor errors of omissions and commissions in the book. The authors welcome constructive criticism and suggestions for the improvement of the book.

COURSES OF STUDIES IN CHEMISTRY (THEORY)
FOR
HIGHER SECONDARY EXAMINATION
(Effective from 2016 Admission Batch)

FIRST YEAR

Unit - I : Some Basic Concepts of Chemistry

General Introduction : Importance and scope of chemistry.

Nature of matter, laws of chemical combination, Dalton's atomic theory: concept of elements, atoms and molecules. Atomic and molecular masses. and equivalent mass of elements, acid, base, salt, oxidants and reductants, mole concept and molar mass, percentage composition, empirical and molecular formula, chemical reactions, stoichiometry and calculations based on stoichiometry.

Unit - II : Structure of Atom

Discovery of Electron, Proton and Neutron, atomic number, isotopes and isobars. Thomson's model and its limitations. Rutherford's model and its limitations, Bohr's relationship, Heisenberg uncertainty principle, concept of orbitals, quantum numbers, shape of s, p and d orbitals, rules for filling electrons in orbitals - Aufbau principle, Pauli's exclusion principle and Hund's rule, electronic configuration of atoms, stability of half filled and completely filled orbitals.

Unit -III : Classification of Elements and Periodicity in Properties

Significance of classification, brief history of the development of periodic table, modern periodic law and the present form of periodic table, periodic trends in properties of elements - atomic radii, ionic radii, inert gas radii. Ionization enthalpy, electron gain enthalpy, electronegativity, valency and oxidation state, Nomenclature of elements with atomic number greater than 100.

Unit - IV : Chemical Bonding and Molecular Structure

Valence electrons, ionic bond, covalent bond; bond parameters, Lewis structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization, involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules (qualitative idea only), hydrogen bond.

Unit - V : State of Matter : Gases and Liquids

Three states of matter, intermolecular interactions, types of bonding, melting and boiling points, role of gas laws in elucidating the concept of the molecule, Boyle's law, Charle's law, Gay Lussac's law, Avogadro's law, ideal behaviour, empirical derivation of gas equation. Avogadro's number, ideal gas equation, Deviation from ideal behaviour, liquefaction of gases, critical temperature, kinetic energy and molecular speeds (elementary idea). Liquid state: vapour pressure, viscosity and surface tension (qualitative idea only, no mathematical derivations.)

Unit - VI : Chemical Thermodynamics

Concept of System and types of systems, surroundings, work, heat, energy, extensive and intensive properties, state functions.

First law of thermodynamics - internal energy and enthalpy, heat capacity and specific heat, measurement of ΔU and ΔH , Hess's law of constant heat summation, enthalpy of bond dissociation, combustion, formation, atomization, sublimation phase transition, ionization, solution and dilution. Second law of Thermodynamics (brief introduction)

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Third law of thermodynamics (brief introduction)

Unit - VII : Equilibrium

Equilibrium in physical and chemical processes, dynamic nature of equilibrium, law of mass action, equilibrium constant, K_c , K_p and K_x and their relationship factors affecting equilibrium. Le Chatelier's principle, ionic equilibrium-ionization of acids and bases strong and weak electrolytes, degree of ionization, ionization of poly basic acids, acid strength, concept of pH, Henderson Equation. hydrolysis of salts (elementary idea), buffer solution, solubility product, common ion effect (with illustrative examples), numerical problems.

Unit - VIII : Redox Reaction

Concept of oxidation and reduction, redox reactions, oxidation number, balancing redox reactions, in terms of loss and gain of electrons and change in oxidation number, applications of redox reactions.

Unit - IX : Hydrogen

Position of hydrogen in periodic table, occurrence, isotopes, preparation, properties and uses of hydrogen, hydrides-ionic, covalent and interstitial; physical and chemical properties of water, heavy water, hydrogen peroxide - preparation, reactions and structure and use, hydrogen as a fuel.

Unit - X : s-Block Elements (Alkali and Alkaline Earth Metals)

Group 1 and Group 2 Elements

General introduction, electronic configuration, occurrence, anomalous properties of the first element of each group, diagonal relationship, trends in the variation of properties (such as ionization enthalpy, atomic and ionic radii), trends in chemical reactivity with oxygen, water, hydrogen and halogens, uses.

Preparation and Properties of some important Compounds :

Sodium Carbonate, Sodium Chloride, Sodium Hydroxide and Sodium Hydrogencarbonate, Biological importance of Sodium and Potassium. Calcium Oxide and Calcium Carbonate and their industrial uses, biological importance of Magnesium and Calcium.

Unit - XI : Some p-Block Elements

General Introduction to p-Block Elements

Group 13 Elements : General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous properties of first element of the group, Boron-physical and chemical properties, some important compounds, Borax, Boric acid Boron Hydrides, Aluminium: Reactions with acids and alkalis, uses.

Group 14 Elements : General introduction, electronic configuration, occurrence, variation of properties, oxidation states, trends in chemical reactivity, anomalous behaviour of first elements. Carbon-catenation, allotropic forms, physical and chemical properties, use of some important compounds: oxides. Important compounds of Silicon and a few uses: Silicon Tetrachloride. Silicones, Silicates and Zeolites, their uses.

Unit - XII : Organic Chemistry - Some Basic Principles and Technique

General introduction, methods of purification, qualitative and quantitative analysis, classification and IUPAC nomenclature of organic compounds. Electronic

displacements in a covalent bond: inductive effect, electromeric effect, resonance and hyperconjugation, homolytic and heterolytic fission of a covalent bond free radicals, carbocations, carbanions, electrophiles and nucleophiles, types of organic reactions.

Unit - XIII : Hydrocarbons

Classification of Hydrocarbons

Aliphatic Hydrocarbons

Alkanes - Nomenclature, isomerism, conformation (ethane only), methods of preparation, physical properties, chemical reactions including free radical mechanism of halogenation, combustion and pyrolysis.

Alkenes - Nomenclature, structure of double bond (ethene) geometrical isomerism, physical properties, methods of preparation, chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markownikov's addition and peroxide effect), ozonolysis, oxidation, mechanism of electrophilic addition.

Alkynes - Nomenclature, structure of triple bond (ethyne), physical properties, methods of preparation, chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.

Aromatic Hydrocarbons : Introduction, IUPAC nomenclature, benzene: resonance, aromaticity chemical properties: mechanism of electrophilic substitution: nitration, sulphonation, halogenation Friedel Craft's alkylation and acylation, directive influence of functional group in monosubstituted benzene. Carcinogenicity and toxicity.

Unit - XIV : Environmental Chemistry

Environmental pollution - air, water and soil pollution, chemical reactions in atmosphere, smog, major atmospheric pollutants, acid rain, ozone and its reactions, effects of depletion of ozone layer, green house effect and global warming-pollution due to industrial wastes, green chemistry as an alternative tool in reducing pollution, strategies for control of environmental pollution.

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UNIT – I

SOME BASIC CONCEPTS OF CHEMISTRY

CHAPTER - 1 INTRODUCTION

Chemistry is one of the major disciplines of science. It deals with the study of the composition, structure and properties of matter along with the changes involved in matter. In other words, chemistry is defined as the science of matter and its transformations.

Chemistry has been further classified into following main different branches.

1. **Inorganic chemistry** : It deals with the study of all the elements and their compounds except the covalently bonded compounds of carbon.
2. **Organic chemistry** : It deals with the study of the carbon compounds derived from living organisms, except oxides of carbon, carbides, carbonates and bicarbonates. In other words, organic chemistry is defined as the study of hydrocarbons and their derivatives.
3. **Physical chemistry** : It deals with the fundamental principles governing various chemical phenomena.
4. **Analytical chemistry** : It deals with the identification, separation and qualitative determination of the composition of different substances.
5. **Industrial chemistry** : It deals with the chemistry involved in various chemical industry.
6. **Biochemistry** : It deals with the study of chemical changes, which take place in living organisms.
7. **Nuclear chemistry** : It deals with the study of structure and processes involved in nuclei of atoms.
8. **Polymer chemistry** : It deals with the study of structure, synthesis and reactions of macromolecules.

1.1 **IMPORTANT CONTRIBUTIONS OF CHEMISTRY :**

The present day chemistry is providing man with more comforts for a better, healthier and happier life. It is of great importance in industry, medicines, synthetic fibres, food stuffs, fertilizers and generation of power.

The important contributions of chemistry to the modern world are :

- (i) **In foodstuff** : Food enriched with vitamins helps us for the improvement of our health. The modern methods of processing food and selection of diets have solved malnutrition problem. The satisfactory production and protection of food grains have been achieved by the application of chemical fertilizers and pesticides such as D.D.T, Gammexene etc.

- (ii) **In housing :** Chemical substances, like cement, paints, varnishes, plastic, metals and their alloys are useful in building the modern house.
- (iii) **In medicine :** A number of medicines like quinine, antibiotics, insulin, streptomycin etc. have helped human beings in leading healthy life. Now radioactive isotopes are used in diagnosis of diseases.
- (iv) **In industry :** Chemical industries like steel, fertilizers, artificial fibres, synthetic rubber, petrochemicals, cement etc. have helped us to achieve self sufficiency in the respective fields.
- (v) **In warfare :** Powerful explosives like T.N.T, R.D.X and poisonous gases like phosgene are the contributions of chemistry. Atom bomb and hydrogen bomb can destroy the whole mankind. However, these are now used for peaceful purposes like generation of power and utilisation in telecommunications.
- (vi) **Pollution control :** The effluents are chemically treated before mixing with air and water to prevent pollution.

Besides the above, chemistry will have a wide range of applications in the 21st century for modern living and better future.

1.2 UNITS OF MEASUREMENT SYSTEM OF UNITS :

The system of units commonly used are : (1) French system or C.G.S. System, (2) British system or F.P.S. System, (3) Metre-Kilogram Second or M.K.S. System (4) International system of units or S.I.System.

1. **C.G.S. System :** In this system the units of length, mass and time are centimetre, gram and second respectively. The CGS System is widely used because its small and large units are multiples of ten. However, now a days S.I. units are preferred.

The units in C.G.S. system for expressing mass, volume and length are explained in following table.

Units for mass, volume and length.

Physical(Quantity)	Kilo	Hecto	Deca	Deci	Centi	Milli
Mass (in gm)	1000	100	10	0.1	0.01	0.001
Volume (in litres)	1000	100	10	0.1	0.01	0.001(1ml)
Length (in metres)	1000	100	10	0.1	0.01 (1cm)	0.001

2. **F.P.S. System :** In this system the units of length, mass and time are foot, pound and second respectively.
3. **M.K.S. System :** The unit of mass in this system is kilogram, the unit of length is metre and the unit of time is second.
4. **International System of Units (S.I.Units) :** This is the recent version of the metric system (M.K.S) and is supposed to be used throughout the world. This system consists of seven fundamental units with the help of which the derived units for all other possible quantities can be determined.

- (a) **Fundamental Units :** There are seven fundamental units.

Fundamental quantity and units

Physical quantity	Unit	Symbol
Length	Metre	m
Mass	Kilogram	Kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
Luminous intensity	Candela	Cd
Amount of substance	Mole	mol

- (b) **Derived Units :** There are many derived units. Only few of them which are mostly useful in the study of chemistry are :

- (i) **Pressure:** It is defined as the force per unit area. Hence pressure is expressed in Nm^2 .
- (ii) **Volume :** Volume of a solid is expressed in m^3 , whereas the volume of a liquid is generally expressed in litres.

$$1 \text{ litre} = 10^{-3} \text{ m}^3$$

Names and Symbols for some S.I.derived units.

Physical quantity	Symbol	Units	Special name of S.I.Units	Symbol for S.I.Units
Area	A	m^2		
Density	P	Kg.m^{-3}		
Force	F	Kg.m.s^{-2}	Newton	N
Pressure	P	$\text{Kg.m}^{-1}.s^{-2}$	Pascal	Pa
Energy	E	$\text{Kg.m}^2.s^{-2}$	Joule	J
Viscosity coefficient	μ	$\text{Kg.m}^{-1}.s^{-1}$		
Surface tension	r	Kg.s^{-2}		
Electric potential	V	$\text{Kg.m}^2.s^{-2}A^{-1}$	Volt	V
Electric resistance	R	$\text{Kg.m}^2.s^{-2}A^{-2}$	Ohm	Ω
Electric charge	I	—	Coulomb	C
Frequency	ν	s^{-1} (cycles per second)	Hertz	Hz

Multiples of SI Units : Knowledge of some units which are not S.I. Units but are commonly used and are fractions or multiples of S.I. Units is useful in various fields of chemistry. Such units and their relation with S.I. Units is described in the following table.

Some Units and their relation with S.I.Units

Physical quantity	Unit	Symbol	Relation with S.I.Unit
Length	Angstrom	A°	10^{-10} m
Length	Micron	μ	10^{-6} m
Length	Picometre	pm	10^{-12} m
Force	dyne	dyne	10^{-5} N
Pressure	bar	bar	10^5 Nm^{-2}
Energy	erg	erg	10^{-7} J
Area	barn	b	10^{-25} m^2
Volume	litre	l	$10^{-3} \text{ m}^3 = 1 \text{ dm}^3$

Temperature measurement :

Temperature is measured with the help of thermometer. Three scales are used for measuring temperature.

- (i) **Centigrade scale :** The thermometer with centigrade scale has a zero mark for the temperature of ice at one atmospheric pressure. The mark 100°C indicates the temperature of boiling water at one atmospheric pressure. The space between any two consecutive divisions (representing 1°C) is further divided into 10 subdivisions.
- (ii) **Fahrenheit scale :** In this scale, the temperature of ice at one atmospheric pressure has a mark 32°F while that of boiling water is 212°F .

Centigrade and Fahrenheit scales are related as follows.

$$F = \frac{9}{5} C + 32$$

Example : Convert 25°C into a temperature on Fahrenheit scale.

Solution : Temperature on centigrade scale = 25°C

Hence, temperature on Fahrenheit scale

$$\begin{aligned} &= \frac{9}{5} \times 25 + 32 \\ &= 77^{\circ}\text{F} \end{aligned}$$

- (iii) **Absolute scale :** It is also known as Kelvin scale. On this scale, the temperature of ice at one atmospheric pressure is 273°A or 273K . This scale is related to centigrade scale in the following way;

Temperature on centigrade scale + 273

= Temperature on absolute or kelvin scale.

Hence, $0^{\circ}\text{C} = 273^{\circ}\text{A}$ or 273 K .

and $- 273^{\circ}\text{C} = 0^{\circ}\text{A}$ or Absolute zero.

1.3 **MATTER**

Matter : Matter is defined as anything that has definite mass and that occupies space.

Examples : Water, air, gases, wood, solutions of salts etc. are examples of matter. All these substances possess definite mass and occupy some space.

Classification of matter : Matter is classified into the following two categories.

1. **Homogeneous matter :** Matter that has uniform composition and identical properties throughout the phase is called homogeneous matter. It consists of only one phase.

Examples : Water, sulphur, sugar, oxygen, copper etc.

2. **Heterogeneous matter :** Matter, which is made of two or more components, that are physically distinct is called heterogeneous matter. It has neither uniform composition nor identical properties. It consists of two or more number of phases.

Example : (i) Mixture of salt and sand.

(ii) Mixture of water and benzene.

Elements, Compounds and Mixtures :

1. **Element :** An element is the simplest form of matter which can not be broken down into still simpler form by any physical or chemical means.

Modern concept of element : According to the modern concept, an element can be broken down into its simplest form called atom in which all the properties of element are observed. For example, if a piece of iron is divided and subdivided continuously a stage will be reached when further subdivision will not be possible. The last portion will however exhibit all the properties of iron, that is, it will be attracted by a magnet.

So far 116 elements have been discovered.

Classification of elements :

Elements have been classified into the following three categories depending upon their physical properties.

- (i) **Metals :** All metals are solids except mercury, which is a liquid. Metals are good conductors of heat and electricity and possess high melting and boiling points.

Examples : copper, silver, gold etc.

- (ii) **Non-metals :** Non-metals exist in all the three states of matter. They are bad conductors.

Examples : Solid non-metal – Sulphur, iodine, carbon

Liquid non-metal – Bromine

Gaseous non-metal – Chlorine, oxygen, nitrogen etc.

- (iii) **Metalloids :** Elements which have the properties of metals as well as non-metals are called semi-metals or metalloids.

Example : Bismuth, arsenic, tin etc.

Compound : A compound may be defined as a substance formed by the chemical union of two or more substances in certain fixed proportion by mass. The compound so formed differs entirely in properties from those of its constituents.

Example : Water, carbondioxide, sodium chloride etc.

A compound is always homogeneous and on decomposition it produces the substances from which it is obtained.

Mixture : A mixture is formed by simply mixing two or more elements or compounds in any proportion. Here, the properties of elements or compounds forming the mixture do not change at all.

Mixture can be homogeneous or heterogeneous.

Examples of homogeneous mixture :

- (i) Mixture of two miscible liquids (water and alcohol)
- (ii) Mixture of a solid and a liquid (solution of any salt)
- (iii) Mixture of two or more gases (air)
- (iv) Mixture of two or more solids (steel, brass etc.)

Examples of heterogeneous mixture :

- (i) Gun powder is a mixture of nitre, sulphur and charcoal
- (ii) Salt and sand

1.4 **ATOMS AND MOLECULES :**

We know that matter is composed of very minute particles, called molecules. But it has been found that, a molecule is not the ultimate particle but is made up of two or more particles, called atoms. So, an atom is the ultimate particle of an element while a molecule is the ultimate particle of a compound.

Atom : An atom is defined as the smallest particle of an element which may or may not have independent existence.

- Example :**
- (i) Atoms of copper, iron, silver etc. have independent existence.
 - (ii) Atoms of hydrogen, oxygen etc. do not have independent existence.

However, now a days atom is not considered as indivisible, rather, it can be further sub-divided into more simpler substances, called the fundamental particles. The fundamental particles present in an atom are electron, proton and neutron.

Molecule : A molecule is defined as the smallest particle of an element or a compound which has independent existence.

Molecules can be classified into two main types :

- (a) **Homoatomic molecules** : In this case, two or more atoms of the same element combine to form molecules.

Examples :

- (i) Monoatomic molecules : Monoatomic molecules contain single atoms of the same element. Noble gas elements, He, Ne, Ar are monoatomic molecules.
- (ii) Diatomic molecules : Diatomic molecules contain two atoms of the same element. Oxygen and nitrogen are diatomic molecules
- (iii) Triatomic molecules : Triatomic molecules contain three atoms of the same element. Ozone (O_3) is a triatomic molecule.

- (b) **Heteroatomic molecules** : In this case, two or more atoms of the different elements combine to form molecules.

Examples : (i) Molecule of water (H_2O)

(ii) Molecule of sulphuric acid (H_2SO_4)

1.5 STATES OF MATTER :

Matter exists in any one of the three states, such as solid, liquid and gas, depending upon temperature, pressure and its nature.



- (i) **Solid state :**

Matter in the solid state has definite shape and volume.

Since solids are rigid and hard, they show very small change in volume by the application of pressure and temperature. However, on strong heating, solid melts. Solids also possess high densities due to the strong electrostatic force of attraction between the atoms in a molecule.

Example : Silver, copper, sugar etc.

- (ii) **Liquid state :** Matter in the liquid state has definite volume but no definite shape. It acquires the shape of the container in which it is kept.

By the application of pressure and temperature, the volume of the liquid changes appreciably. The forces of attraction between the atoms here is comparatively less than solid.

Examples : Water, alcohol etc.

- (iii) **Gaseous state :** Matter in the gaseous state has neither definite shape nor definite volume. The gases occupy the entire available space and also acquire the shape of the vessel.

Temperature and pressure have a marked effect on the volume of a gas. By the application of pressure a gas can be compressed or expanded. They possess low values of densities as compared to solids and liquids due to very weak forces of attraction.

Distinction between solid, liquid and gaseous state

The main distinction between the three states of matter.

Property	Solid	Liquid	Gas
1.State of aggregation	The molecules are closely packed.	1. The molecules are loosely packed	1. The molecules are at a sufficient distance apart.
2. Intermolecular forces	The forces of attraction are maximum	2. The forces of attraction are less than those in case of solids	2. Very weak forces of attraction.
3. Molecular motion	The molecules possess vibratory motion.	3. Molecules have translatory as well as vibratory motion.	3. Molecules have random motion. They possess translatory, vibratory and rotatory motion.
4. Density	The density is high	4. The density is less than those of solids	4. Very small value of density.
5. Shape and volume	It has definite shape and volume	5. It has definite volume but no definite shape	5. It has neither definite shape nor definite volume.
6. Compressibility	Solids are least compressible	6. The compressibility of liquids is more than solids.	6. Gases are highly compressible.
7. Diffusion	Solids do not diffuse	7. Liquids have a small tendency for diffusion.	7. Gases diffuse easily.

1.6 SYMBOL

Symbol is a chemical notation to represent the name of an element in an abbreviated form. It also represents one atom of the element or one mole of the element. For example, the symbol 'C' represents the element Carbon, 1 atom of carbon or 1 mole of carbon atoms.

Elements and their symbols

Name	Symbol	Name	Symbol
Argon	Ar	Hydrogen	H
Aluminium	Al	Helium	He
Arsenic	As	Holmium	Ho
Antimony (Stibium)	Sb	Hafnium	Hf
Astatine	At	Hahnium	Ha
Actinium	Ac	Iron (ferrum)	Fe
Americium	Am	Iodine	I
Beryllium	Be	Indium	In
Boron	B	Iridium	Ir
Bromine	Br	Krypton	Kr
Barium	Ba	Kurchatovium	Ku
Bismuth	Bi	Lithium	Li
Berkelium	Bk	Lanthanum	La
Carbon	C	Lutetium	Lu
Chlorine	Cl	Lead	Pb
Calcium	Ca	Lawrencium	Lr
Chromium	Cr	Magnesium	Mg
Cobalt	Co	Manganese	Mn
Copper (Cuprum)	Cu	Molybdenum	Mo
Cadmium	Cd	Mercury (Hydrargyrum)	Hg
Cesium	Cs	Mendelevium	
Cerium	Ce	Nitrogen	N
Curium	Cm	Neon	Ne
Californium	Cf	Nickel	Ni
Dysprosium	Dy	Niobium	Nb
Europium	Eu	Neodymium	Nd
Erbium	Er	Neptunium	Np
Einsteinium	Es	Nobelium	No
Fluorine	F	Oxygen	O
Francium	Fr	Osmium	Os
Fermium	Fm	Phosphorus	P
Gallium	Ga	Potassium (Kalium)	K
Germanium	Ge	Palladium	Pd
Gold (Aurum)	Au	Praseodymium	Pr
Gadolinium	Gd	Promethium	Pm

Name	Symbol	Name	Symbol
Platinum	Pt	Titanium	Ti
Polonium	Po	Technetium	Tc
Protactinium	Pa	Tin (Stannum)	Sn
Plutonium	Pu	Tellurium	Te
Rubidium	Rb	Terbium	Tb
Ruthenium	Ru	Thulium	Tm
Rhodium	Rh	Tantalum	Ta
Rhenium	Re	Tungsten (wolfram)	W
Radon	Rn	Thallium	Tl
Radium	Ra	Thorium	Th
Sodium (Natrium)	Na	Uranium	U
Silicon	Si	Vanadium	V
Sulphur	S	Xenon	Xe
Scandium	Sc	Yttrium	Y
Selenium	Se	Ytterbium	Yb
Strontium	Sr	Zinc	Zn
Silver (Argentum)	Ag	Zirconium	Zr
Samarium	Sm		

As is evident from the symbols of different elements, the initial letter of the name of the element in capital usually represents the element. For example, H stands for hydrogen, C stands for carbon, O stands for oxygen, etc.

The initial letter C above cannot represent the elements Chlorine, Calcium, Chromium, Cobalt, Copper, Cadmium, etc. The initial letter C being used for carbon, for above elements, the initial letter in capital along with a small letter from the name of the elements represents the element. So the symbols Cl, Ca, Cr, Co, Cu, Cd are used respectively to represent them.

For some metals, the latin names of the elements (written in parentheses against names of elements in table above) are used as symbol.

Certain elements have been named after the scientists, important laboratories, cities, countries and planets. Given below is the list of elements whose symbols are derived from the names of scientists, laboratories, etc.

Elements after the names of Scientists, Laboratories etc.

Element	Scientist	Symbol
Curium	Madam Curie	Cm
Einsteinium	Alfred Einstein	Es
Fermium	Enrico Fermi	Fm
Mendelevium	Mendeleef	Md
Nobelium	Alfred Nobel	No
LABORATORY		
Californium	University of California	Cf
CITY		
Berkelium	Berkeley	Bk
COUNTRY		
Americium	America	Am
	Gallium	
	Galia (old name of France)	Ga
Germanium	Germany	Ge
Polonium	Poland	Po
PLANET		
Uranium	Uranus	U
Neptunium	Neptune	Np
Plutonium	Pluto	Pu

1.7 VALENCY

According to the **old concept**, Valency of an element denotes the combining capacity of its atoms to form compounds.

Hydrogen being the lightest element, its valency is chosen as one and the reference. The valencies of other elements are compared with that of hydrogen.

For example, one atom of chlorine combines with one atom of hydrogen to form one molecule of hydrogen chloride, HCl. So the valency of chlorine is one.

One atom of oxygen combines with two atoms of hydrogen to form one molecule of water, H_2O . Hence the valency of oxygen is two.

One atom of nitrogen combines with three atoms of hydrogen to form one molecule of ammonia, NH_3 . Thus the valency of nitrogen is three.

Valencies of some elements

Element	Valency	Element	Valency
Hydrogen	1	Magnesium	2
Chlorine	1	Calcium	2
Sodium	1	Nitrogen	3
Potassium	1	Aluminium	3
Oxygen	2	Carbon	4

When elements have valencies 1, 2, 3, 4, 5, 6, etc. they are said to be monovalent or univalent, divalent, trivalent, tetravalent, pentavalent, hexavalent respectively.

Thus, valency is a number that describes the combining capacity of an element. It does not carry any plus or minus sign. Valency is helpful in writing the formula of the compounds, In any compound, the valency of an element is always a whole number.

Formulae of organic compounds cannot be written and explained on the basis of this concept of valency.

The **modern concept of valency** is related to the number of electrons lost, gained or shared with an atom of an element in order to attain the stable configuration of the nearest inert gas element.

For example, in sodium chloride NaCl, sodium loses one electron to attain the stable configuration of neon, Ne. Chlorine gains one electron and attains the stable configuration of inert gas argon, Ar. Therefore, in sodium chloride valency of sodium is one and that of chlorine is one. In hydrogen chloride HCl, hydrogen shares its only electron with one electron of chlorine. After sharing hydrogen attains the stable configuration of inert gas helium, He and chlorine attains the stable configuration of argon, Ar. Therefore the valency of hydrogen is one and that of chlorine is one.

Variable valency :

Certain elements having more than one valency are said to exhibit variable valencies.

Variable valencies of some elements

Element	Valency	Element	Valency
Arsenic	3,5	Manganese	2, 3, 4, 6, 7
Antimony	3,5	Mercury	1, 2
Chlorine	1, 3, 5, 7	Nitrogen	1, 2, 3, 4, 5
Copper	1, 2	Phosphorus	3, 5
Cobalt	2,3	Platinum	2, 4, 6
Gold	1, 3	Sulphur	2, 4, 6
Iron	2,3	Tin	2, 4

While naming a particular compound the lower valency is referred to as **-ous** and higher valency as **-ic**. The following metallic elements combine with chlorine to form metal chlorides, exhibiting their variable valencies.

Some metallic elements with variable valencies in their chlorides

Metal chloride	Systematic name	Formula	Valency of the metal
Ferrous chloride	Iron (II) chloride	FeCl ₂	2
Ferric chloride	Iron (III) chloride	FeCl ₃	3
Cuprous chloride	Copper (I) chloride	CuCl or Cu ₂ Cl ₂	1
Cupric chloride	Copper (II)chloride	CuCl ₂	2
Mercurous chloride	Mercury (I) chloride	HgCl or Hg ₂ Cl ₂	1
Mercuric chloride	Mercury (II) chloride	HgCl ₂	2
Stannous chloride	Tin (II) chloride	SnCl ₂	2
Stannic chloride	Tin (IV) chloride	SnCl ₄	4

Non-metallic elements such as nitrogen, N exhibits variable valencies of 1, 2, 3, 4, 5 in its oxides like N₂O, NO, N₂O₃, NO₂, N₂O₅ respectively.

1.8 RADICALS

A radical in the molecule of a compound behaves as a single unit with a cluster of atoms. Radicals possess electrical charge.

A **simple radical** contains one or more atoms of the same element. For example, oxide O²⁻ and peroxide, O₂²⁻.

Valencies of some simple radicals

Radical	Valency	Radical	Valency
Hydrogen, H ⁺	1	Chloride, Cl ⁻	1
Sodium, Na ⁺	1	Bromide, Br ⁻	1
Potassium, K ⁺	1	Oxide O ²⁻	2
Magnesium Mg ²⁺	2	Sulphide S ²⁻	2
Calcium Ca ²⁺	2	Nitride N ³⁻	3
Aluminium Al ³⁺	3	Phosphide P ³⁻	3
Hydride, H ⁻	1	Carbide C ⁴⁻	4

A **compound radical** consists of two or more atoms of different elements. For example ammonium NH₄⁺, nitrate NO₃⁻, sulphate SO₄²⁻, phosphate PO₄³⁻, etc. When radicals contain oxygen atoms, the suffixes, **-ite** and **-ate** are used. The names of radicals ending in 'ite' contains less number of oxygen atoms than radicals ending in -ate. For example, nitrite NO₂⁻ and nitrate NO₃⁻.

Valencies of some compound radicals

Radical	Valency	Radical	Valency
Ammonium, NH_4^+	1	Manganate, MnO_4^{2-}	2
Hydroxide, OH^-	1	Chromate, CrO_4^{2-}	2
Carbonate, CO_3^{2-}	2	Dichromate, $\text{Cr}_2\text{O}_7^{2-}$	2
Bicarbonate HCO_3^-	1	Arsenate, AsO_4^{3-}	3
Bisulphide, HS^-	1	Arsenite, AsO_3^{3-}	3
Sulphite, SO_3^{2-}	2	Antimonate, SbO_4^{3-}	3
Bisulphite, HSO_3^-	1	Pyroantimonate, $\text{H}_2\text{Sb}_2\text{O}_7^{2-}$	2
Nitrite, NO_2^-	1	Borate, BO_3^{3-}	3
Nitrate, NO_3^-	1	Metaborate, BO_2^-	1
Sulphate, SO_4^{2-}	2	Meta aluminate, AlO_2^-	1
Bisulphate, HSO_4^-	1	Aluminate, AlO_3^{3-}	3
Phosphate, PO_4^{3-}	3	Zincate, ZnO_2^{2-}	2
Phosphite, PO_3^{3-}	3	Hypochlorite, ClO^-	1
Metaphosphate, PO_3^-	1	Chlorite, ClO_2^-	1
Pyrophosphate, $\text{P}_2\text{O}_7^{4-}$	4	Chlorate, ClO_3^-	1
Molybdate, MoO_4^{2-}	2	Perchlorate, ClO_4^-	1
Permanganate, MnO_4^-	1		

Radical bearing one, two, three, four units of charges are called univalent, divalent, trivalent, tetra or quadrivalent radicals respectively.

A salt has usually two parts or radicals. The electropositive part or basic radical is the cation, whereas the electronegative part or acid radical is the anion. For example in common salt i.e. sodium chloride the basic radical is Na^+ and the acid radical is Cl^- .

1.9 FORMULA

The **formula of a compound** represents the number of atoms of each element present in one molecule of the compound. The formula of the compound sodium chloride is NaCl , which means that one molecule of sodium chloride contains one atom of sodium and one atom of chlorine. A chemical formula also states the name of a compound as in the case of symbols.

For some elements, the molecule of the element exists. In such case, the **formula of an element** denotes the number of atoms occurring in one molecule of the element.

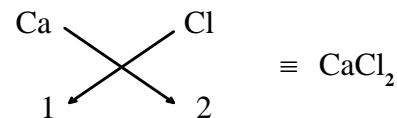
The formula H_2 , O_3 , P_4 , etc, indicate that two atoms of hydrogen are present in a molecule of the element hydrogen, three atoms of oxygen are present in a molecule of ozone, four atoms of phosphorus are present in a molecule of phosphorus respectively.

If we know the valency of each element in a compound we can easily write its formula. The symbol of the positive part is written to the left hand side and the symbol of the negative part to its right. The valency of each element is placed as subscript by the side of the symbol of other element as shown below. Subscript 1 is not often written.

Example - 1

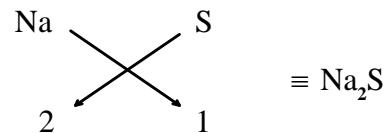
What is the formula of calcium chloride ?

Solution : The valency of calcium is 2 and that of chlorine is 1. Criss - crossing the valency number and using them as subscripts, we have the formula :



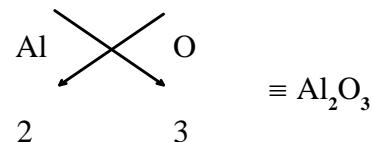
Example - 2 What is the formula of sodium sulphide ?

Solution : The valency of sodium is 1. and that of sulphur is 2. Criss - Crossing the valency number, we can write the formula :



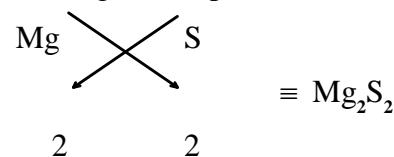
Example - 3 A compound consists of aluminium and oxygen. What is its formula ?

Solution : Aluminium has a valency number of 3. oxygen has a valency number of 2. Criss - crossing the valency numbers and using them as subscript, we have the formula :

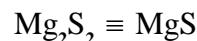


Example - 4 What is the formula of magnesium sulphide ?

Solution : Magnesium has a valency number of 2, and that of sulphur is 2. Therefore the formula of magnesium sulphide is MgS as explained below :

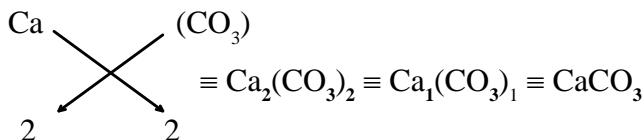


This formula tells us that the ratio of magnesium to sulphur atoms is 2 : 2. This is, of course, is the same as a ratio of 1 : 1 and the formula becomes :



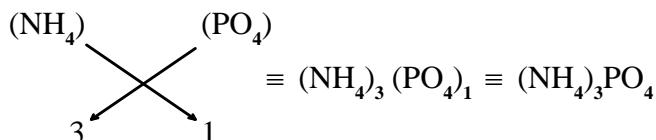
Example - 5 To write the formula of calcium carbonate.

Solution : The valency number of calcium is 2 and that of carbonate radical is 2. Criss-crossing the valency numbers, we write the formula :



Example - 6 What is the formula of ammonium phosphate ?

Solution : Ammonium has the valency Number 1 and that of phosphate radical is 3. Criss-crossing the valency numbers the formula of the compound may be written :



Correctness of a formula :

Since a compound contains two parts that is the basic and the acid part, the correctness of its formula may be tested as follows.

- (i) The number of the basic part is multiplied with its valency.
- (ii) The number of the acid part is multiplied with its valency.
- (iii) If both the values of the products are equal, then the formula is found to be correct.

Testing the correctness of a formula.

Formula	No. of basic parts x valency	No. of acid parts x valency	Remark on correctness.
CaCl_2	$1 \times 2 = 2$	$2 \times 1 = 2$	correct
Na_2PO_4	$2 \times 1 = 2$	$1 \times 3 = 3$	wrong
$\text{Al}_2(\text{SO}_4)_3$	$2 \times 3 = 6$	$3 \times 2 = 6$	correct.
$(\text{NH}_4)_3\text{SO}_4$	$3 \times 1 = 3$	$1 \times 2 = 2$	wrong
$\text{Mg}(\text{NO}_3)_2$	$1 \times 2 = 2$	$2 \times 1 = 2$	correct

Structural formula :

Sometimes, the formulae of compounds are written graphically indicating how the atoms in a molecule are linked with each other. The **structural formula** may also be called as **graphic formula**. In a compound, atoms of elements present are assumed to possess one or more bonds which are represented by small straight lines. A single bond is represented by a small straight line. Two straight lines mean a double, bond three lines, a triple bond etc.

Structural or graphic formulae of some compounds

Compound	Molecular formula	Structural formula
Hydrogen chloride	HCl	H – Cl
Methane	CH ₄	<pre> H H – C – H H </pre>
Carbon dioxide	CO ₂	O = C = O
Ethylene	C ₂ H ₄	<pre> H H C = C H H </pre>
Hydrogen cyanide	HCN	H – C ≡ N
Acetylene	C ₂ H ₂	H – C ≡ C – H

1.10 [NAMING OF COMPOUNDS]

The way of naming is called **nomenclature**.

A binary compound contains only two elements. Out of the two elements, one may be a metal and the other, a nonmetal or both may be non-metals.

The following sequence is followed to name a binary compound that contains a metal and a nonmetal.

1. The name of the metallic part is mentioned first.
2. The stem of the name of the second element i.e. the nonmetal ends with "ide".
3. If the binary compound contains metal of variable valency, the metal is followed by a Roman numeral in bracket to indicate its valency state. In common method of naming, the lower valency state of the metal is indicated by suffix "**-ous**" and its higher valency state by suffix "**-ic**".
4. Although the metal hydroxides and ammonium chloride contain three elements and they are not binary compounds, they end in "**-ide**", e.g, sodium hydroxide NaOH, ammonium chloride NH₄Cl.

Name of some binary compounds containing metals of fixed valency states.

Formula	Name of the first element (metal)	Stem name of the second element ending with '-ide'	Name of the compound
NaCl	Sodium	Chlor + (-ide)	Sodium chloride
KBr	Potassium	Brom +(-ide)	Potassium bromide.
CaO	Calcium	Ox + (-ide)	Calcium oxide
MgS	Magnesium	Sulph +(-ide)	Magnesium sulphide
AlN	Aluminium	Nitr + (-ide)	Aluminium nitride.

Name of some binary compounds containing metals of variable valency states.

Formula	Valency of the metal	Conventional name	Systematic name
PbCl ₂	2	Plumbous chloride	Lead(II) chloride
PbCl ₄	4	Plumbic chloride	Lead (IV) chloride
As ₂ S ₃	3	Arsenous sulphide	Arsenic (III) sulphide
As ₂ S ₅	5	Arsenic sulphide	Arsenic(V) sulphide
Sb ₂ O ₃ or Sb ₄ O ₆	3	Antimonous oxide	Antimony (III) oxide
Sb ₂ O ₅	5	Antimonic oxide	Antimony (V) oxide
MnO	2	Manganous oxide	Manganese (II) oxide
Mn ₂ O ₃	3	Manganic oxide	Manganese (III) oxide
AuCl	1	Aurous chloride	Gold (I) chloride
AuCl ₃	3	Auric chloride	Gold (III) chloride

In order to name a binary compound containing two **nonmetals**, number of each of the atoms are indicated by Greek prefixes. The prefix hemi, mono, sesqui, di, tri, tetra etc are used for $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, 3, 4 atoms respectively. The prefix "mono" is usually not mentioned when naming the compound. There are some exceptions to the name of binary compounds such as water H₂O, ammonia NH₃, etc.

Name of binary compounds composed of nonmetals.

Formula	Name of first nonmetal with Greek prefix	Greek prefix plus the stem name of the second nonmetal ending with '-ide'	Name of the compound
BCl ₃	Boron	tri-chlor-ide	Boron trichloride
CO ₂	Carbon	di-ox-ide	Carbon dioxide
CCl ₄	Carbon	tetra-chlor-ide	Carbon tetrachloride
N ₂ O	Di-nitrogen	oxide	Dinitrogen oxide
N ₂ O ₃	Di-nitrogen	tri-ox-ide	Dinitrogen trioxide
N ₂ O ₅	Di-nitrogen	penta-ox-ide	Dinitrogen pentoxide
PCl ₃	Phosphorus	tri-chlor-ide	Phosphorus trichloride
PCl ₅	Phosphorus	penta-chlor-ide	Phosphorus pentachloride
SO ₂	Sulphur	di-ox-ide	Sulphur dioxide
SO ₃	Sulphur	tri-ox-ide	Sulphur trioxide

The above procedure is followed to name binary compounds containing hydrogen and nonmetals. Such a compound existing in gaseous or liquid state remains soluble in water and the resulting aqueous solution is acidic in nature.

To name its acid the prefix hydro is used followed by the stem of the name of the non-metal with the suffix "-ic" and the word acid.

Name of some binary compounds of hydrogen and nonmetals

Formula	Name of the compound in the gaseous or liquid state	Name of the compound in aqueous state i.e. acid.
HCl	Hydrogen chloride	Hydrochloric acid
HBr	Hydrogen bromide	Hydrobromic acid
H ₂ S	Hydrogen sulphide	Hydrosulphuric acid
H ₂ Se	Hydrogen selenide	Hydroselenic acid

Inorganic oxy-acids contain hydrogen, oxygen and another element, called a parent element. The name of the oxy-acid is derived from the parent element ending in -ous or - ic. The acid with less number of oxygen ends with -ous and the acid with more number of oxygen ends with - ic. The oxy-acid in which the valency of the parent element is higher than the - ic acid and contains one more oxygen is called per-ic acid. An oxy-acid containing the parent element of lower valency than the -ous acid is called hypo -ous acid.

Name of some oxyacids and their sodium salts

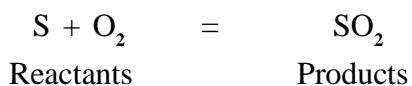
Oxy-acid	Sodium salt	
HNO ₂	Nitrous acid	NaNO ₂ Sodium nitrite
HNO ₃	Nitric acid	NaNO ₃ Sodium nitrate
H ₂ SO ₃	Sulphurous acid	Na ₂ SO ₃ Sodium sulphite
H ₂ SO ₄	Sulphuric acid	Na ₂ SO ₄ Sodium sulphate
HOCl	Hypochlorous acid	NaOCl Sodium hypochlorite
HClO ₂	Chlorous acid	NaClO ₂ Sodium chlorite
HClO ₃	Chloric acid	NaClO ₃ Sodium chlorate
HClO ₄	Perchloric acid	NaClO ₄ Sodium perchlorate

The name of the salts is based upon the name of the acid form which it is derived. The salt derived from the acid ending in -ous ends in -ite. A salt derived from an acid ending in -ic, ends in -ate. The salt of a hypo -ous acid is named as a hypo -ite salt.

1.11 **CHEMICAL EQUATION**

A chemical equation states a chemical reaction represented by symbols and chemical formulae.

When sulphur burns in air it combines with oxygen in air to produce sulphur dioxide due to the chemical combination of sulphur and oxygen.

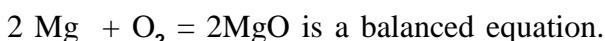


The chemical substances on the left hand side and right hand side of an equation are called reactants and products respectively. The above chemical equation also expresses that one atom of sulphur reacts with one molecule of oxygen to form one molecule of sulphur dioxide. Again the equation indicates that one mole of sulphur reacts with one mole of oxygen to produce one mole of sulphur dioxide. On examining this equation we observe that the total mass of the reactants is equal to the total mass of the products i.e the total mass is conserved as per law of conservation of matter.

Let us look at another reaction. Magnesium burns in air to produce magnesium oxide and is represented by the equation :



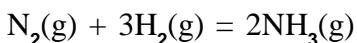
In this reaction there is loss of oxygen from the product side which is not in accordance with law of conservation of matter. The equation is called a skeleton equation and needs to be balanced. The equation would be balanced if we could place number 2 before MgO and number 2 before Mg. Thus,



A skeleton equation is balanced by placing numbers, also called **coefficients** before the formulae of the substances in the reaction. In the left hand side there are two magnesium atoms and two oxygen atoms and in the right hand side there are also same number of magnesium and oxygen atoms.

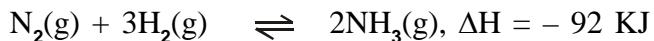
In a balanced equation therefore, the number of atoms of different elements appearing as reactants are equal to number of atoms of the same elements present as products.

Let us look at one more example. The following chemical equation



says that 1 mole of gaseous nitrogen combines with 3 moles of gaseous hydrogen to produce 2 moles of gaseous ammonia. This also says that 1 volume of gaseous nitrogen combines with

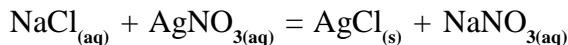
3 volumes of gaseous hydrogen to form 2 volumes of gaseous ammonia. The equation may be elaborately written as :



The reaction is a reversible one and represented by the sign \rightleftharpoons which indicates that the reaction may proceed both in forward or reverse direction. **The reversibility of a reaction is represented by the sign \rightleftharpoons .**

The above reaction evolves heat and we call it a exothermic reaction (the heat changes i.e. ΔH has a -ve value). An endothermic reaction absorb heat and its ΔH value is +ve. However, the heat changes (ΔH) in reactions are mentioned in a **thermochemical equation** whenever necessary.

The gaseous, liquid, solid states and the aqueous solution are given the symbol (g), (l), (s) and (aq) respectively For example the reaction of sodium chloride and silver nitrate is represented as follows :



In the laboratory carbon dioxide gas is prepared by the action of dilute hydrochloric acid on calcium carbonate. The reaction is represented by the equation :



When gas is evolved in a reaction, a vertical arrow \uparrow is sometimes used. In a reaction when a precipitate is formed, a downward arrow \downarrow is often used.

The required conditions of temperature, pressure, catalyst etc, are often mentioned in the equation as shown below.



Limitations of a chemical equation

The conditions such as temperature, pressure and the catalyst those bring about a chemical reaction are sometimes mentioned in the chemical equation.

The concentration of the reactants and products are never mentioned in an equation. An equation cannot furnish informations about all experimental conditions required for the reaction. The heat evolved or heat absorbed in a reaction are not ordinarily stated. A chemical equation does not speak about the speed with which the reaction proceeds and also the time needed for completion of the reaction.

Balancing of chemical equations

Any chemical equation must be written in the balanced form, since the number atoms on the reactant side must be equal to the number of atoms on the product side due to conservation of atoms. There are five different methods for balancing a chemical equation.

- (a) Hit and trial method
- (b) Partial equation method
- (c) Algebraic method
- (d) Oxidation number method
- (e) Ion electron method

(a) Hit and trial method

Simple equations are balanced by hit and trial method. The following steps may be employed to balance the equation in order to equalize atoms of each kind on both sides of the skeleton equation.

- (i) The skeleton equation be written to indicate the reactants and products.
- (ii) The biggest formula is selected and the different atoms present in it be balanced with the same atoms on the other side.
- (iii) Elementary gaseous reactants be written in atomic state, N, O etc. and they should be balanced at last.
- (iv) Atoms of elements which occur in maximum number of places be balanced then.
- (v) The balanced equation in the atomic state is changed into the molecular form and all the reactants and products are expressed in whole number multiples.

While balancing the equations, methods of addition, subtraction, multiplication and division are used.

Example 1

Potassium chlorate when heated decomposes to potassium chloride and oxygen gas is liberated.

Step 1 Skeleton equation is written as



Step 2 Biggest formula here is KClO_3 and it is balanced.



Example 2

Iron pyrite burns in oxygen to produce ferric oxide and sulphur dioxide

Step 1 $\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$ (Skeleton equation)

Step 2 $2\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2$ (iron balanced)



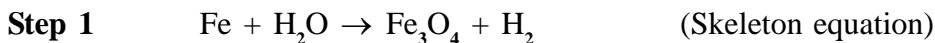
Step 3 $2\text{FeS}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ (atomic state of equation)

Step 4 $2\text{FeS}_2 + 11\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ (oxygen balanced)

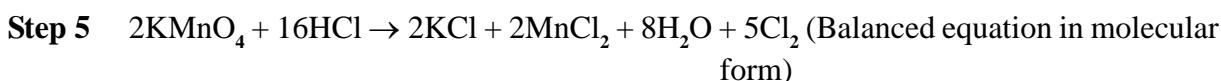
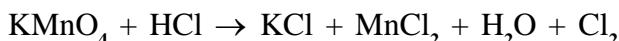
Step 5 $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$ (balanced equation in molecular form)

Example 3

When steam is passed over red-hot iron, ferroso ferric oxide and hydrogen are produced.

**Example 4**

Balance the skeleton equation

**Partial equation method**

In this method the reaction is thought to take place in several steps and each step is represented by partial equation.

The partial equations are balanced by hit and trial method and may be multiplied by suitable integers to omit the products which do not appear in the final equation.

Finally the partial equations are added to have the balanced equation.

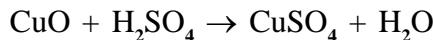
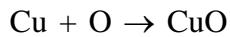
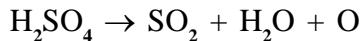
Example 1

Copper and sulphuric acid react to produce sulphur dioxide gas, copper sulphate and water. Balance the reaction by partial equation method.

Solution : The skeleton equation may be written as :

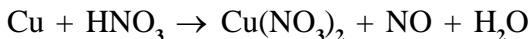


The above reaction is supposed to break up as follows.

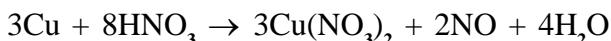
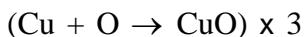
**Example 2**

Metallic copper reacts with moderately concentrated nitric acid to produce cupric nitrate, nitric oxide and water. Balance the reaction by partial equation method.

Solution : The skeleton equation may be written as :



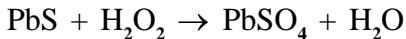
The above reaction is supposed to break up as follows :



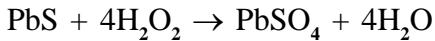
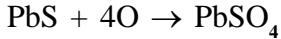
Example 4

Hydrogen peroxide reacts with lead sulphide to produce lead sulphate and water. Balance the equation by partial equation method.

Solution : The skeleton equation is written as :



The above reaction is supposed to break up as follows :

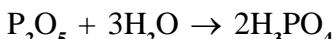
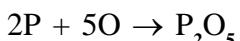
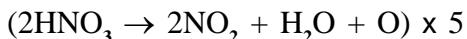


Example 4

Balance the following equation by partial equation method.

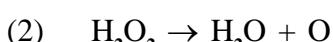
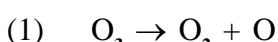


Solution : The above reaction is supposed to occur as follows :



Some important and supposed break up reactions.

The following reactions may be written to be used as first reactions while balancing equations by partial equation method.



- (4) $\text{X}_2 + \text{H}_2\text{O} \rightarrow 2\text{HX} + \text{O}$ (X = Cl, Br or I)

(5) $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$

(6) $2\text{HNO}_3 \rightarrow 2\text{NO}_2 + \text{H}_2\text{O} + \text{O}$ (concentrated HNO_3)

(7) $2\text{HNO}_3 \rightarrow 2\text{NO} + \text{H}_2\text{O} + 3\text{O}$ (Moderate HNO_3)

(8) $2\text{HNO}_3 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{O}$ (dilute HNO_3)

(9) $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{O}$

(10) $\text{MnO}_2 \rightarrow \text{MnO} + \text{O}$

(11) $\text{MnO}_2 + 2\text{HCl} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{O}$

(12) $\text{MnO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{H}_2\text{O} + \text{O}$

(13) $2\text{KMnO}_4 \rightarrow \text{K}_2\text{O} + 2\text{MnO} + 5\text{O}$ (acidic medium)

(14) $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{K}_2\text{O} + \text{Cr}_2\text{O}_3 + 3\text{O}$ (acidic medium)

(15) $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5\text{O}$

(16) $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO})_3 + 4\text{H}_2\text{O} + 3\text{O}$

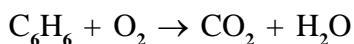
Algebraic method

This method is useful to balance a complicated equation.

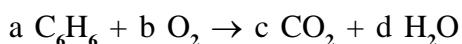
Example 1

Solution : Balance the equation for the combustion of benzene.

The skeleton equation for the combustion of benzene is



Let the balance equation be



According to the conservation of atoms, the number of carbon atoms on the reactant side must be equal to that on the product side.

Similarly, considering hydrogen atoms

and taking oxygen atoms into account

$$2b \equiv 2c + d \dots\dots\dots(3)$$

The above equations can be reduced to

$$c = 6 \text{ a}$$

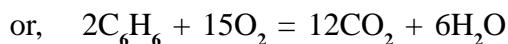
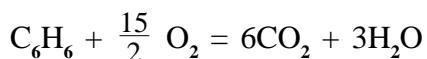
$$d = 3 \text{ } a$$

$$b = \frac{15}{2} a$$

Assuming the smallest value $a = 1$

$$C = 6, d = 3 \text{ and } b = \frac{15}{2}$$

The balanced equation is thus



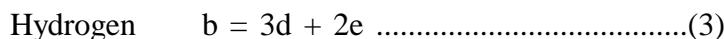
Example 2

Write the balanced equation for the oxidation reaction of phosphorus by nitric acid.

Solution : The skeleton equation for the reaction is written as



Let the balanced equation be



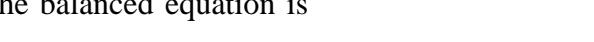
Ouwzen 3b 3c + 4d +



$$d = 4a : c = b, \quad b = 12a + 2e, \quad b =$$

Therefore, $e = 4a$, $b = 20$, $c = b$ and $d = 4a$

Assuming $a = 1$, then $b =$



$$P_4 + 20 HNO_3 \rightarrow 20 NO_2 + 4H_3PO_4 + 4H_2O$$

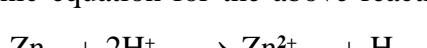
Chemical equations corresponding to **redox chemical reactions** (involving both oxidation and reduction) in aqueous solutions are balanced by oxidation number method.

Baum Reactions

Metallic zinc reacts with dilute hydrochloric acid to liberate hydrogen gas for which

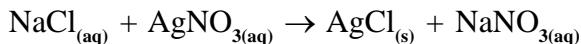


The initial conditions for the simulation are given in Table 1.

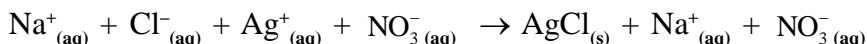


Silver nitrate solution when added to aqueous solution of sodium chloride, silver chloride solid is precipitated.

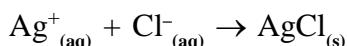
The chemical equation for the precipitation reaction is given below.



The substances NaCl, AgNO₃ and NaNO₃ almost completely dissociate into their ions in aqueous solution. As a result the number of Na⁺_(aq) and NO⁻_{3(aq)} on both the reactant and product side equal and the equation is written as :



and hence, the ionic equation becomes



CHAPTER (1) AT A GLANCE

Symbol : Symbol is a chemical notation to represent the name of an element, one atom of the element or one mole of the element.

Valency : According to the old concept valency of an element denotes the combining capacity of its atoms to form compounds.

According to modern concept, valency is related to the number electrons lost, gained or shared with an atom of an element in order to attain the stable configuration of the nearest inert gas element.

Variable valency : Certain elements having more than one valency are said to show variable valencies.

Radical : A radical in the molecule of a compound behaves as a single unit with a cluster of atoms. Radical possesses electrical charge. A simple radical contains one or more atoms of the same element.

Cation and Anion : A salt has usually two parts or radicals. The electropositive part or basic radical is called the cation. The electronegative part or acid radical is called the anion.

Formula : The formula of a compound represents the number of atoms of each element present in one molecule of the compound. The formula of an element denotes the number of atoms present in one molecule of the element. A formula also represents a quantity of the compound equal in mass to its molecular mass.

Structural or Graphic formula : The structural formula or graphic formula of compounds are written graphically indicating how the atoms in a molecule are linked with each other.

Chemical equation : A chemical equation states a chemical reaction represented by symbols and chemical formulae.

Balanced equation : A skeleton equation is balanced by placing numbers called coefficients before the formulae of the reactants and products mentioned in the reaction. In a balanced equation the number of atoms of different elements appearing as reactants are equal to the number of atoms of the same elements present as products.

QUESTIONS**(A) Very short answer type (1 mark each)****Write the formulae of the following compounds**

1. Sodium phosphate
2. Silver nitrate
3. Aluminium nitride
4. Aluminium phosphate
5. Sulphurous acid
6. Nitrogen trioxide
7. Potassium permanganate
8. Mercurous chloride
9. Sodium bicarbonate
10. Carbonic acid
11. Manganese dioxide
12. Silicon fluoride
13. Sodium thiosulphate
14. Boric acid
15. Antimonous sulphide
16. Mercurous nitrate
17. Nitrogen pentoxide
18. Hydrogen peroxide
19. Manganous sulphate
20. Cuprous chloride
21. Potassium pyroantimonate
22. Nitrous acid
23. Lead dioxide
24. Ammonium dichromate
25. Sodium tetraborate
26. Auric chloride
27. Potassium manganate
28. Phosphoric acid
29. Nitrosyl chloride
30. Sodium zincate
31. Perchloric acid
32. Stannous chloride
33. Potassium chromate
34. Sodium silicate
35. Barium peroxide
36. Chloric acid
37. Mercuric chloride
38. Stannic sulphide
39. Bismuth oxychloride
40. Calcium carbide
41. Potassium ferrocyanide
42. Potassium ferricyanide
43. Ferric ferricyanide
44. Diammine silver chloride
45. Zinc sulphide
46. Magnesium nitride
47. Ferric sulphate
48. Lead acetate
49. Sodium meta-aluminate
50. Chromium sulphate
51. Potassium cobaltinitrite.
52. Strontium nitrate
53. Lead iodide
54. Beryllium chloride
55. Lithium oxide.
56. Magnesium nitride

(B) Short answer type (2 marks each)**(i) Define the following terms**

1. Symbol. 2. Valency 3. formula 4. Radical

(ii) Explain the following terms

1. Variable valency 2. Compound radical
3. Molecular formula 4. Empirical formula
5. Structural formula.

(iii) Write down the formulae and chemical names of the following

- | | |
|-------------------------|-------------------------|
| 1. Dry ice | 25. slaked lime |
| 2. Sand | 26. lime water |
| 3. Oil of vitriol | 27. chalk |
| 4. Baking soda | 28. marble |
| 5. Caustic soda | 29. Gypsum |
| 6. soda lime | 30. Plaster of paris |
| 7. Soda ash | 31. Bleaching powder |
| 8. Washing soda | 32. Sal-ammoniac |
| 9. Common salt | 33. Smelling salt |
| 10. Table salt | 34. Borax |
| 11. Chili salt petre | 35. Alumina |
| 12. Nitre cake. | 36. Potash alum |
| 13. Salt cake | 37. Green vitriol |
| 14. Glauber's salt | 38. Mohr's salt |
| 15. Sodamide | 39. Blue vitriol |
| 16. Water glass | 40. White vitriol |
| 17. Hypo | 41. Lunar caustic |
| 18. Micro cosmic salt | 42. Quick silver |
| 19. Caustic potash | 43. Calomel |
| 20. Nitre | 44. Corrosive sublimate |
| 21. Potash or pearl ash | 45. Litharge |
| 22. Milk of magnesia | 46 Red lead |
| 23. Epsom salt | 47. Sugar of lead |
| 24. lime or quick lime | 48. White lead. |

(iv) Balance the following equations by Hit and trial method

1. $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$
2. $\text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaAlO}_2 + \text{H}_2$
3. $\text{Si} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2$
4. $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$
5. $\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3$
6. $\text{Mg} + \text{HNO}_3 \rightarrow \text{Mg}(\text{NO}_3)_2 + \text{H}_2$
7. $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow \text{FeO} + \text{CO}_2$
8. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$
9. $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
10. $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{NH}_3$
11. $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$
12. $\text{NH}_3 + \text{Cl}_2 \rightarrow \text{NH}_4\text{Cl} + \text{N}_2$
13. $\text{NH}_3 + \text{Cl}_2 \text{ (excess)} \rightarrow \text{NCl}_3 + \text{HCl}$
14. $\text{CaOCl}_2 + \text{NH}_3 \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{N}_2$
15. $\text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbO} + \text{NO}_2 + \text{O}_2$
16. $\text{Hg}_2(\text{NO}_3)_2 \rightarrow \text{Hg} + \text{NO}_2 + \text{O}_2$
17. $\text{Na} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{H}_2$
18. $\text{HNO}_3 + \text{H}_2\text{S} \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{S}$
19. $\text{HNO}_3 + \text{HI} \rightarrow \text{NO} + \text{I}_2 + \text{H}_2\text{O}$
20. $\text{H}_2\text{S} + \text{SO}_2 \rightarrow \text{H}_2\text{O} + \text{S}$
21. $\text{P}_4 + \text{H}_2\text{O} + \text{NaOH} \rightarrow \text{NaH}_2\text{PO}_2 + \text{PH}_3$
22. $\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
23. $\text{CuSO}_4 + \text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + \text{H}_2\text{SO}_4$
24. $\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
25. $\text{NaOH} + \text{F}_2 \rightarrow \text{NaF} + \text{H}_2\text{O} + \text{O}_2$
26. $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{NO}$
27. $\text{Al} + \text{Fe}_3\text{O}_4 \rightarrow \text{Al}_2\text{O}_3 + \text{Fe}$
28. $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl}$

ANSWERS

- | | | | | |
|----|---|--|--|--|
| A. | 1. Na_3PO_4 | 2. AgNO_3 | 3. AlN | 4. AlPO_4 |
| | 5. H_2SO_3 | 6. N_2O_3 | 7. KMnO_4 | 8. Hg_2Cl_2 |
| | 9. NaHCO_3 | 10. H_2CO_3 | 11. MnO_2 | 12. SiF_4 |
| | 13. $\text{Na}_2\text{S}_2\text{O}_3$ | 14. H_3BO_3 | 15. Sb_2S_3 | 16. $\text{Hg}_2(\text{NO}_3)_2$ |
| | 17. N_2O_5 | 18. H_2O_2 | 19. MnSO_4 | 20. Cu_2Cl_2 |
| | 21. $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ | 22. HNO_2 | 23. PbO_2 | 24. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ |
| | 25. $\text{Na}_2\text{B}_4\text{O}_7$ | 26. AuCl_3 | 27. K_2MnO_4 | 28. H_3PO_4 |
| | 29. NOCl | 30. Na_2ZnO_2 | 31. HClO_4 | 32. SnCl_2 |
| | 33. K_2CrO_4 | 34. Na_2SiO_3 | 35. BaO_2 | 36. HClO_3 |
| | 37. HgCl_2 | 38. SnS_2 | 39. BiOCl | 40. CaC_2 |
| | 41. $\text{K}_4[\text{Fe}(\text{CN})_6]$ | 42. $\text{K}_3[\text{Fe}(\text{CN})_6]$ | 43. $\text{Fe}[\text{Fe}(\text{CN})_6]$ | 44. $\text{Ag}(\text{NH}_3)_2\text{Cl}$ |
| | 45. ZnS | 46. Mg_3N_2 | 47. $\text{Fe}_2(\text{SO}_4)_3$ | 48. $\text{Pb}(\text{CH}_3\text{COO})_2$ |
| | 49. NaAlO_2 | 50. $\text{Cr}_2(\text{SO}_4)_3$ | 51. $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ | 52. $\text{Sr}(\text{NO}_3)_2$ |
| | 53. PbI_2 | 54. BeCl_2 | 55. Li_2O | 56. Mg_3N_2 |

- B.(iii)**
1. CO_2 , Carbon dioxide
 2. SiO_2 , Silicon dioxide
 3. H_2SO_4 , Sulphuric acid
 4. NaHCO_3 , Sodium bicarbonate
 5. NaOH , Sodium hydroxide
 6. $\text{NaOH} + \text{Ca}(\text{OH})_2$, Mixture of sodium hydroxide and calcium hydroxide
 7. Na_2CO_3 , Sodium carbonate
 8. Na_2CO_3 , Sodium carbonate
 9. NaCl , Sodium chloride
 10. NaCl , Sodium chloride
 11. NaNO_3 , Sodium nitrate
 12. NaHSO_4 , Sodium bisulphate
 13. Na_2SO_4 , Sodium sulphate
 14. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Sodium sulphate decahydrate.
 15. NaNH_2 , Sodamide.
 16. Na_2SiO_3 , Sodium silicate
 17. $\text{Na}_2\text{S}_2\text{O}_3$, Sodium thiosulphate
 18. $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, Sodium ammonium hydrogen phosphate tetrahydrate.
 19. KOH , Potassium hydroxide
 20. KNO_3 , Potassium nitrate

21. K_2CO_3 , Potassium carbonate
 22. $Mg(OH)_2$, Magnesium hydroxide.
 23. $MgSO_4 \cdot 7H_2O$, Magnesium sulphate heptahydrate
 24. CaO , Quick lime
 25. $Ca(OH)_2$, Calcium hydroxide suspension
 26. $Ca(OH)_2$, Dissolved calcium hydroxide
 27. $CaCO_3$, Calcium carbonate
 28. $CaCO_3$, Calcium carbonate
 29. $CaSO_4 \cdot 2H_2O$, Calcium sulphate dihydrate
 30. $2CaSO_4 \cdot H_2O$ or $CaSO_4 \cdot \frac{1}{2}H_2O$, Calcium sulphate half hydrate.
 31. $CaOCl_2$, Calcium chlorohypochlorite.
 32. NH_4Cl , Ammonium chloride
 33. $(NH_4)_2CO_3$, Ammonium carbonate
 34. $Na_2B_4O_7 \cdot 10H_2O$, Sodium tetraborate decahydrate
 35. Al_2O_3 , Aluminium oxide
 36. $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, Hydrated potassium aluminium sulphate .
 37. $FeSO_4 \cdot 7H_2O$, Ferrous sulphate heptahydrate
 38. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, Ferrous ammonium sulphate hexahydrate
 39. $CuSO_4 \cdot 5H_2O$, Copper sulphate pentahydrate
 40. $ZnSO_4 \cdot 7H_2O$, Zinc sulphate heptahydrate
 41. $AgNO_3$, Silver nitrate
 42. Hg , Metallic mercury
 43. Hg_2Cl_2 , Mercurous chloride
 44. $HgCl_2$, Mercuric chloride
 45. PbO , Lead oxide (yellow)
 46. Pb_3O_4 , Lead oxide(Red)
 47. $Pb(CH_3COO)_2$, Lead acetate
 48. $2PbCO_3 \cdot Pb(OH)_2$, Basic lead carbonate.
- B.(iv)**
1. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
 2. $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$
 3. $Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + H_2$
 4. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$
 5. $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

6. $\text{Mg} + 2\text{HNO}_3 \rightarrow \text{Mg}(\text{NO}_3)_2 + \text{H}_2$
7. $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$
8. $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
9. $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$
10. $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$
11. $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$
12. $8\text{NH}_3 + 3\text{Cl}_2 \rightarrow 6\text{NH}_4\text{Cl} + \text{N}_2$
13. $\text{NH}_3 + 3\text{Cl}_2(\text{excess}) \rightarrow \text{NCl}_3 + 3\text{HCl}$
14. $3\text{CaOCl}_2 + 2\text{NH}_3 \rightarrow 3\text{CaCl}_2 + 3\text{H}_2\text{O} + \text{N}_2$
15. $2\text{Pb}(\text{NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$
16. $\text{Hg}_2(\text{NO}_3)_2 \rightarrow 2\text{Hg} + 2\text{NO}_2 + \text{O}_2$
17. $2\text{Na} + 2\text{NH}_3 \rightarrow 2\text{NaNH}_2 + \text{H}_2$
18. $2\text{HNO}_3 + \text{H}_2\text{S} \rightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} + \text{S}$
19. $2\text{HNO}_3 + 6\text{HI} \rightarrow 2\text{NO} + 3\text{I}_2 + 4\text{H}_2\text{O}$
20. $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3\text{S}$
21. $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$
22. $2\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
23. $3\text{CuSO}_4 + 2\text{PH}_3 \rightarrow \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$
24. $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
25. $4\text{NaOH} + 2\text{F}_2 \rightarrow 4\text{NaF} + 2\text{H}_2\text{O} + \text{O}_2$
26. $3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$
27. $8\text{Al} + 3\text{Fe}_3\text{O}_4 \rightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$

□□□

CHAPTER - 2

BASIC CONCEPTS ATOMS & MOLECULES

2.1 LAWS OF CHEMICAL COMBINATIONS

The laws of chemical combinations helped in the development of the atomic theory and later the molecular theory. These laws govern chemical reactions.

Law of conservation of mass

Matter is neither created nor destroyed during any transformation of matter. In any chemical reaction the total mass of the reactants is equal to the total mass of the products.

This law has been verified by repeated experiments on chemical changes using delicate balances to measure the weights of reactants and products. In 1774, scientist Lavoisier formulated the law. This law is also applicable in case of a physical change.

Landolt's experiment

Landolt conducted many experiments to verify the law of conservation of mass. One of the experiments is discussed below.

In a specially designed H-shaped glass tube (Fig 2.1) aqueous solution of silver nitrate and sodium chloride were taken as shown. The open ends of the tube were sealed and the tube was weighed.

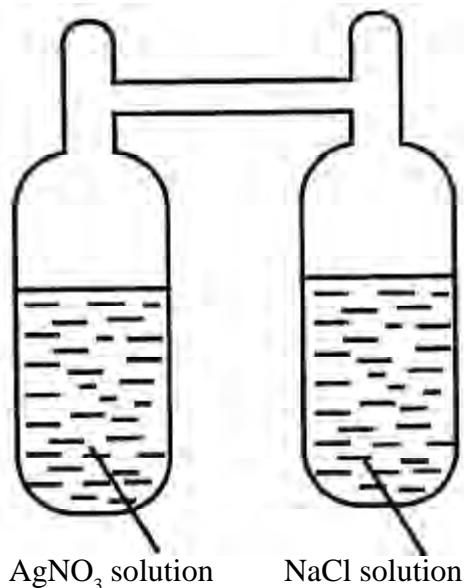
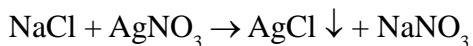


Fig. 2.1 Landolt's experiment

Then the two solutions were thoroughly shaken and mixed. During mixing, the reactants combine to form white AgCl precipitate and NaNO₃ solution.



Now the tube was weighed again and it was observed that the weight remained un-changed. Thus, the mass was found to be the same as before and the law was verified.

Example : 0.22 g of a hydrocarbon containing carbon and hydrogen only, on complete combustion with oxygen resulted 0.9 gm of water and 0.44 gm of carbon dioxide. Show that these results are in accordance with the law of conservation of mass (C = 12, H = 1, O = 16)

The molecular mass of carbon dioxide CO₂ and water H₂O calculated from their respective formula.

$$\text{Molecular mass of CO}_2 = 12 + 32 = 44$$

$$\text{Molecular mass of H}_2\text{O} = 2 + 16 = 18$$

$$\text{Now mass of carbon in } 0.44 \text{ g of CO}_2 = \frac{12 \times 0.44}{44} = 0.12 \text{ g. and}$$

$$\text{mass of hydrogen in } 0.9 \text{ g. of H}_2\text{O} = \frac{2 \times 0.9}{18} = 0.1 \text{ Og.}$$

Hence, the total mass of C and H after combustion

$$= 0.12 + 0.10 = 0.22 \text{ g}$$

This total mass 0.22 g of C and H becomes equal to the same mass 0.22g of hydrocarbon used in the combustion. Thus, the results are in accordance with the law of conservation of mass.

Law of definite or constant proportions

According to Proust, the law states that :

A given compound always contains the same elements combined in the same proportions by mass.

When a pure sample of water collected from any source is analysed, it is found that one part by mass of water contains $\frac{1}{9}$ part i.e. 11.1 % hydrogen and $\frac{8}{9}$ part i.e. 88.9 % oxygen. The ratio of mass of the two elements hydrogen and oxygen is always 1:8.

Example : 2.75 g of cupric oxide was reduced by hydrogen and the weight of copper so obtained was 2.20 g. In another experiment 2.36 g of copper was dissolved in nitric acid and the resulting copper nitrate was converted to cupric oxide which weighed 2.95 g by ignition. Show that these results illustrate the law of definite proportion.

2.20 g of copper was obtained from 2.75 g of cupric oxide. Therefore, the weight of oxygen that combined with copper was (2.75 – 2.20 =) 0.55 g.

Hence, 2.20 g of copper combined with 0.55 g of oxygen.

$$\text{So 1 g of copper combines with } \frac{0.55}{2.20} = 0.25 \text{ g of oxygen.}$$

Again the other data reveal that,

2.36 g of copper combines with $(2.95 - 2.36) = 0.59$ g of oxygen

So 1 g of copper combines with $\frac{0.59}{2.36} = 0.25$ g of oxygen.

Thus from whatever sources cupric oxide may be obtained, 1g of copper always combines with 0.25 g of oxygen to form cupric oxide.

Therefore, in the formation of cupric oxide, the ratio of masses of copper to oxygen is always 4:1.

Law of multiple proportions

The law was formulated by John Dalton.

Whenever two elements combine to form more than one compound the masses of the elements that combine with a constant mass of the other element are in a ratio of simple whole numbers.

Hydrogen combines with oxygen to form water and hydrogen peroxide separately.

On analysis it is evident that :

In water, 1 part by mass of hydrogen combines with 8 parts by mass of oxygen. In hydrogen peroxide 1 part by mass of hydrogen combines with 16 parts by mass of oxygen.

So in H_2O and H_2O_2 , one part by mass of hydrogen combines with 8 and 16 parts by-mass of oxygen respectively. It means that the masses of oxygen that combine with constant mass of hydrogen (in both the compounds) are in a ratio 8 : 16 or 1 : 2.

Example 1

1.5 g of each of two oxides of a metal on reduction resulted 1.331 g and 1.196 g of metal. Show that the data illustrate the law of multiple proportions.

Weight of oxygen in two oxides are

$$1.5 \text{ g} - 1.331 \text{ g} = 0.169 \text{ g}$$

$$1.5 \text{ g} - 1.196 \text{ g} = 0.304 \text{ g}$$

In the first oxide, 1.331 g of metal combines with 0.169 g of oxygen.

So 1g of metal combines with $\frac{0.169}{1.331} = 0.127$ g of oxygen.

In the second oxide, 1.196 g of metal combines with 0.304 g of oxygen

So 1g of the metal combines with $\frac{0.304}{1.196} = 0.253$ g of oxygen

The mass of oxygen that combines with a fixed or constant mass of the metal (here 1g) are in the ratio of 0.127 : 0.253 and that is 1 : 2. Thus the results are in conformity with the law of multiple proportion.

Example 2

Two chlorides of a metal contains 34% and 51% chlorine respectively. Show that the results are in accordance with law of multiple proportions.

The first chloride contains 34% Cl

Hence, the metal present in it = $100 - 34 = 66\%$

Therefore, 66 g of metal combine with 34 g of chlorine.

So, 1 g of metal combines with $\frac{34}{66} = 0.515$ g of chlorine.

The second chloride contains 51% Cl

Hence, the metal present in it = $100 - 51 = 49\%$.

Therefore, 49 g of metal combine with 51 g of chlorine

So, 1 g of metal combines with $\frac{51}{49} = 1.041$ g of chlorine. Now the varying masses of chlorine which combine with fixed mass of the metal are in a ratio of $0.515 : 1.041 = 1 : 2$

Law of equivalent or reciprocal proportions

The masses of two or more different elements which separately combine with a definite mass of another element are either the same as or simple multiple of the masses of different elements when they combine amongst themselves.

Let two different elements-A and B separately combine with another element C. According to this law, the ratio in which the masses of A and B combine with definite mass of C will be the same or be a simple multiple of the ratio in which A and B combine with each other.

For example, sulphur and oxygen separately combine with hydrogen to form hydrogen sulphide and water respectively.

In hydrogen sulphide : 2 grams of hydrogen combine with 32 grams of sulphur.

In water : 2 grams of hydrogen combine with 16 grams of oxygen. Thus, the masses of sulphur and oxygen which combine separately with a definite mass of hydrogen that is 2 grams of hydrogen bear a simple ratio of 32 : 16 or 2 : 1.

When sulphur and oxygen combine together to form the compound sulphur dioxide, according to the law of reciprocal proportions, the ratio of their masses should be the same i.e. 2 : 1 or a simple multiple of this ratio. In sulphur dioxide we see that 32 grams of sulphur combine with 32 grams of oxygen and the ratio of the masses of sulphur and oxygen is 1 : 1.

Thus the two ratios that is 2 : 1 and 1 : 1 are simple multiple of each other being 2:1.

Example 1

Water and sulphur dioxide contain 88.9% and 50% oxygen respectively. Hydrogen sulphide contains 94.1% sulphur. Show that these figures are in agreement with the law of reciprocal proportions.

In H_2O , 88.9 % oxygen is present.

Hence, $100 - 88.9 = 11.1$ % hydrogen is present.

So, the mass ratio of H : O = $11.1 : 88.9 = 1 : 8$

In H_2S , 94.1 % sulphur is present.

Hence, $100 - 94.1 = 5.9$ % hydrogen is present.

So, the mass ratio of H : S = $5.9 : 94.1 = 1 : 16$

Now the mass ratio of sulphur and oxygen in H_2S and H_2O when combining with fixed mass of hydrogen becomes $16 : 8$ i.e. $2 : 1$.

Now, SO_2 contains 50% oxygen.

Hence, $100 - 50 = 50$ % sulphur is present. So the mass ratio of S : O = $50 : 50 = 1 : 1$ Thus, the above two ratios that is $2 : 1$ and $1 : 1$ are simple multiple of each other being $2 : 1$

Hence, the data are in agreement with law of reciprocal proportions.

Example 2

Carbon dioxide contains 27.3% of carbon. Carbon disulphide contains 15.8% of carbon and sulphur dioxide contain 50% of sulphur. Show that these results illustrate the law of reciprocal proportions.

In CO_2 , 27.3% carbon is present.

Hence, $100 - 27.3 = 72.7$ % oxygen is present.

So, the mass ratio of C : O = $27.3 : 72.7 = 1 : 2.66$

In CS_2 , 15.8% carbon is present.

Hence, $100 - 15.8 = 84.2$ % sulphur is present.

So, the mass ratio of C : S = $15.8 : 84.2 = 1 : 5.33$.

Now, the mass ratio of sulphur and oxygen in CS_2 and CO_2 , when combining with fixed mass of carbon becomes $5.33 : 2.66 = 2 : 1$

Now, SO_2 , contains 50% sulphur

Hence, $100 - 50 = 50$ % oxygen is present.

So the mass ratio of S : O = $50 : 50 = 1 : 1$

Thus, the above ratios that is $2 : 1$ and $1 : 1$ are simple multiple of each other being $2 : 1 :: 1 : 1 = 2 : 1$

Hence, the results illustrate the law of reciprocal proportions.

Law of gaseous volumes

Gases react with one another in simple ratio by volume and if the product of the reaction is gaseous then the volume of the product also bears a simple ratio to the volumes of the combining gases under similar conditions of temperature and pressure. Gay-Lussac, a French scientist stated the law of gaseous volume.

Gay-Lussac's law of combining volumes

When gases combine they do so in simple ratio by volume to each other and to the gaseous products, all the volumes being measured at the same temperature and pressure.

In the synthesis of ammonia 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. Thus, the" volume ratio is nitrogen : hydrogen : ammonia :: 1 : 3 : 2.

2.2 DALTON'S ATOMIC THEORY

According to Greek philosophers matter can be divided again and again till the smallest possible piece of matter, i. e. atom, is reached, The word 'atom' in Greek means (a - tomos) for not cut. In the begining of 19th century, the English chemist John Dalton put forth the atomic theory of matter (1808). This theory was based on the first four laws of chemical combinations as already described. Dalton's theory, deals with the microscopic nature of matter.

Postulates

- (1) Matter is composed of tiny particles called atoms. **Atoms are indestructible i.e. they can neither be created nor destroyed by any chemical reaction.** Atoms cannot be further divided during a chemical reaction. Chemical reactions can only involve rearrangement of atoms leaving the total mass unchanged.

(Dalton named the smallest part of an element as **simple atom** and that of a compound as **compound atom**. However, atom is the smallest particle of an element and molecule, that of a compound. Thus, an element consists of only one kind of atoms.)

- (2) **Element is composed of one kind of atoms.** Atoms of the same element are all alike in shape, size etc. and differ from atoms of another element.
- (3) **Atom of an element possesses a definite mass.** Atoms of different elements are different in mass and exhibit different properties.

(The atomic mass of carbon and oxygen have atomic masses 12 and 16 respectively. Further, these two elements are entirely different in their properties.)

- (4) When two or more different elements chemically combine, they do so by combination of atoms to form molecule.

(The word molecule has been used by replacing "**compound atom**" as suggested by Dalton) **The combination of atoms of different elements to form molecules occurs in simple ratios.**

- (5) The combining ratio of the masses of the elements represents the combining ratio of the masses of the atoms.

Atoms can not be considered indestructible.

In subsequent chapters while studying Atomic structure and Nuclear reactions, it will be shown that atom is further composed of still more microscopic particles. Again it will be shown

in the study of isotopes that it is possible to distinguish atoms of the same element. Isotopes **are** atoms of the same element having different masses.

2.3 DALTON'S ATOMIC THEORY AND THE LAWS OF CHEMICAL COMBINATIONS

Law of conservation of mass

Since atoms are indestructible that is they cannot be created or destroyed in a chemical reaction, all the atoms present in the reactants must be present at the end of the chemical reaction. **Thus chemical reactions are only due to rearrangement of atoms.** Again atom of an element having fixed mass, the total mass of the reactants must be equal to the total mass of the products.

Law of definite proportions

According to the atomic theory atoms of different elements combine to form molecules. Molecules are the smallest particles of compounds. Let atoms of element A combine with atoms of element B to form molecules of the compound AB.

This is possible if equal number of atoms of element A and B combine. This shows that the compound AB always has a definite composition of element A and B i.e. the ratio in this case is 1:1. Again in compounds of elements A and B the molecules may be of the type A_2B , AB_2 , AB_3 , etc. Since the combination of indivisible atoms must occur in whole numbers the ratio of elements of A and B in the above compounds are 2 : 1, 1 : 2, 1 : 3 etc.

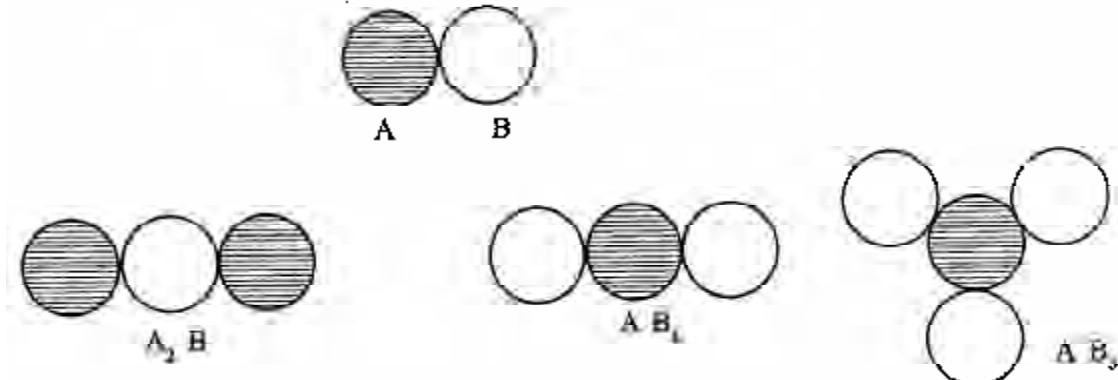


Fig 2.2 Combination of atoms to form molecules

Since atom of an element has a fixed mass the constant composition of elements in a compound leads to a definite ratio of masses of the elements in a compound.

Law of multiple proportions

When the elements A and B combine to form a compound AB, the combining ratio of the atoms A and B is 1 : 1. In the compound AB_2 , similarly, the combining atomic ratio is 1 : 2. In a molecule of the compound AB_2 there are present 1 atom of A and 2 atoms of B. Since atom of an element has fixed mass, the mass B that combines with a certain mass of A in the compounds AB and AB_2 should be in the ratio 1:2.

SOLVED PROBLEMS

Problem 1

Different samples of sodium chloride obtained from sea, lake and rock gave the following results.

- a. Sample A : 5.85g of NaCl gave 3.54g of chlorine
- b. Sample B : 2.92g of NaCl gave 1.77g of chlorine
- c. Sample C : 1.95g of NaCl gave 1.18g of chlorine

Show that the results agree with law of definite proportions

Solution **Sample A** : 5.85g of NaCl contain 3.54g of Cl

$$\text{So, \% of chlorine} = \frac{3.54}{5.85} \times 100 = 60.51$$

$$\text{Hence, \% of Na} = 100 - 60.51 = 39.49$$

Sample B : 2.92g of NaCl contain 1.77g of Cl

$$\text{So, \% of chlorine} = \frac{1.77}{2.92} \times 100 = 60.61$$

$$\text{Hence, \% of Na} = 100 - 60.61 = 39.39$$

Sample C : 1.95g of NaCl contain 1.18g of Cl

$$\text{So, \% of Cl} = \frac{1.18}{1.95} \times 100 = 60.51 \text{ Hence, \% of Na} = 100 - 60.51 = 39.49$$

From the above results it is found that the percentage of Na and Cl are nearly constant in all the three samples. Therefore, the results agree with the law of definite proportion.

Problem 2

Three oxides of manganese contain respectively 30.4%, 36.8% and 40% of oxygen. Show that these results illustrate the law of multiple proportions.

Solution

In the first compound, 30.4g of oxygen combine with

$$100 - 30.4 = 69.6\text{g of manganese}$$

$$\text{So, 1g of oxygen combines with } \frac{69.6}{30.4} = 2.29\text{g of manganese.}$$

In the second compound, 36.8 g of oxygen combines with

$$100 - 36.8 = 63.2\text{g of manganese}$$

$$\text{So, 1g of oxygen combines with } \frac{63.2}{36.8} = 1.72\text{g of manganese}$$

In the third compound, 46.6g of oxygen combines with

$$100 - 46.6 = 53.4 \text{ g of manganese.}$$

$$\text{So, } 1\text{ g of oxygen combines with } \frac{53.4}{46.6} = 1.15\text{ g of manganese}$$

Thus, in the three compounds 1g of oxygen that combines with 2.29g, 1.72g and 1.15g of manganese is 2 : 1.5 : 1 and that is 4 : 3 : 2. This is a ratio of simple whole numbers. Thus, the results are in conformity with the law of multiple proportion.

Problem 3

Water contains 11.11% hydrogen, ammonia contains 82.35% nitrogen and nitrogen trioxide contains 63.15% oxygen. Show that these results can be explained with the help of the law of reciprocal proportions.

Solution

In H_2O , 11.11% hydrogen is present

Hence, $100 - 11.11 = 88.89\%$ oxygen is present

Thus the mass ratio of H : O = 11.11 : 88.89 = 1:8

In NH_3 , 82.35% of nitrogen is present

Hence, $100 - 82.35 = 17.65\%$ hydrogen present.

Thus the mass ratio of H : N = 17.65 : 82.35 = 1 : 4.67

In the two compounds H_2O and NH_3 the weight of nitrogen and oxygen that combine with same wt. that is 1 part by wt. of hydrogen, are in the ratio of

$$4.67 : 8 = 1 : 1.71$$

In nitrogen trioxide, 63.15% oxygen is present

Hence, $100 - 63.15 = 36.85\%$ nitrogen is present.

Thus, the mass ratio of N : O = 36.85 : 63.15 = 1 : 1.71

In both of the above cases the mass ratio of N : O becomes the same i.e

1 : 1.71 which illustrates the validity of the law of reciprocal proportions.

CHAPTER (2.1 - 2.3) AT A GLANCE**Law of conservations of mass**

Matter is neither created nor destroyed during any transformation of matter. In any chemical reaction the total mass of the reactants is equal to the total mass of the products.

Law of definite proportions or constant proportions

A given compound always contains the same elements combined in the same proportion by mass.

Law of multiple proportions

Whenever two elements combine to form more than one compound, the masses of the elements that combine with a constant mass of the other element are in a ratio of simple whole numbers.

Law of equivalent or reciprocal proportions

The masses of two or more different elements which separately combine with a definite mass of another element are either the same as or simple multiple of the masses of different elements when they combine amongst themselves.

Gay-Lussac's law of combining volumes

When gases combine, they do so in simple ratio by volume to each other and to the gaseous products, all the volumes being measured at the same temperature and pressure.

QUESTIONS**A. Very short answer type (1 mark each)****State true or false**

1. Atoms can be divided.
2. Copper oxide is formed from metallic copper with a net increase in mass.
3. Mass and energy are interconvertible.
4. The law of reciprocal proportions is also called law of equivalent proportions.
5. Law of conservation of mass was formulated by Lavoisier.
6. Atoms of one element can be changed into another element.
7. Gay-Lussac's law of combining volumes is applicable to the formation of SO₂ from sulphur.
8. Matter is destructible.
9. Atoms of different elements are different in all respects.
10. Atoms of the same element are similar in all respects.
11. The law of definite proportions is also called the law of constant proportions.
12. The law of reciprocal proportions was enunciated by Richter.
13. John Dalton formulated the law of multiple proportions.
14. Atoms of different elements always combine in simple ratio to form their compounds.

15. Proust formulated the law of definite proportions.
16. According to the law of definite proportions, a chemical compound obtained from different sources has different composition.

B. Short answer type (2 marks each)

1. State the law of multiple proportions. [CHSE 1991, 1994, 2001 IR]
2. State the law of reciprocal proportions [CHSE 1997]
3. Define law of conservation of mass
4. State the Gay-Lussac's law of combining volumes.
5. State the law of definite proportions.

C. Long answer type (10 marks each) (Statement with explanation 7 marks, Problem 3 marks)

1. State the postulates of Dalton's atomic theory. How this theory explains the laws of chemical combinations ?
2. State the law of reciprocal proportions.
Water and sulphur dioxide contain 88.9% and 50% oxygen respectively. Hydrogen sulphide contains 94.1% sulphur. Show that these figures are in agreement with the law-of reciprocal proportions.
3. State and explain the law of multiple proportions.
1.5 grams of each of the two oxides of an element on reduction produced 1.331 grams and 1.196 grams of the elements respectively. Show that the results are in agreement with the law of multiple proportions.
4. State and explain the law of conservation of mass.
6.3 grams of sodium bicarbonate are added to 15.0 grams of acetic acid solution and the residue is found to weigh 18.0 grams. What mass of carbon dioxide is released during the reaction ?
[Hints : $\text{NaHCO}_3 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} + \text{CO}_2$. In the reaction mass of the residue = mass of CH_3COONa + mass of H_2O]
5. State and explain the law of definite proportions.
0.09g of carbon burns in oxygen to give 0.33g of carbon dioxide. Carbon dioxide is also obtained by burning 0.225g of carbon in 0.6g of oxygen. Show that the above data illustrate the law of constant proportions.
6. State Gay-Lussac's law of gaseous volumes and give two examples of the reactions which illustrate the law.

D. NUMERICAL PROBLEMS

1. How much silver nitrate would be required to react with 1. 16gms of sodium chloride to produce 1.70 gms of sodium nitrate and 2.87 gms of silver chloride ? Which law of chemical combinations holds good in this case ? [Hint : mass of AgNO_3 + mass of NaCl = mass of AgCl + mass of NaNO_3]
2. Weight of copper oxide obtained by treating 2.16g of metallic copper with nitric acid and subsequent ignition was 2.7g. In another experiment, 1.15g of copper oxide on reduction produced 0.92g of copper. Show that these results illustrate the law of constant proportions.

3. In an experiment 0.6g of carbon when heated with excess of oxygen produced 1.12 litres of carbon monoxide at NTP. In another experiment 2.24 litres of carbon dioxide upon reduction with 1.2g of carbon produced 4.48 litres of carbon monoxide at NTP. Show that the results illustrate the law of definite proportions.

$$\begin{aligned} \text{[Hint : } 2\text{C} + \text{O}_2 &= 2\text{CO} \\ &= 2 \times 22.4 \text{ litres of CO} = 2 \times 28 = 56 \text{ g.} \end{aligned}$$



The calculation will be based on the concepts of mole and molar volume which is discussed in chapter-6]

4. Carbon and oxygen are known to form two compounds. The carbon content in one of these is 42.9% while in the other is 27.3%. Show that the data are in agreement with the law of multiple proportions.
5. Three oxides of a metal M are found to contain 24.26, 29.95 and 49.95 percent of oxygen. Show that these results are in agreement with law of multiple proportions.
6. Phosphorus chloride contains 22.57% phosphorus, phosphine contains 8.82% hydrogen and hydrogen chloride contains 97.23% chlorine. Show that these figures agree with the law of reciprocal proportions.
7. KI contains 23.6% potassium. KC1 contains 52% potassium. IC1 contains 77.8% iodine. Show that these data are in agreement with law of reciprocal proportions.

ANSWERS

- A. 1. False 2. True. 3. True 4. True 5. True 6. True 7. False 8. False 9. False 10. False 11. True
12. True 13. True 14. False 15. True 16. False.
- C. 2. Reference : Example 1 of law of reciprocal proportions .
3. Reference : Example 1 of the law of multiple proportions.
4. 3.3g.
5. C : O mass ratio 1 : 2.67.
- D. 1. 3.41g , The law of conservation of mass.
2. C = 80% O = 20%
3. In both the experiments C : O ratio = 3:4.
4. The weights oxygen combining with fixed weight of carbon are in a simple whole number ratio of 1 : 2.
5. The ratio of weights of the metal M that combines with one part by weight of oxygen is 3:2:1.
6. The ratio weights of Cl and H which combine with fixed weight of phosphorus is 35.5 : 1 and the ratio weights of Cl and H in HC1 is also 35.5 : 1.
7. The ratio weights of I : Cl which combine with fixed weight of K is 3.52 : 1, where as the ratio weights of I : Cl is 3.50 : 1. Both the values of I : Cl ratio- weights are within the limits of experimental error.

2.4 ATOMIC MASS

It is analysed that water contains 88.9% mass of oxygen and 11.1% mass of hydrogen. Thus the mass of hydrogen and oxygen is about 1 : 8. The molecular formula of water is H_2O . It is evident that there are 2 atoms of hydrogen and one atom of oxygen in a molecule of water. It leads to the fact that 1 atom of oxygen is 16 times as heavy as that of 1 atom of hydrogen. Since hydrogen is the lightest element, if the mass of a hydrogen atom is regarded as 1 then the mass of oxygen atom is found more correctly as 15.88. Considering the mass of hydrogen atom as the reference, the **relative atomic masses** of other elements may be expressed as mentioned below.

The atomic mass or the relative atomic mass of an element is a number which expresses how many times the mass of one atom of the element is heavier than the mass of one atom of hydrogen.

$$\text{Atomic mass of an element} = \frac{\text{Mass of 1 atom of the element}}{\text{Mass of 1 atom of hydrogen}}$$

The atomic mass of nitrogen is 14. This means that one atom of nitrogen is 14 times heavier than one atom of hydrogen.

If, however, an oxygen atom was chosen as the reference and assigned the value 16.000, then the atomic masses of majority of elements become whole numbers or near whole numbers.

Thus, oxygen was taken as the accepted standard.

The atomic mass or relative atomic mass of an element is the ratio of the mass of an atom to $\frac{1}{16}$ th of the mass of oxygen atom. These masses are expressed in atomic mass units (amu). The atomic mass of hydrogen is 1.008 amu in this scale.

It has been stated earlier that isotopes of an element are atoms of the same element having different masses. Natural oxygen is known to consist of three isotopes of masses, 16, 17 and 18. Hence chemical atomic mass scale based upon the mass of natural oxygen as 16 is of less validity from the standpoint of determining isotopic masses accurately. Thus, a physical atomic scale based upon the oxygen –16(^{16}O) was devised.

The physical atomic mass of an element is the ratio of the mass of one atom of the element to $\frac{1}{16}$ of the mass of one atom of ^{16}O .

On this scale the atomic mass of natural oxygen is 16.0043 amu.

The atomic masses of most elements are very accurately determined in a mass spectrometer by using volatile compounds of carbon as reference. Thus the mass of carbon –12 isotope (^{12}C)

was accepted as the standard by IUPAC (International Union of Pure and Applied Chemistry) in 1961. The physical atomic mass scale based on ^{12}C as a reference is expressed as

$$\frac{\text{Mass of 1 atom of the element}}{\frac{1}{12}\text{th of the mass of } ^{12}\text{C}}$$

Carbon has two other isotopes of masses 13 and 14. Thus the present scale is based on ^{12}C equal to 12. This scale is used for both chemical atomic masses and isotopic masses.

The atomic mass or the relative atomic mass of an element is a number which expresses how many times the mass of one atom of the element is heavier than $\frac{1}{12}$ th of the mass of carbon -12 (^{12}C).

$$\text{Atomic mass of an element} = \frac{\text{Mass of 1 atom of the element}}{\frac{1}{12}\text{th of the mass of } ^{12}\text{C}}$$

Relative atomic mass is expressed in the unit (a.m.u), atomic mass unit.

Gram atomic mass

The gram atomic mass or the gram - atom of an element is its relative atomic mass expressed in grams.

For example, the relative atomic mass of helium is 4.003. Hence its gram - atomic mass is 4.003g. 1 g - atom of helium represents 4.003 g of helium.

Table 2.1 Relative atomic masses of elements based upon carbon -12, $^{12}\text{C} = 12.000$ amu.

Element	Relative atomic mass (amu)	Element	Relative atomic mass (amu)
Hydrogen	1.007967	Magnesium	24.312
Helium	4.003	Aluminium	26.98
Lithium	6.939	Silicon	28.086
Beryllium	9.102	Phosphorus	30.974
Boron	10.81	Sulphur	32.064
Carbon	12.01115	Chlorine	35.453
Nitrogen	14.007	Argon	39.948
Oxygen	15.99943	Potassium	39.102
Fluorine	19.00	Calcium	40.08
Neon	20.183	Scandium	44.956
Sodium	22.9898	Titanium	47.90

Element	Relative atomic mass (amu)	Element	Relative atomic mass (amu)
Vanadium	50.942	Gadolinium	157.25
Chromium	52.00	Terbium	158.924
Manganese	54.94	Dysprosium	162.50
Iron	55.85	Holmium	164.93
Cobalt	58.933	Erbium	167.26
Nickel	58.71	Thulium	168.934
Copper	63.54	Ytterbium	173.04
Zinc	65.37	Lutetium	174.97
Gallium	69.72	Hafnium	178.49
Germanium	72.59	Tantalum	180.948
Arsenic	74.92	Tungsten	183.85
Selenium	78.96	Rhenium	186.23
Bromine	79.909	Osmium	190.20
Krypton	83.80	Iridium	192.20
Rubidium	85.47	Platinum	195.09
Strontium	87.62	Gold	196.97
Yttrium	88.905	Mercury	200.59
Zirconium	91.22	Thallium	204.37
Niobium	92.91	Lead	207.19
Molybdenum	95.94	Bismuth	208.98
Technetium	99†	Polonium	210†
Ruthenium	101.07	Astatine	210†
Rhodium	102.905	Radon	222†
Palladium	106.4	Francium	223†
Silver	107.87	Radium	226†
Cadmium	112.40	Actinium	227
Indium	114.82	Thorium	232.038
Tin	118.69	Protactinium	231†
Antimony	121.75	Uranium	238.03
Tellurium	127.60	Neptunium	237†
Iodine	126.90	Plutonium	242†
Xenon	131.30	Americium	243†
Caesium	132.91	Curium	247†
Barium	137.34	Berkelium	249†
Lanthanum	138.91	Californium	251†
Cerium	140.12	Einsteinium	254†
Praseodymium	140.907	Fermium	253†
Neodymium	144.24	Mendelevium	256†
Promethium	147†	Nobelium	254†
Samarium	150.35	Lawrencium	257†
Europium	151.96		

† symbol indicates the mass number of the longest lived or best known isotope.

Absolute mass of an atom

The atom is so small that its exact weight cannot be measured accurately. The absolute mass of an atom is the mass of one atom in gram.

$$\text{Absolute mass of an atom in gram} = \frac{\text{Atomic mass in gram}}{\text{Avogadro number, } (6.023 \times 10^{23})}$$

Table 2.2 Atomic mass and absolute atomic mass of atoms of some elements

Element	Atomic mass (amu)	Absolute mass of an atom (gm)
H	1.008	$\frac{1.008}{6.023 \times 10^{23}} = 1.67 \times 10^{-24}$
C	12	$\frac{12}{6.023 \times 10^{23}} = 1.99 \times 10^{-23}$
N	14	$\frac{14}{6.023 \times 10^{23}} = 2.32 \times 10^{-23}$
O	16	$\frac{16}{6.023 \times 10^{23}} = 2.66 \times 10^{-23}$

Atomic mass, isotopes and isobars

F. W. Aston, an English physicist determined the relative mass of atoms in the mass spectrograph. It is found that some naturally occurring elements contain atoms that are chemically identical but have different masses.

Atoms of the same element having different masses are called **isotopes**.

In case of existing isotopes of an atom, it is significant to find the **average atomic mass of the atom**.

Chlorine has two isotopes of atomic mass 35 and 37 occurring in the ratio 3 : 1. Therefore, the average mass of chlorine is

$$\frac{(3 \times 35) + (1 \times 37)}{3 + 1} = 35.5$$

Atoms of different elements having the same atomic mass are called **isobars**.

Argon has one isotope having atomic mass 40 and one of the isotopes of potassium has atomic mass 40. These two atoms of different elements argon and potassium are called **isobars**.

2.5 DETERMINATION OF RELATIVE ATOMIC MASS BY DULONG AND PETIT'S METHOD

The French Scientists Dulong and Petit studied the relationship between specific heat and atomic mass of elements.

Dulong and Petit's law states that the product of the relative atomic mass of an element and its specific heat is approximately equal to 6.4 for all solid elements at

ordinary temperature (except carbon silicon, boron & beryllium). This product is called the atomic heat.

Mathematically, it can be stated :

$$\text{Relative atomic mass} \times \text{Specific heat} \approx 6.4$$

The specific heat is usually expressed in calorie per degree per gram of the element. If however, the specific heat is expressed in joule, then

$$\text{relative atomic mass} \times \text{specific heat} \approx 26.8.$$

Dulong and Petit's law can be applied to determine the approximate relative atomic mass of an element. In order to find out the correct relative atomic mass of an element, the following steps are adoptd.

- (1) The approximate relative atomic mass of the element is calculated from the known specific heat of the element with the help of Dulong and Petit's law.

$$\text{Approximate relative atomic mass} = \frac{6.4}{\text{Specific heat}}$$

- (2) The equivalent mass of the element is determined from the experiment.
- (3) The approximate relative atomic mass is divided by the equivalent mass to get an approximate valency.

$$\text{Relative atomic mass (approx)} = \text{Equivalent mass} \times \text{Valency (approx)}$$

$$\text{or Valency (approx)} = \frac{\text{Relative atomic mass (approx)}}{\text{Equivalent mass}}$$

- (4) The approximate valency is converted to the nearest whole number.
- (5) The correct relative atomic mass of the element is calculated from the product of equivalent mass and the valency (whole number)

$$\text{Relative atomic mass} = \text{Equivalent mass} \times \text{Valency}$$

NUMERICAL PROBLEMS

Example 1 The equivalent mass of a metal is 32.2. Its specific heat is 0.095. Determine the relative atomic mass of the metal.

Solution The approximate relative atomic mass of the metal

$$= \frac{6.4}{0.095} = 67.4$$

$$\text{The approximate valency of the metal is } \frac{67.4}{32.2} = 2.1$$

When converted to nearest whole number becomes 2.

$$\text{Hence the relative atomic mass of the metal} = \text{Eq.mass} \times \text{Valency} = \\ 32.2 \times 2 = 64.4$$

Example 2 The equivalent mass and specific heat of a metal is 9.0 and 0.214 respectively. Calculate

the atomic mass of the metal.

Solution The approximate atomic mass of the metal. = $\frac{6.4}{0.214} = 29.9$

$$\text{The approximate valency of the metal} = \frac{\text{Atomic mass of the metal}}{\text{Eq.mass of the metal}}$$

$$= \frac{29.9}{9} = 3.32$$

When converted to the nearest whole number becomes 3.

Hence, the atomic mass of the metal = Eq.mass \times Valency = $9.0 \times 3 = 27$

Determination of atomic masses from physical measurement

The atomic masses of elements are determined and the existence of isotopes is proved by experiments performed in a **Mass Spectrograph**.

In 1919 the instrument mass spectrograph was devised by scientists Thomson and Aston who studied the deflection of positive ions by simultaneously applying electric and magnetic fields.

In this method, atoms of gaseous elements are converted into ions in a discharge tube. The positive rays thus formed are passed through two slits S_1, S_2 and then subjected to the influence of electric (E_1, E_2) and magnetic fields M (Fig 2.3)

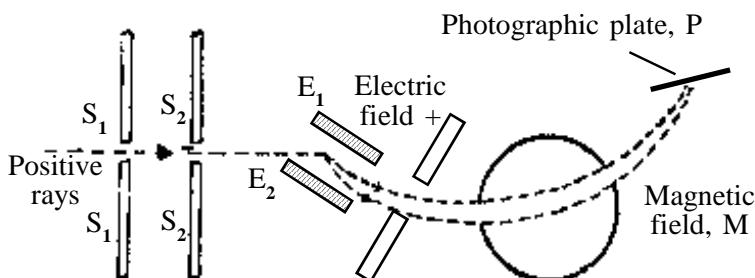


Fig.2.3 Mass spectrograph.

The narrow beam of positive ions with different masses deflect into different extents. Ions of heavier mass suffer less deflection. The impressions of the deflections are recorded on a photographic plate, **P**.

Thomson produced positive ions by taking neon gas in a discharge tube and analysed it in the mass spectrogram. Thomson found a very faint trace due to singly charged neon of atomic mass 22 along with parabolic trace due to singly charged neon of atomic mass 20. He concluded that neon has two isotopes of atomic masses 20 and 22.

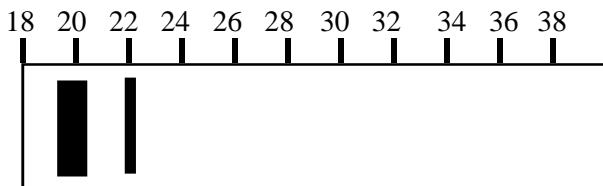


Fig 2.4 Spectrogram

From the position of the lines, the relative masses of the positive ions are calculated (Fig.2.4). Several lines may be recorded for the elements consisting of isotopes.

An element recording lines at mass numbers A_1 and A_2 and thickness of lines remaining in the ratio of n_1 and n_2 , the atomic mass becomes.

$$\frac{n_1 A_1 + n_2 A_2}{n_1 + n_2}$$

CHAPTER (2.4) AT A GLANCE

The atomic mass or the relative atomic mass of an element

The atomic mass or the relative atomic mass of an element is a number which expresses how many times the mass of one atom of the element is higher than $\frac{1}{12}$ th of the mass of carbon –12(^{12}C).

Atomic mass unit (a.m.u.)

The relative atomic mass is expressed with the unit a.m.u., that is atomic mass unit.

The gram atomic mass or the gram-atom

The gram atomic mass or the gram-atom of an element is its relative atomic mass expressed in grams.

Absolute mass of an atom

The absolute mass of an atom is the mass of one atom in grams.

$$\text{Absolute mass of an atom in grams} = \frac{\text{Atomic mass in gram}}{\text{Avogadro number } (6.023 \times 10^{23})}.$$

Isotopes are atoms of the same element having different masses.

Average atomic mass

It can be calculated by taking into account of the number of isotopes of an atom and the isotopic occurrence of its mass ratio.

Relationship among atomic mass, equivalent mass and valency of an element

Atomic mass = Equivalent mass × Valency

Dulong and Petit's law

Dulong and Petit's law states that the relative atomic mass of an element and its specific heat is approximately equal to 6.4 (atomic heat) for all elements at ordinary temperature (except Be, B, C, Si)

Relative atomic mass × Specific heat \approx 6.4 (Atomic heat) (approx)

Mass Spectrograph

The atomic masses of elements can be determined in a mass spectrograph.

Solved Problems

Problem 1

0.875 g of a metal produced 1.095 g of its oxide. The specific heat of the metal is 0.09. Determine the exact atomic mass of the metal.

Solution :

The mass of oxygen that combined with 0.875 g of metal = $1.095 - 0.875 = 0.22$ g

Hence 0.22 g of oxygen combined with 0.875 g of metal

or 8 g of oxygen combines with $\frac{0.875}{0.22} \times 8 = 31.82$, which is the equivalent mass of the metal.

Now the approximate atomic mass of the metal = $\frac{6.4}{0.09} = 71.1$

The approximate valency of the metal = $\frac{71.1}{31.2} = 2.23$

When converted to the nearest whole number becomes 2.

Hence, the atomic mass of the metal = Eq.mass × Valency = $31.82 \times 2 = 63.64$

Problem 2

The specific heat of a metal M is 0.25 and its equivalent mass is 12. What is its correct atomic mass ? Mention the formula of its chloride.

Solution : The approximate atomic mass of the metal = $\frac{6.4}{0.25} = 25.6$

The approximate valency of the metal = $\frac{25.6}{12} = 2.13$ and therefore the nearest whole number valency becomes 2. Hence the correct atomic mass of the metal = $.12 \times 2 = 24$.

Since the valency of the metal is 2, the formula of its chloride becomes MCl_2 .

Problem 3

Specific heat of an element is 0.057. Its equivalent mass is 37.8. What is its exact atomic mass ? (CHSE 1994 A)

Solution : The approximate atomic mass of the metal = $\frac{6.4}{0.057} = 112.28$

$$\text{The approximate valency of the metal} = \frac{\text{Approx. atomic mass of element}}{\text{Eq.mass of the element}} = \frac{112.28}{37.8}$$

= 2.97 and converted to the nearest whole number valency 3.

$$\begin{aligned}\text{Now the exact atomic mass of the element} &= \text{Equivalent mass} \times \text{Valency} \\ &= 37.8 \times 3 = 113.4\end{aligned}$$

Problem 4

The chloride of a metal M contains 23.2% of metal. Its specific heat is 0.224. What is the accurate atomic mass of the metal ? (CHSE 1992)

Solution : In 100g of metal chloride the mass of metal = 23.2 g

So, the mass of chlorine = $100 - 23.2 = 76.8$ g

76.8g of chlorine combines with 23.2 g of the metal

$$\text{Hence, equivalent mass of the metal} = \frac{23.2 \times 35.45}{76.8} = 10.71$$

Specific heat of the metal = 0.224

$$\text{The approximate atomic mass of the metal} = \frac{6.4}{0.224} = 28.57$$

$$\text{The approximate valency} = \frac{28.57}{10.71} = 2.67$$

and making the valency a whole number it becomes 3.

$$\begin{aligned}\text{Now the accurate atomic mass of the metal} &= \text{Eq.mass} \times \text{Valency} = 10.71 \times 3 \\ &= 32.13\end{aligned}$$

QUESTIONS

A. Very short answer type (1 mark each)

1. Atomic mass of which element is taken as standard when defining the relative atomic mass of other elements.
2. Define isotopes.
3. What value has the relative atomic mass of oxygen ?
4. What is the mass of 1 atom of carbon ?
5. The equivalent mass of a trivalent metal is 9. What will its relative atomic mass ?
6. What is the value of atomic heat ?
7. What is the unit of specific heat ?
8. Does the specific heat change with temperature ?
9. Mention the relationship among atomic mass, molecular mass and atomicity.

10. How many atoms are present in 1 gram atom of the element ?
11. State Dulong and Petit's law (CHSE 2001 ER)

B. Short answer type (2 marks each)

1. An oxide of a bivalent metal contains 40% oxygen. Calculate its atomic mass.
2. What is the difference between relative atomic mass and gram atomic mass ?
3. What is the mass of 3 atoms of nitrogen ?
4. What is the relationship among equivalent mass, atomic mass and valency ?
5. Explain atomic mass unit.
6. The specific heat of an element is 0.214 cal/gm. What is its approximate atomic weight ?
7. Explain average atomic mass.
8. Differentiate between atomic mass and absolute mass of an atom.
9. "Equivalent mass of an element may vary" – Explain with example.
10. State Dulong and Petit's law. How can it be used to calculate the exact atomic mass of a solid element.

C. Long answer type (7 marks each)

1. State and explain Dulong and Petit's law. Define atomic mass.
Specific heat of an element is 0.057. Its equivalent mass is 37.8. What is its exact atomic mass ?
2. State Dulong Petit's law. Describe how the atomic mass of an element is determined by the use of the law. A certain metal oxide contains 60% of oxygen. The specific heat of the metal is 0.401. Calculate the exact atomic mass, equivalent mass and valency of the metal.
3. State and explain Dulong and Petit's law. The chloride of a metal 'M' contains 23.2% of metal. Its specific heat is 0.224. What is the accurate atomic mass of the metal ?

D. Numerical Problems

1. A certain metal forms an oxide containing 60% of oxygen. The specific heat of the metal is 0.401. Calculate the valency of the metal.
2. 0.1g of a metal M, when dissolved in dil HCl evolved 124.2 ml of hydrogen at NTP. The specific heat of the metal is 0.214. Calculate the atomic mass of the metal. What are the formulae of the oxide and chloride of the metal ?
3. An element forms an oxide containing 47% oxygen. The specific heat of the element is 0.22. Calculate the relative atomic mass of the element.

4. 0.108g of a metal when treated with excess of dilute H_2SO_4 liberated 40.2 ml of hydrogen gas at $17^\circ C$ and 770 mm pressure. Aqueous tension at $17^\circ C$ is 14.4 mm pressure. The specific heat of the metal is 0.095. Determine the relative atomic mass of the metal.
5. The chloride of a metal contains 79.8% of chlorine. The specific heat of the metal is 0.224. Calculate the correct relative atomic mass of the metal.

ANSWER

- A. 1. Carbon, ^{12}C . 3.16 amu 4. $1.99 \times 10^{-23}g$ 5. 27 6. 6.4 approx.
 7. cal/gm/ $^\circ C$. 8. Yes. 9. Molecular mass = At.mass \times Atomicity
 10. 6.023×10^{23} atoms.
- B. 3. $6.96 \times 10^{-23}g$ 4. Atomic mass = Equivalent mass \times Valency 6. 29.9
- C. 1. 113.4 (Ref : solved problem no 3. in this Chapter)
- D. 1. 3 2. At.mass = 27, M_2O_3 and MCl_3 3. 27.06 4. 64.4 5. 26.94

2.6 [MOLECULAR MASS :]

The molecular mass or the relative molecular mass of an element or a compound is expressed as the mass of one molecule of the element or compound as compared to $\frac{1}{12}$ th of the mass of one atom of carbon -12 ($^{12}C = 12.000$) in the physical atomic mass unit scale.

The relative molecular mass of an element or compound

$$= \frac{\text{Mass of 1 molecule of the element or compound}}{\frac{1}{12} \text{th of the mass of } ^{12}C}$$

The gram-molecular mass or the gram-mole or the molar mass of a substance is its relative molecular mass expressed in grams.

For example, the relative molecular mass of oxygen is 32.

So, 1 gram-molecule of oxygen represents 32 g.

The relative molecular mass of a compound is the sum of the relative atomic masses of all constituent elements.

Based on the carbon–12 standard in the physical atomic mass scale, the mass of oxygen atom is $15.99943 \approx 16$.

The relative molecular mass of oxygen (O_2) is $2 \times 16 = 32$ amu.

Thus, one gram-molecule of oxygen represents 32 g.

The relative molecular masses of some compounds have already been calculated in Chapter – 1 of this book.

Table 2.3 Relative molecular masses and gram molecular masses of some elements and compounds.

Molecule/compound	Formula	Relative molecular mass	Gram molecular mass	No.of molecules.
Hydrogen	H_2	2 a.m.u	2 g	6.023×10^{23}
Nitrogen	N_2	28 a.m.u	28 g	6.023×10^{23}
Chlorine	Cl_2	71 a.m.u	71 g	6.023×10^{23}
Water	H_2O	18 a.m.u	18 g	6.023×10^{23}
Carbon dioxide	CO_2	44 a.m.u	44 g	6.023×10^{23}
Hydrogen peroxide	H_2O_2	34 a.m.u	34 g	6.023×10^{23}
Sodium hydroxide	$NaOH$	40 a.m.u	40 g	6.023×10^{23}

Determination of Relative molecular mass

Various methods are used to determine the relative molecular masses.

DETERMINATION OF RELATIVE MOLECULAR MASS OF VOLATILE LIQUIDS BY VICTOR MEYER'S METHOD.

A known weight of a volatile liquid is vapourised which displaces an equal volume of air. From this volume of collected air and weight of liquid, the vapour density and then the relative molecular mass of the liquid is calculated.

Victor Meyer's apparatus consists of a long cylindrical glass vessel having a bulb at the bottom , a side tube and a funnel fitted with a cork at the top.

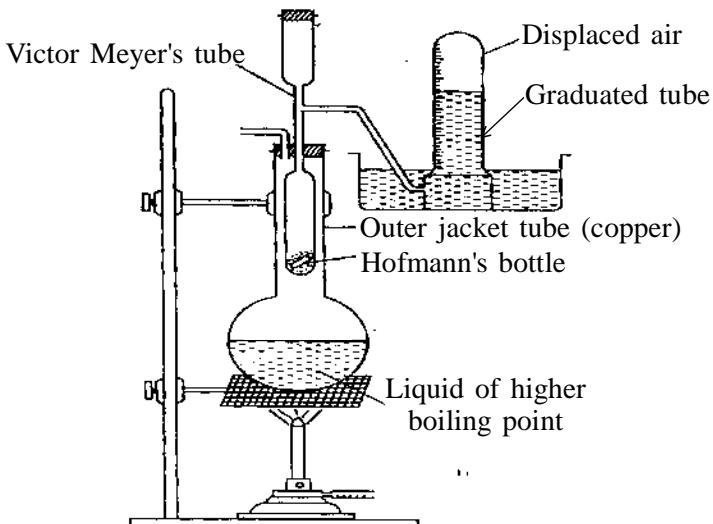


Fig: 2.5 Victor Meyer's apparatus

In the bulb at the bottom small amount of asbestos is placed so that the bottom of the cylindrical glass vessel does not crack when the **Hofmann's bottle** is dropped. This cylindrical glass vessel is kept inside an **outer jacket-tube** made of copper ending in a bulb at the lower end. The glass vessel is kept in position by a cork fitted to the outer jacket tube. A bent tube is also fitted to the cork for the exit of the vapours of boiling liquid in the outer jacket. A liquid whose boiling point is about $25\text{--}30^{\circ}\text{C}$ higher than the boiling point of the volatile liquid (whose relative molecular mass is to be determined) is taken in the outer jacket-tube. For the determination of relative molecular mass of low boiling liquid, usually water is taken in the outer jacket-tube. The top of the funnel of the cylindrical glass vessel is closed with a cork.

To start with the experiment the liquid in the outer jacket-tube is heated to boiling. Now the side tube of the cylindrical glass vessel is dipped under water in a trough. When no more bubbles appear, the apparatus has attained a steady temperature. Then a graduated tube filled with water is inverted over the end of the side tube. In the mean while a known weight of the volatile liquid (about 0.1 to 0.2 g) is taken in a small bottle fitted with a loose stopper known as **Hofmann's bottle**. This bottle is quickly dropped into the cylindrical glass vessel and the mouth of the funnel of the glass vessel is closed with the cork. Since the Hofmann's bottle is loosely stoppered, the stopper opens and the volatile liquid vapourises quickly. The vapour so produced displaces the same volume of air that is collected in the graduated tubes at the room temperature and pressure. When the water level in the graduated tube remains constant for quite sometime, the graduated tube is removed with the thumb at its open end with care so that the water level is constant. Then the graduated tube is carefully lowered in a water jar and the volume of air is noted by making the level of water inside and outside the tube the same. The room temperature and the atmospheric pressure is also noted.

Now since the volume of the vapour from a known weight of a volatile liquid at a particular temperature and pressure is known, the vapour density and the molecular mass of the volatile liquid can be calculated as follows :

Calculation

Let mass of the volatile liquid = m g

Volume of air collected = V_1 cc = The volume the vapour of the volatile liquid.

Atmospheric pressure = P_1 mm of mercury

Room temperature = t_1° , C = $(t_1 + 273)^{\circ}$ A = T_1

Aqueous tension at t_1° C = f mm

So, pressure of dry air = $(P_1 - f)$ mm

In order to calculate the vapour density of the vapour from the volatile liquid, the volume of vapour of the volatile liquid V_1 be converted to V i.e. the volume of vapour at NTP.

$$P = 760 \text{ mm} \quad T = 273^{\circ}\text{A}$$

V = The volume of vapour of the volatile liquid at NTP = ?

From the combined gas equation $\frac{PV}{T} = \frac{P_1V_1}{T_1}$

$$V = \frac{P_1V_1}{T_1} \times \frac{T}{P} = \frac{(P_1 - f) \times V_1 \times 273}{(t_1 + 273) \times 760} = \text{Volume of vapour of the volatile liquid.}$$

Method- 1

Direct calculation of relative molecular mass from the idea of molar volume.

Now, weight of Vcc of vapour at NTP = m g

$$\text{So, weight of } 22,400 \text{ cc of the vapour at NTP} = \frac{M}{V} \times 22,400 \text{ g}$$

= The relative molecular mass of the volatile liquid.

Method- 2

The relative molecular mass = 2 x V.D.

The vapour density (V.D) of the vapour is given by

$$\text{V.D} = \frac{\text{Weight of Vcc of the vapour at NTP}}{\text{Weight of the same Vcc of the hydrogen gas at NTP}}$$

$$= \frac{m}{V \times 0.000089} \quad (\text{Since weight of } 1\text{cc of hydrogen gas at NTP is } 0.000089 \text{ g})$$

Now the relative molecular mass M = $2.016 \times \text{V.D.}$

$$= 2 \times \text{V.D.} \quad (\text{Since } 2.016 \approx 2, \text{ we consider})$$

Method- 3

The relative molecular mass can be calculated from the gas equation $PV = \left(\frac{g}{M}\right) RT$

Since the entire amount of volatile liquid is converted to its vapour, the mass of the vapour is also the mass of the volatile liquid.

$$\text{From the gas equation, } PV = \left(\frac{g}{M}\right) RT$$

where g is the mass of vapour whose relative molecular mass is M .

$$\text{In this case, Pressure} = P_1 \text{ mm} = (P_1 - f) \text{ mm} = \frac{P_1 - f}{760} \text{ atms.}$$

$$\text{Volume} = V_1 \text{ cc} = \frac{V_1}{1000} \text{ litres. } R = 0.082 \text{ litre-atm. degree}^{-1} \text{ mol}^{-1}.$$

$$T_1 = (t_1 + 273)^0 \text{ A}$$

$$\text{Substituting these values in } PV = \left(\frac{g}{M}\right) RT, \text{ Here } P_1 V_1 = \left(\frac{g}{M}\right) RT_1$$

$$\text{or, } M = \frac{g \cdot RT_1}{P_1 V_1} = \frac{m \times 0.082 \times (273 + t_1) \times 760 \times 1000}{(P_1 - f)V_1}$$

= The relative molecular mass of the volatile liquid.

NUMERICAL PROBLEMS

Example 1 : In an experiment 0.61 g. of a volatile liquid displaces 122.9 ml of moist air at 20°C and 757.5 mm Hg pressure. If aqueous tension at 20°C is 17.4 mm, calculate the vapour density and molecular mass of the substance.

Solution Given, mass of volatile liquid $m = 0.61 \text{ g}$

Volume of moist air collected = Say $V_1 = 122.9 \text{ ml}$

Atmospheric pressure = 757.5 mm of mercury

Temperature = $t_1 = 20^{\circ}\text{C} = (20 + 273)^0\text{A} = 293^0\text{A}$.

Aqueous tension at $20^{\circ}\text{C} = 17.4 \text{ mm.}$

Thus, the pressure of dry air = $P_1 = (757.5 - 17.4) = 740.1 \text{ mm}$

$$P = 760 \text{ mm } T = 273^0\text{A}$$

and $V = \text{Volume of the vapour of the volatile liquid at NTP} = ?$

$$\text{Applying the combined gas equation, } \frac{PV}{T} = \frac{P_1 V_1}{T_1}$$

$$V = \frac{P_1 V_1}{T_1} \times \frac{T}{P} = \frac{740.1 \times 122.9 \times 273}{293 \times 760} = 111.51 \text{ ml}$$

$$\text{Now vapour density, V.D} = \frac{\text{Wt. of Vml. of the vapour at NTP}}{\text{Wt. of same volume of hydrogen at NTP}}$$

$$= \frac{0.61}{111.51 \times 0.000089} = 61$$

and therefore, the molecular mass = $2 \times \text{V.D} = 2 \times 61 = 122$

Example 2 : 0.309 g of a compound is found to occupy 488 ml at 25°C and 737 ml pressure. What is the molecular mass of the compound ?

Solution Given, the mass of the compound = 0.309 g

Volume of the gas occupied, $V_1 = 488\text{ml}$.

$$\text{Temperature } t_1^{\circ}\text{C} = (25 + 273)^{\circ}\text{A} = 298^{\circ}\text{A} = T_1$$

$P_1 = 737 \text{ mm}$ (since no aqueous tension is given, the pressure of the gas is to be considered as pressure of dry gas)

Normal pressure = $P = 760 \text{ mm}$, Normal temperature = $T = 273^{\circ}\text{A}$.

$$\text{From combined gas equation } \frac{PV}{T} = \frac{P_1V_1}{T_1}, V = \frac{P_1V_1}{T_1} \times \frac{T}{P}$$

Now, the volume of gas occupied at NTP = V

$$\text{So, } V = \frac{P_1V_1}{T_1} \times \frac{T}{P} = \frac{737 \times 488 \times 273}{298 \times 760} = 433.53 \text{ ml.}$$

Now, 433.53 ml of the gas at NTP is liberated from 0.309 g of the compound.

$$\text{Hence } 22,400 \text{ ml of the gas at NTP} = \frac{0.309}{433.53} \times 22,400 = 16$$

Therefore, the molecular mass of the compound is 16.

Example 3 In Victor Meyer's experiment 0.235 g of a liquid is vapourised and the volume of air displaced measured in a gas burette is 42cc at 23°C and 730 mm pressure. The vapour pressure of water at 23°C is 21 mm. Calculate the molecular weight of the substance.

Solution Pressure of dry air = The pressure exerted by vapour

$$= (730 - 21) = 709 \text{ mm} = \frac{709}{760} \text{ atm.}$$

$$\text{Volume of the air displaced} = \text{Volume of the vapour} = 42\text{cc} = \frac{42}{1000} \text{ litres}$$

$$\text{Temperature} = (23 + 273) = 296^{\circ}\text{A}$$

$$\text{Mass of the vapour} = \text{mass of the liquid} = 0.235 \text{ g}$$

$$\text{Applying the gas equation } PV = \left(\frac{g}{M}\right) RT$$

$$\text{Now, the molecular weight } M = \frac{gRT}{PV}$$

$$= \frac{0.235 \times 0.082 \times 760 \times 1000 \times 296}{709 \times 42} = 145.6.$$

$$(\text{Since } R = 0.082 \text{ litre-atm. degree}^{-1} \text{ mol}^{-1})$$

Therefore, the molecular weight of the substance is 145.6

CHAPTER (2.6) AT A GLANCE

Molecular mass :

The molecular mass or the relative molecular mass of an element or a compound is the mass of one molecule of the element or the compound compared with $\frac{1}{12}$ th of the mass of one atom of carbon-12 ($^{12}\text{C} = 12.000$).

Gram - molecular mass :

The gram-molecular mass or the gram-mole or the molar mass of a substance is its relative molecular mass expressed in grams.

The relative molecular mass is the sum of the relative atomic masses of all the constituent elements.

The unit of the relative molecular mass is a.m.u. (atomic mass unit)

The relative molecular masses of volatile liquids can be determined by Victor Meyer's Experiment.

The following important relationships are used to calculate the relative molecular masses.

1. Mass of 22,400 ml of vapour at NTP = The relative molecular mass of the volatile liquid.
2. The relative molecular mass = $2 \times \text{V.D}$ (Vapour density)
3. The relative molecular mass can be calculated by applying gas equation

$$\text{PV} = \left(\frac{\text{g}}{\text{M}}\right)\text{RT} \quad (\text{where g} = \text{mass of the substance}, \text{M} = \text{molecular mass})$$

Solved Problems :

Problem 1 0.1 gm of a volatile substance on vapourisation in Victor Meyer's experiment displaced 123 ml of moist air at 15°C and 740 mm pressure. Calculate the molecular mass of the substance. (Aqueous tension at $15^{\circ}\text{C} = 12.7$ mm. (CHSE 1997 A)

Solution Given : Mass of the substance = 0.1 g

Measured : Pressure, $P_1 = (740 - 12.7) = 727.3$ mm

Temperature, $T_1 = (15 + 273) = 288^{\circ}\text{A}$

Volume $V_1 = 123$ ml.

At NTP, pressure, $P = 760$ mm Temperature, $T = 273^{\circ}\text{A}$ Volume $V = ?$

Applying combined gas equation

$$\frac{\text{PV}}{\text{T}} = \frac{\text{P}_1\text{V}_1}{\text{T}_1} \quad \text{or,} \quad \text{V} = \frac{\text{P}_1\text{V}_1}{\text{T}_1} \times \frac{\text{T}}{\text{P}} = \frac{727.3 \times 123 \times 273}{288 \times 760} = 111.5 \text{ ml} = \text{Volume at NTP.}$$

Now, 111.5 ml of the vapour is liberated from 0.1 g of the substance

$$\text{Hence, } 22,400 \text{ ml of the vapour will be liberated from : } \frac{0.1}{111.5} \times 22,400 \text{ ml} = 20.1$$

Therefore, the molecular mass of the volatile substance is 20.1

Problem 2 In a Victor Meyer's experiment 0.6 g of a volatile substance displaced 115 ml of air at 20°C and 756 mm pressure. Calculate the molecular weight of the substance (Aqueous tension at 20°C = 17.4 mm). (CHSE 1989 A)

Solution Mass of volatile substance = 0.6 g

Observed : Volume $V_1 = 115 \text{ ml}$, pressure $P_1 = (756 - 17.4) = 738.6 \text{ mm}$

Temperature $T_1 = 20 + 273 = 293^\circ\text{A}$

At NTP, $P = 760 \text{ mm}$ $T = 273^\circ\text{A}$ $V = ?$

$$\text{Applying the combined gas laws } \frac{PV}{T} = \frac{P_1V_1}{T_1}$$

$$\text{or, } V = \frac{P_1V_1}{T_1} \times \frac{T}{P} = \frac{738.6 \times 115 \times 273}{293 \times 760} = 104.13 \text{ ml}$$

Now, 104.13 ml of vapour at NTP weigh 0.6 g.

$$\text{So, } 22,400 \text{ ml of at NTP weigh} = \frac{0.6 \times 22,400}{104.13} = 128.07 \text{ g.}$$

Therefore, the molecular weight of the substance is 128.07

Problem 3 One litre of hydrogen at NTP weighs 0.09 g. 100ml of another gas at NTP weigh 0.0765 g. Calculate the vapour density and the relative molecular mass of the gas.

Solution Weight of 100 ml of gas at NTP = 0.0765 g

Therefore, weight of 1000 ml or 1 litre of the gas at NTP = 0.765 g

Weight of 1 litre of hydrogen at NTP = 0.09 g.

$$\text{Vapour density of the gas} = \frac{\text{Wt. of 1 litre of gas}}{\text{Wt of 1 litre of H}_2} = \frac{0.765}{0.09} = 8.5$$

Hence, the relative molecular mass = $2 \times \text{V.D} = 2 \times 8.5 = 17$.

Problem 4 A certain gas occupies 0.418 litre at 27°C and 740 mm of mercury. If the same weighs 3.0 g, what is the molecular mass of the gas?

Solution $P = 740 \text{ mm} = \frac{740}{760} \text{ atm}$ $V = 0.418 \text{ l}$

$T = 27 + 273 = 300^\circ\text{A}$, $\text{g} = 3.0 \text{ g}$, $R = 0.082 \text{ litre - atm. per degree per mole.}$

$$\text{Applying the relation } PV = \frac{g}{M} RT \quad \text{or} \quad M = \frac{gRT}{PV}$$

$$\text{and incorporating the above values } M = \frac{3 \times 0.082 \times 300 \times 760}{740 \times 0.418} = 181.3$$

Hence, the relative molecular mass of the gas is 181.3

QUESTIONS**A. Very short answer type (1 mark each)**

1. One gram mol. of oxygen will weigh how many grams ?
2. What unit is used for vapour density ?
3. Which method is suitable for determining the molecular mass of volatile substances ?
4. How many molecules are present in one gram molar volume of a gas ?
5. Why is asbestos or glass wool placed in the Victor Meyer's cylindrical glass vessel ?
6. What is the relationship between molecular mass and vapour density of a gas or vapour ?
7. Why should the Victor Meyer's tube be dried before start of the experiment ?
8. After inserting Hofmann's bottle, why should the Victor Meyer's tube is corked at once ?
9. What is the vapour density of N_2O ?
10. Which will weigh more, one gram mol of oxygen or 24 gms of nitrogen ?
11. What is the vapour density of ozone ?

B. Short answer type (2 marks each)

1. Define molecular mass.
2. Explain gram molecular mass.
3. What is the difference between normal density and relative vapour density ?
4. Is there any difference between the molecular weight and mass of one molecule of a gas ? Explain.
5. Explain why some gases show abnormal density.

C. Long answer type (10 marks each)

1. Describe Victor Meyer's method for determining the molecular mass of a substance.
0.1 gm of a volatile substance on vapourisation in Victor Meyer's experiment displaced 123 ml moist air at 15°C and 740 mm pressure. Calculate the molecular mass of the substance. (Aqueous tension at $15^\circ\text{C} = 12.7 \text{ mm}$) (CHSE 1997 A)
2. Define vapour density. How will you determine the vapour density of a volatile substance ?
3. Derive the relationship between molecular mass and vapour density of a gas from Avogadro's hypothesis.
0.796 g of a metal oxide was heated in a cuvett of dry hydrogen when. 0.18 g of water was formed. Calculate the equivalent mass of the metal. (CHSE, 2001 ER)

ANSWERS

- A. 1. 30g 2. No unit and V.D. is a number 3. Victor Meyer's method 4. 6.023×10^{23} molecules. 5. The glass vessel does not crack when Hofmann's bottle is dropped into it. 6. Molecular mass = $2 \times$ V.D. 7. Because there will be error in the volume of vapour collected, if some moisture remains in the tube. 8. Because the vapours of volatile liquid will immediately escape. 9. 22 10. 1 gm mole of oxygen 11. 24gms of nitrogen.
- C. 1. 20.1 (Reference : Solved problem **No.1** in this chapter)

NUMERICAL PROBLEMS

1. 3.01 g of a gas occupies 1.3 litres at 0°C and 760 mm pressure. Calculate the molecular mass of the gas.
(Ans. 51.44)
2. In the Victor Meyer's experiment, 0.0926 g of a volatile liquid resulted 28 ml of its vapour at 16°C and 753.5mm pressure. Find out the vapour density and molecular weight of the liquid (Aqueous tension at $16^\circ\text{C} = 13.5$ mm)
(Ans : 79.8)
3. In the Victor Meyer's apparatus 0.23 gm of a volatile substance displaced air which measured 112 ml at STP. Calculate the vapour density and molecular weight of the substance.
(Ans : V.D = 23, Mol. wt = 46)
4. 33.6 cc of phosphorus vapour weighs 0.062 gm at 546°C and 760 mm pressure. The atomic weight of phosphorus is 31. What is the molecular weight of phosphorus ? How many atoms are present in one molecule of phosphorus ?
(Ans : Mol. wt. 124, 4 atoms)

2.7 EQUIVALENT MASS

The equivalent mass of an element is a number which expresses how many parts by mass of the element combines with or displaces from a compound 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.45 parts by mass of chlorine.

One equivalent of any substance reacts with one equivalent of the other substance to produce one equivalent of each of the products. Thus, it is evident that all substances combine or appear on the basis of an equivalence.

The equivalent mass or equivalent weight expressed in gram is called gram-equivalent mass or gram-equivalent weight.

Many metals such as zinc, magnesium, aluminium etc. react with acids liberating hydrogen gas.

Now, one mole of hydrogen gas occupies 22.4 litres at NTP, and weighs 2.016g.

Hence, 11.2 litres of hydrogen gas at NTP would weigh 1.008g.

Therefore, in the displacement method, **that mass of the metal in grams which would liberate**

11.2 litres of hydrogen at NTP would be the gram equivalent mass of the metal.
Relation between equivalent mass, valency and relative atomic mass of an element.

Table 2.4 Relation of relative atomic mass and equivalent mass with valency

Element	Relative atomic mass(A)	Equivalent mass(B)	(A)/(B) Valency
Sodium	22.997	22.997	1
Magnesium	24.32	12.16	2
Zinc	65.38	32.69	2
Aluminium	26.97	8.99	3
Hydrogen	1.008	1.008	1
Oxygen	16.000	8.000	2

From the table 8.1, it is clear that the ratio of the relative atomic mass to the equivalent mass of an element is equal to its valency.

Therefore, the relative atomic mass of the element = the equivalent mass of the element \times valency

Variable equivalent mass

Some metals such as copper, iron show variable valency. Copper has valencies 1 and 2. Iron shows valencies 2 and 3. Elements showing variable valency have equivalent masses corresponding to each of its valency. For such elements the equivalent mass of an element depends upon its valency shown by the element in a particular compound. For example, the element iron forms two oxides, ferrous oxide FeO and ferric oxide Fe_2O_3 . The valencies of iron in these two compounds are 2 and 3 respectively. The relative atomic mass of iron is 55.85. And hence the equivalent masses of iron in FeO is $55.85/2 = 27.92$ and in Fe_2O_3 is $55.85/3 = 18.62$.

DETERMINATION OF EQUIVALENT MASS OF METALS :

Hydrogen displacement method

Metals such as zinc, magnesium, aluminium, iron, tin etc, displace hydrogen gas from dilute acids. A known amount of the metal is allowed to react with dilute acid and the volume

of evolved hydrogen gas, measured under atmospheric pressure and at room temperature, is converted to the volume at NTP.

It has been mentioned earlier that the gram-equivalent mass of a metal is that weight of the metal in grams which would liberate 11.2 litres of hydrogen gas at NTP.

EQUIVALENT MASS OF ZINC BY HYDROGEN DISPLACEMENT METHOD

Experiment

A piece of AR grade (analytical reagent) zinc ($< 0.1\text{g}$) of about 0.08g in weight placed in a watch glass is weighed out accurately. This piece of zinc, placed on a piece of and in contact with platinum foil is kept immersed in a beaker under water. The zinc metal along with the platinum foil is covered with an inverted small funnel such that the stem of the funnel remained immersed under water. An eudiometer tube (graduated tube) is filled with bench sulphuric acid and then the open end of the eudiometer tube closed with thumb is inverted over the funnel so that the stem of the funnel remained inside the tube. A little concentrated sulphuric acid is added to the water in the beaker. The zinc metal reacted with sulphuric acid liberating hydrogen gas. The gas is collected by downward displacement of acid in the eudiometer tube. When the metal is completely dissolved in the acid and no more gas evolved, the tube is removed by closing the mouth of the tube with the thumb. The tube, the open end of which is closed with the thumb is then plunged inside a tall jar of water in an inverted position. The thumb is slowly released and the tube is held with a piece of paper in position. The tube is not held with hand, since the body temperature will expand the gas. The tube is allowed to remain for sometime in the tall jar so that the gas in the tube is to attain the room temperature i.e. the temperature of water. Then the volume of the hydrogen gas collected is read out by adjusting the tube so that the surface of water level both inside and outside the tube became the same. The room temperature and the atmospheric pressure are noted. Since the gas is collected over water, the pressure exerted by dry hydrogen gas is less than the atmospheric pressure by an amount, the aqueous tension of water vapour. This aqueous tension of water vapour is also noted at room temperature.

Reaction :

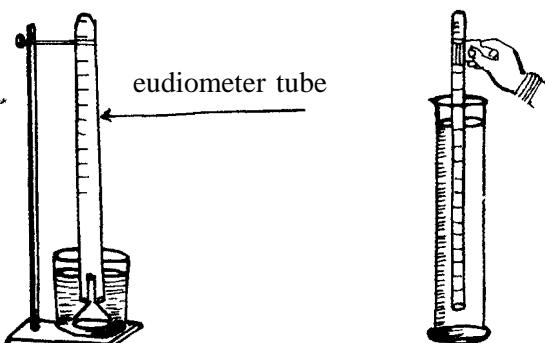
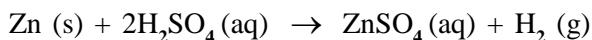


Fig 2.6 Determination of equivalent mass of zinc

(a) Calculation of Volume of hydrogen at NTP

Let the weight of zinc taken be Wg.

The volume of hydrogen gas collected at room temperature $t^{\circ}\text{C}$ and atmospheric pressure Pmm of mercury be $V_1\text{cc}$.

The aqueous tension due to water vapour at $t^{\circ}\text{C}$ is f mm of mercury.

Therefore, the pressure exerted by dry hydrogen gas is $(P - f)$ mm of mercury.

Thus, $V_1\text{cc}$ of dry hydrogen gas is collected at $t^{\circ}\text{C}$ and under $(P - f)$ mm of mercury pressure.

This volume is converted to the volume V_{cc} at NTP.

Here, $P_1 = (P - f)$, $T_1 = (t + 273)$, V_1 = measured volume of gas

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1}$$

$$\text{or, } V = \frac{P_1 V_1}{T_1} \times \frac{T}{P}$$

$$\text{or, } V = \frac{(P - f) \times V_1 \times 273}{(t + 273) \times 760}$$

(b) Calculating equivalent mass :

Method 1

Now V_{cc} of dry hydrogen gas at NTP is liberated from Wg of zinc.

So, 11.2 litres i.e 11,200cc of hydrogen gas at NTP is liberated from $= \frac{W}{V} \times 11,200$ g of zinc.

Hence, the equivalent weight of zinc $= \frac{W}{V} \times 11,200$

Method 2

1cc of hydrogen at NTP weighs 0.000089 g.

So, V_{cc} of hydrogen at NTP weigh $V \times 0.000089$ g.

Now $V \times 0.000089$ g of hydrogen is displaced by Wg of metal

Hence, 1.008 g of hydrogen displaced by $\frac{W}{V \times 0.000089} \times 1.008$ g

So, equivalent mass of metal $= \frac{W}{V \times 0.000089} \times 1.008$

NUMERICAL PROBLEMS

Example 1

0.27 g of a metal on treatment with dilute H_2SO_4 produced 112 ml of hydrogen at NTP.

What is the equivalent mass of the metal ?

Solution :

112 ml of hydrogen gas at NTP is liberated from 0.27g of the metal.

11,200 ml of hydrogen gas is liberated from

$$\frac{0.27}{112} \times 11,200 = 27$$

Example 2

0.425g of a metal liberated 436.5 ml of moist hydrogen at 17°C and 745.4 mm when reacted with HCl. Determine the equivalent mass of the metal. (Aqueous tension at 17°C is 14.4mm)

Solution : Volume of moist hydrogen $V_1 = 436.5$ ml

Pressure P_1 = pressure observed – aqueous tension = $745.4 - 14.4 = 731$ mm

Temperature $T_1 = 17 + 273 = 290^\circ\text{A}$

At NTP : volume = V, pressure, P = 760 mm, Temperature T = 273°A

$$\text{Now, } \frac{PV}{T} = \frac{P_1V_1}{T_1} \quad \text{or,} \quad V = \frac{P_1V_1T}{T_1P}$$

$$= \frac{731 \times 436.5 \times 273}{290 \times 760} = 395.2 \text{ ml}$$

1 ml of H_2 at NTP weighs 0.000089 gm

So, 395.2 ml of H_2 at NTP weighs $0.000089 \times 395.2 = 0.035$ gm

Now 0.035 gm of H_2 displaced by 0.425 g of the metal.

Therefore 1.008 gm of H_2 displaced by $\frac{0.425}{0.035} \times 1.008 = 12.24$ gm of metal.

Hence, The equivalent mass of the metal is 12.24.

Determination of equivalent mass of a metal by indirect oxidation method.

A metal is oxidised to its oxide either by heating the metal in air or by an indirect way. If a known amount of a metal is converted to its oxide, then the amount of the metal which was combined with 8g of oxygen can be calculated and that weight of metal is its equivalent mass.

EQUIVALENT MASS OF COPPER BY INDIRECT OXIDATION METHOD

The metal copper does not readily and quantitatively produce its oxide when heated directly in excess of air. Hence, a known amount of copper is treated with nitric acid to dissolve the metal. The copper nitrate solution so produced is heated to dryness. Thereafter this dry copper nitrate is strongly heated to decompose to cupric oxide. From the weight of the oxide, as has been said, the equivalent mass of copper is calculated.

Experiment

A porcelain crucible with its lid is cleaned, dried, heated for sometime, and then cooled in a desiccator. The weight of the crucible with its lid is determined. The procedure

of heating, cooling and then weighing the crucible along with the lid is repeated till they weigh constant weight. Then a piece of copper wire weighing about 1g is placed in the crucible and weighed. Thus the weight of copper can be known. The crucible is kept nearly covered when concentrated nitric acid is added dropwise to react with copper wire. Brown fumes are evolved and reaction appears to be vigorous. Addition of nitric acid dropwise is continued until the metal dissolved completely. When no more brown fumes appear, the reaction has apparently ceased.

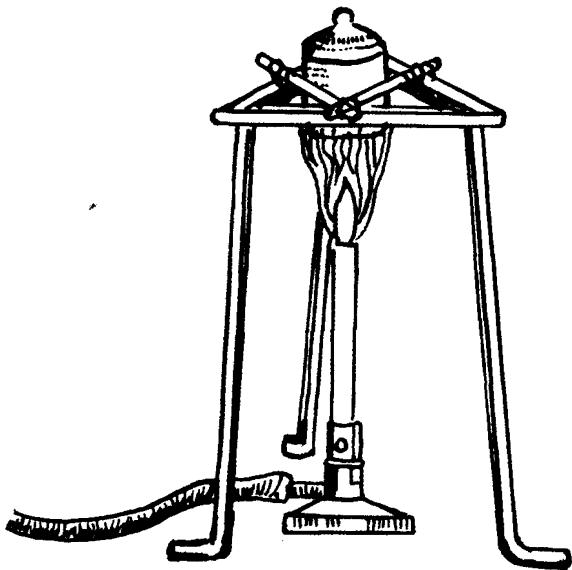
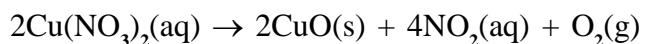


Fig 2.7 Determination of equivalent mass by oxide formation method.

Now the solution is slowly evaporated on water bath to dryness. Care is taken so that there is no loss of solution due to spouting. The residue so obtained, green in colour, is copper nitrate. Then the crucible with its lid is strongly heated on a clay pipe triangle when copper nitrate completely decomposes to cupric oxide, black in colour. Heating is then discontinued, the crucible is cooled in a desiccator, and its weight is determined. The procedure of heating, cooling and weighing along with cupric oxide is repeated till a constant weight is obtained.

Reaction



Calculation

$$\text{Weight of crucible with lid} = W_1\text{g} \quad (\text{constant weight})$$

$$\text{Weight of crucible with lid and copper wire} = W_2\text{g}$$

$$\text{Weight of crucible with lid and black cupric oxide} = W_3\text{g} \quad (\text{constant weight}).$$

$$\text{Thus, the weight of copper} = (W_2 - W_1)\text{g},$$

$$\text{the weight of cupric oxide} = (W_3 - W_1)\text{g}$$

Hence, the weight of oxygen = $(W_3 - W_1) - (W_2 - W_1) = (W_3 - W_2)$ g

So, $(W_3 - W_2)$ g of oxygen combines with $(W_2 - W_1)$ g of copper

Hence, 8g of oxygen will combine with $\left(\frac{W_2 - W_1}{W_3 - W_2} \right) \times 8$ g of copper.

Therefore, equivalent weight of copper is $8 \left(\frac{W_2 - W_1}{W_3 - W_2} \right)$

Relationship among atomic mass, equivalent mass and valency of an element.

Consider an element X with its atomic mass A, equivalent mass E and valency V.

Hydrogen being lightest its atomic mass is 1.008. Now, A parts by mass of the element will combine with $V \times 1.008$ parts by mass of hydrogen.

So, 1.008 parts by mass of hydrogen will combine with A/V parts by mass of the element and by definition this is equal to equivalent mass E of the element.

$$\text{Hence } \frac{A}{V} = E \text{ or } A = E \times V$$

Therefore Atomic mass = Equivalent mass \times Valency

NUMERICAL PROBLEMS

Example 1 3.5 g of copper was dissolved in excess concentrated nitric acid and the solution was evaporated to dryness. The copper nitrate so formed was ignited to its oxide which weighed 4.4 g. Calculate the equivalent mass of copper.

Solution : Weight of copper = 3.5 g

Weight of copper oxide = 4.4 g

Therefore, weight of oxygen = $(4.4 - 3.5) = 0.9$ g

Hence, 0.9 g of oxygen combines with 3.5 g of copper

So, 8 g of oxygen combines with $\frac{3.5 \times 8}{0.9} = 31.1$ g

Thus, Equivalent mass of copper is 31.1.

Example 2 0.84g of a divalent metal on burning in air produced 1.4g of metal oxide. Calculate the equivalent mass and the relative atomic mass of the element.

Solution : Weight of the metal = 0.84g

Weight of the metal oxide = 1.4g

Therefore, the weight of oxygen = $(1.4 - 0.84) = 0.56$ g

0.56g of oxygen combines with 0.84g of the metal.

So, 8g of oxygen will combine with $\frac{0.84}{0.56} \times 8 = 12$ g

Hence the equivalent mass of the metal = 12.

Since the metal is divalent its valency is 2,

and its relative atomic mass becomes $12 \times 2 = 24$.

Equivalent mass of a compound

Equivalent mass of a compound is a number which expresses what mass of the compound contain 1.008 parts by mass of hydrogen or 8.0 parts by mass of oxygen or 35.45 parts by mass of chlorine.

Thus, 98 parts by mass of H_2SO_4 contain 2.016 parts by mass of hydrogen.

So, 49 parts by mass of H_2SO_4 contain 1.008 parts by mass of hydrogen.

Therefore, equivalent mass of H_2SO_4 is 49.

In the case of NaCl , 58.45 parts by mass NaCl contain 35.45 parts by mass of chlorine.

Therefore, the equivalent mass of NaCl is 58.45.

Equivalent mass of a compound may be calculated by the expression,

$$\frac{\text{Molecular mass of the compound}}{\text{The total number of charges on the cations or anions}}$$

NUMERICAL PROBLEMS

Example 1 Calculate the equivalent mass of sodium carbonate.

Solution :

$$\begin{aligned}\text{Molecular mass of } \text{Na}_2\text{CO}_3 &= 2 \times 23 + 12 + 3 \times 16 \\ &= 46 + 12 + 48 = 106\text{g}\end{aligned}$$

Total number of charges of cation i.e. sodium (two numbers of sodium ions each having one charge) = 2

$$\text{Now, equivalent mass of } \text{Na}_2\text{CO}_3 = \frac{106}{2} = 53.$$

Example 2 Calculate the equivalent mass of barium chloride.

Solution :

$$\text{Molecular mass of } \text{BaCl}_2 = 137 + 2 \times 35.45 = 207.9 \approx 208$$

There are one barium cation having charges 2 which becomes the total charges.

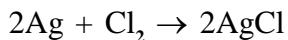
$$\text{Now, equivalent mass of } \text{BaCl}_2 = \frac{208}{2} = 104$$

Equivalent mass of metals

1. Chloride formation method

A metal may directly combine with chlorine to form metal chloride.

For example, silver reacts with chlorine to form silver chloride



In this case the mass of metal and the mass of metal chloride are accurately determined and the equivalent mass of the metal is calculated as below.

$$\text{Equivalent mass of metal} = \frac{\text{Mass of metal} \times 35.45}{\text{Mass of chlorine}}$$

Equivalent mass of silver can also be determined by completely dissolving silver metal in dilute nitric acid. The silver nitrate thus formed is treated with dil HCl to precipitate silver chloride. The weight of silver and weight of silver chloride are accurately measured and then the equivalent mass of silver is calculated.

$$\text{Weight of silver} = x \text{ gram}$$

$$\text{Weight of silver chloride} = y \text{ gram}$$

$$\text{Therefore, weight of chlorine} = (y - x) \text{ g}$$

$$\text{Thus, } (y - x) \text{ g of chlorine combines with } x \text{ g of silver}$$

$$\text{Hence, } 35.45 \text{ g of chlorine will combine with } \left(\frac{x}{y-x}\right) \times 35.45 \text{ g}$$

$$\text{Equivalent weight of silver} = 35.45 \left(\frac{x}{y-x}\right)$$

Example 1

2.7 g of silver when heated with excess of chlorine resulted 3.586 g of silver chloride. Calculate the equivalent mass of silver.

Solution : The mass of chlorine that combined with silver = $3.586 - 2.7 = 0.886$ g

$$\begin{aligned} \text{So, } \text{Equivalent mass of silver} &= \frac{\text{Mass of silver}}{\text{Mass of chlorine}} \times 35.45 \\ &= \frac{2.7}{0.886} \times 35.45 = 108.03 \end{aligned}$$

Example 2

1.62 g of silver was dissolved in nitric acid. The solution was then treated with hydrochloric acid to precipitate 2.15 g of silver chloride. Determine the equivalent weight of silver.

Solution : Weight of silver = 1.62g

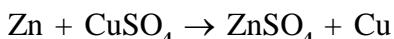
$$\text{Weight of silver chloride} = 2.15 \text{ g}$$

$$\text{Therefore, weight of chlorine} = (2.15 - 1.62) = 0.53 \text{ g}$$

$$\text{So, equivalent weight of silver} = \frac{1.62}{0.53} \times 35.45 = 108.36$$

2. Metal to metal displacement method

More electropositive metals like Zn, Fe, Al etc. displace less electropositive metals like Cu, Ag, Au etc., from their salt solutions.



In such methods, the masses of displacing metal and displaced metal take place in equivalent amounts and are in the ratio of their equivalent masses.

$$\text{Here, } \frac{\text{Mass of Zn}}{\text{Mass of Cu}} = \frac{\text{Equivalent mass of Zn}}{\text{Equivalent Mass of Cu}}$$

Example :

2.06 g of zinc displace 2.0 g of copper from copper sulphate solution. If the equivalent mass of Zn is 32.5, find out the equivalent mass of copper.

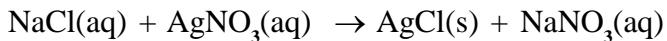
$$\text{Solution } \frac{\text{Mass of Zn}}{\text{Mass of Cu}} = \frac{\text{Equivalent mass of Zn}}{\text{Equivalent mass of Cu}}$$

$$\text{or, } \frac{2.06 \text{ g}}{2.00 \text{ g}} = \frac{32.5}{\text{Equivalent mass of Cu}}$$

$$\text{So, } \text{Equivalent mass of Cu} = \frac{32.5 \times 2.00}{2.06} = 31.55$$

3. Double decomposition method

In this method, a known amount of a water soluble salt such as NaCl or KCl solution is acidified with dilute nitric acid and treated with silver nitrate solution to precipitate AgCl. The weight of AgCl is accurately determined.



The following expression is used to calculate the equivalent mass of the metal.

$$\frac{\text{Weight of metal chloride}}{\text{Weight of silver chloride}} = \frac{\text{Eq.mass of metal} + \text{Eq.mass of chlorine}}{\text{Eq.mass of silver} + \text{Eq.mass of chlorine}}$$

Example :

0.2 g of a metal chloride dissolved in water was treated with excess of silver nitrate solution to precipitate 0.5g of silver chloride. Calculate the equivalent mass of the metal. (Equivalent mass of silver and that of chlorine are 108 and 35.45 respectively).

Solution : Let the equivalent mass of the metal be x.

$$\text{Weight of metal chloride} = 0.2 \text{ g}$$

$$\text{Weight of silver chloride} = 0.5 \text{ g}$$

$$\text{Equivalent mass of silver} = 108$$

$$\text{Equivalent mass of chlorine} = 35.45$$

$$\text{Therefore, Equivalent mass of silver chloride is } (108 + 35.45) = 143.45$$

$$\frac{\text{Weight of metal chloride}}{\text{Weight of silver chloride}} = \frac{\text{Eq.mass of metal} + \text{Eq.mass of chlorine}}{\text{Eq.mass of silver} + \text{Eq.mass of chlorine}}$$

$$\text{or, } \frac{0.2}{0.5} = \frac{x + 35.45}{108 + 35.45} = \frac{x + 35.45}{143.45}$$

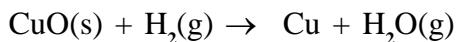
$$\text{or, } x + 35.45 = \frac{143.45 \times 0.2}{0.5} = 57.4$$

$$\text{or, } x = 57.4 - 35.45 = 21.95$$

Hence the equivalent mass of the metal is 21.95

4. Reduction of the oxide method

A known weight of a metal oxide is heated in a current of hydrogen gas to the corresponding metal. The equivalent mass of the metal can be known from the weight of metal oxide, weight of the metal and the weight of oxygen.



5. Decomposition of a metal carbonate into its oxide

Metal carbonates such as NiCO_3 and CuCO_3 on heating produce their oxides.



The equivalent mass of such metals can be calculated with the help of the following expression.

$$\begin{aligned} \frac{\text{Weight of the metal carbonate}}{\text{Weight of the metal oxide}} &= \frac{\text{Equivalent mass of the metal carbonate}}{\text{Equivalent mass of the metal oxide}} \\ &= \frac{\text{Equivalent mass of the metal} + 30}{\text{Equivalent mass of the metal} + 8} \end{aligned}$$

Equivalent mass of oxygen is 8 and that of carbonate (CO_3^{2-})

$$= \left(\frac{12+16 \times 3}{2} \right) = 30$$

Example :

1.05g of a metallic carbonate on heating produced 0.5g of the oxide. Calculate the equivalent mass of the metal.

Solution :

Weight of the metal carbonate = 1.05g

Weight of the metal oxide = 0.5g

Let the equivalent mass of the metal be x,

$$\text{Therefore, } \frac{\text{Weight of the metal carbonate}}{\text{Weight of the metal oxide}} = \frac{\text{Equivalent mass of the metal carbonate}}{\text{Equivalent mass of the metal oxide}}$$

$$\text{or, } \frac{1.05}{0.5} = \frac{x + 30}{x + 8}$$

$$\text{or, } x + 30 = 2.1(x + 8)$$

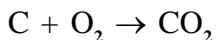
$$\text{or, } 1.1x = 13.2$$

$$\text{or, } x = 12$$

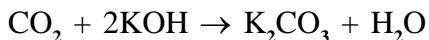
Hence, the equivalent mass of the metal is 12.

Equivalent mass of nonmetals

In determination of the equivalent mass of nonmetals like carbon and sulphur, a known amount of the nonmetal is burnt in excess of air.



The oxide of the nonmetal so formed is absorbed in an suitable solution. Here, CO_2 is absorbed in caustic potash solution.



There would be an increase in weight of the solution, and from this increase in weight, the weight of the nonmetal oxide can be determined.

The equivalent mass of the nonmetal can be calculated from the known weight of the nonmetal, the weight of the metal oxide and the weight of oxygen.

In the case of nonmetals such as chlorine, bromine etc, which react with hydrogen easily, the equivalent mass of the nonmetal can be calculated from the percentage composition of the compound of the nonmetal and hydrogen.

Nonmetals like phosphorus which chemically combine with chlorine, the equivalent mass of the nonmetal can be determined from the percentage composition of the nonmetal chloride.

CHAPTER (2.7) AT A GLANCE

Equivalent mass The equivalent mass of an element is a number which expresses how many parts by mass of the element combines with or displaces 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.45 parts by mass of chlorine.

Equivalents One equivalent of any substance reacts with one equivalent of the other substance to produce one equivalent of each of the products. All substances combine or appear on the basis of an equivalent.

Gram equivalent mass The equivalent mass expressed in grams is called gram equivalent mass.

Solved Problems

Problem 1 0.08 g of a metal produces 22.4 ml of dry hydrogen at NTP. What is its equivalent mass?

Solution 22.4 ml of dry hydrogen at NTP was obtained from 0.08 g of metal.

$$\text{So } 11,200 \text{ ml of hydrogen gas is produced from } \frac{0.08}{22.4} \times 11,200 = 40 \text{ g}$$

Therefore, the equivalent mass of the metal = 40

Problem 2 0.205 g of a metal on treatment with an acid gave 106.60 ml of moist hydrogen collected at 755 mm pressure and 17°C. Calculate the equivalent mass of the metal (Aqueous tension at 17°C = 14.4 mm).

Solution Volume of moist hydrogen 106.60 ml = V_1 (say)

$$\text{pressure } P_1 = (755 - 14.4) = 740.6$$

$$\text{Temperature } T_1 = 17 + 273 = 290^\circ\text{A}$$

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1} \text{ or } V = \frac{P_1 V_1 T}{T_1 P} = \frac{740.6 \times 106.6 \times 273}{290 \times 760} = 97.79 \text{ ml}$$

Now, 97.79 ml of hydrogen gas at NTP is liberated from acid by 0.205 g of metal.

So, 11,200 ml of hydrogen gas at NTP is liberated by,

$$\frac{0.205}{97.79} \times 11,200 = 23.48 \text{ g of metal}$$

Therefore, the equivalent mass of the metal is 23.48.

Problem 3 0.325 gm. of a metal when dissolved in dil H_2SO_4 liberated 0.01 gm of hydrogen. What is the equivalent weight of the metal? (CHSE 1996 A)

Solution 0.01 gm of hydrogen is equivalent to 0.325 gm of the metal.

Therefore 1.008 gm of hydrogen will be equivalent to $\frac{0.325}{0.01} \times 1.008 = 32.76$ gm of the metal.

Hence, the equivalent weight of the metal is 32.76.

Problem 4 1.62 g of a metal was dissolved in nitric acid to prepare its nitrate. On strong heating of the nitrate, 2.02 g of oxide was obtained. Find out the equivalent weight of the metal.

Solution Weight of the metal = 1.62 g

Weight of its oxide = 2.02 g

Hence, the weight of oxygen that combined with the metal = $(2.02 - 1.62) = 0.40 \text{ g}$

Now, 0.40 g of oxygen combined with 1.62 g of the metal

So, 8.0 g of oxygen combines with $\frac{1.62}{0.40} \times 8 = 32.4 \text{ g of the metal.}$

Therefore, equivalent weight of the metal is 32.4.

Problem 5 Calculate the equivalent mass of the metal whose oxide contains 35.2% oxygen.

Solution Mass of oxide of the metal = 100 g

$$\text{Mass of oxygen} = 35.2 \text{ g}$$

$$\text{Hence, the mass of the metal} = (100 - 35.2) = 64.8 \text{ g.}$$

Now, 35.2 g of oxygen combines with 64.8 g of the metal.

$$\text{Therefore } 8.0 \text{ g of oxygen will combine with } \frac{64.8}{35.2} \times 8 = 14.72 \text{ g of the metal.}$$

So the equivalent mass of the metal is 14.72.

Problem 6 0.51 gm of a metal combines with oxygen to give 0.68 gm of metal oxide.

Calculate the equivalent weight of the metal. (CHSE 1989)

Solution Weight of the metal = 0.51 gm

$$\text{Weight of the metal oxide} = 0.68 \text{ gm}$$

$$\text{The weight of oxygen} = 0.68 - 0.51 = 0.17 \text{ gm}$$

$$\text{The equivalent weight of the metal} = \frac{0.51}{0.17} \times 8 = 24$$

Problem 7 0.54 g. of a metal gave 0.7175 g of the metal chloride. Determine the equivalent weight of the metal.

Solution The weight of combined chlorine = $0.7175 - 0.54 = 0.1775 \text{ g.}$

$$\text{Hence, equivalent weight of the metal} = \frac{0.54 \times 35.5}{0.1775} = 108$$

Problem 8 1.08 g of copper displace 3.67 g of silver from silver nitrate solution. find the equivalent mass of copper, that of silver being 108.

Solution Here, $\frac{\text{Eq.mass of copper}}{\text{Eq. mass of silver}} = \frac{\text{Weight of copper}}{\text{Weight of silver displaced}}$

$$\text{or, } \frac{\text{Eq.mass of Cu}}{108} = \frac{1.08}{3.67}$$

$$\text{or, Eq.mass of copper} = \frac{1.08}{3.67} \times 108 = 31.78.$$

Problem 9 1.52 g of a metal hydroxide gave 0.995 g. of its oxide. Calculate the equivalent mass of the metal.

Solution $\frac{\text{Eq. mass of metal} + \text{Eq.mass of OH}}{\text{Eq. mass of metal} + \text{Eq.mass of O}} = \frac{1.52}{0.995}$

$$(\text{Eq mass of OH} = \frac{17}{1} = 17 \text{ and eq.mass of O} = \frac{16}{2} = 8)$$

$$\text{So, } \frac{\text{Eq. mass of metal} + 17}{\text{Eq. mass of metal} + 8} = \frac{E + 17}{E + 8} = \frac{1.52}{0.995}$$

Solving, $E = 9.06$, and that is the equivalent mass of the metal.

Problem 10

0.5 g of a metal combines with 142 ml of oxygen at NTP. Calculate the equivalent mass of the metal.

Solution 22,400 ml of oxygen weigh 32 g

Hence, 142 ml of oxygen weigh $\frac{32}{22,400} \times 142 = 0.20$ g

Thus 0.20 g of oxygen combines with 0.5 g metal.

Hence 8 g of oxygen combine with $\frac{0.5}{0.2} \times 8 = 20$ g of the metal.

Therefore, the equivalent mass of the metal is 20.

QUESTIONS

A. Very short answer type (1 mark each)

1. Which method is used to determine the equivalent mass of zinc. ?
2. What mass of an element combines with 8 parts by mass of oxygen ?
3. How many gram-equivalents will be 40 g of Ca. ?
4. Which method is used to determine the equivalent mass of copper ?
5. What is the equivalent weight of NaOH ?
6. Does the equivalent mass of an element change with temperature ?
7. What is the equivalent mass of hydrogen ?
8. Atomic weight of a metal is 52 and its valency is 3. What is the equivalent weight of the metal ?
9. What is the equivalent mass of OH^- ?
10. What equivalent of oxygen will measure 5.6 litres of oxygen at NTP ?

B. Short answer type (2 marks each)

1. Two metals A and B have the same equivalent mass but the atomic mass of A is twice that of B. How can it be explained ?
2. What is the relationship between atomic mass and equivalent mass of oxygen ?
3. Define equivalent mass.
4. Explain gram equivalent mass.

5. What is the equivalent mass of sodium carbonate ?
6. Why cannot the equivalent mass of copper be determined by hydrogen displacement method ?
7. 74.5 g of a metal chloride contains 35.5 g of chlorine. What is the equivalent mass of the metal ?
8. Explain why the equivalent mass of copper is different in Cu_2O and CuO .
9. X g of an element combines with oxygen to give Y g of its oxide. What is the equivalent mass of the element ?
10. Explain that iron shows variable equivalent weight in its compounds.

C. Long answer type (7 marks each)

1. Define equivalent weight. How will you determine the equivalent weight of zinc by hydrogen displacement method ?
0.325 g of a metal when dissolved in dil H_2SO_4 liberated 0.01 g of hydrogen. What is the equivalent weight of the metal ?
2. Define equivalent mass of an element. How would you determine the equivalent mass of copper ?
3. Define equivalent mass. What is the difference between equivalent mass and gram equivalent ?
4. How will you determine the equivalent mass of zinc by hydrogen displacement method ?

D. Numerical problems :

1. If 1.2 g of a metal displaces 1.12 litres of hydrogen at NTP, what would be the equivalent weight of the metal ?
2. 0.01 g of a metal when dissolved in HCl liberates 10.65 ml of hydrogen collected over water at 27°C . The barometric pressure is 760 mm Hg. Aqueous tension at 27°C is 25 mm of Hg. Calculate the equivalent weight of the metal.
3. 2.943 g of a metal when treated with excess dil H_2SO_4 the volume of hydrogen collected was 1083.6 ml at 15°C and 752.5 mm of pressure. Calculate the equivalent mass of the metal. (Aqueous tension at $15^\circ\text{C} = 12.5$ mm)
4. 0.54 g of a metal gave 0.90 g of its oxide. Calculate the equivalent mass of the metal.
5. An oxide of a metal contains 52.9% metal. Calculate its equivalent mass.
6. 4.74 g of cupric oxide on being heated in a current of hydrogen gave 3.78 g of the metal. Calculate the equivalent mass of copper.
7. The chloride of a metal contained 52.85% of metal. What is the equivalent mass of the metal ?

8. 0.13 g of aluminium displaces 0.47 g of copper from copper sulphate solution. The equivalent mass of copper is 31.75. Calculate the equivalent mass of aluminium.
9. 0.5054 g of a metal nitrate is converted into 0.373 g of its chloride. The equivalent weight of nitrate group (NO_3^-) is 62. Calculate the equivalent weight of the metal.
10. What mass of the metal of equivalent mass 12 will give 0.475 g of its chloride ?

ANSWERS

- A. 1. Hydrogen displacement method 2. Equivalent mass 3. 2 4. Oxide formation method
 5. 40 6. No 7. 1.008 8. 17.33 9. 17 10. 1
- B. 1. Valency of metal A is double that of valency of B.
 2. Atomic mass of oxygen = Equivalent mass of oxygen \times Valency of oxygen (i.e.2)
 5. 53. 6. Copper cannot displace H_2 from an acid. 7. 39 9. $\frac{8x}{y-x}$
- C. 1. 32.76 (Ref : solved problem No.3)
- D. 1. 12 2. 12 3. 32.2 4. 12 5. 8.98 6. 31.5 7. 39.78 8. 8.8 9. 39.1 10. 0.12 g

2.8 EQUIVALENT MASSES OF ACIDS, BASES AND SALTS

- (a) **Equivalent mass of acid :** Equivalent mass of an acid is a number which shows how many parts by mass of the acid contain one part by mass of replaceable hydrogen.

Molecular mass of $\text{HCl} = 36.5$ (At. mass of H=1, Cl = 35.5). Thus, 36.5 parts by mass of HCl contain 1 part by mass of replaceable hydrogen. Hence, equivalent mass of HCl is 36.5.

Molecular mass of $\text{H}_2\text{SO}_4 = 98$ (At mass of H = 1, S = 32, O = 16).

Thus, 98 parts by mass of H_2SO_4 contain 2 parts by mass of replaceable hydrogen. Hence, equivalent mass of $\text{H}_2\text{SO}_4 = \frac{98}{2} = 49$.

Basicity of the acid is the number of replaceable hydrogen atoms it contains. Therefore,

$$\text{Equivalent mass of the acid} = \frac{\text{Molecular mass of the acid}}{\text{Basicity of the acid}}$$

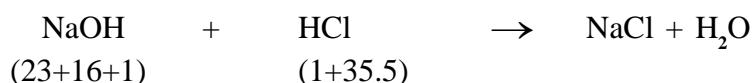
[**Note :** Acetic acid (CH_3COOH) contains four hydrogen atoms in all, but the number of replaceable hydrogen in it is only one. Therefore the equivalent mass of acetic acid is its molecular mass].

Table 2.5 Equivalent mass of some acids.

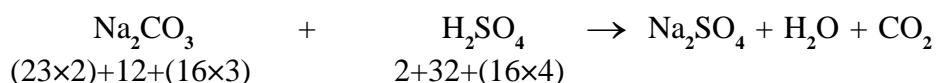
Acid	Formula	Basicity	Molecular mass	Equivalent mass.
Hydrochloric	HCl	1	36.5	$\frac{36.5}{1} = 36.5$
Nitric	HNO ₃	1	63.0	$\frac{63.0}{1} = 63.0$
Sulphuric	H ₂ SO ₄	2	98.0	$\frac{98.0}{2} = 49.0$
Phosphoric	H ₃ PO ₄	3	98.0	$\frac{98.0}{3} = 32.66$
Acetic	CH ₃ COOH	1	60.0	$\frac{60.0}{1} = 60.0$
Oxalic (anhydrous)	COOH COOH	2	90.0	$\frac{90.0}{2} = 45.0$
Oxalic (hydrated)	COOH. .2H ₂ O COOH	2	126.0	$\frac{126.0}{2} = 63.0$

(b) **Equivalent mass of base :** Equivalent mass of a base is a number which shows how many parts by mass of a base can just be neutralised by one equivalent mass of an acid.

Consider the reaction

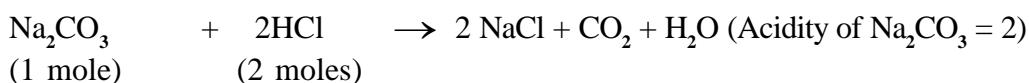
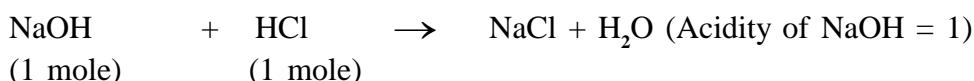


Thus, 40 parts by mass of NaOH is completely neutralised by 36.5 parts by mass of HCl i.e. one equivalent mass of HCl. Therefore, the equivalent mass of NaOH is 40.



Thus, 106 parts by mass of Na₂CO₃ is completely neutralised by 98 parts by mass of H₂SO₄ i.e. two equivalent mass of H₂SO₄. Therefore, equivalent mass of Na₂CO₃ = $\frac{106}{2} = 53$.

The number of moles of monobasic acid which can completely neutralise one mole of the base determines the **acidity** of the base. **Acidity** of the base can also be defined as the number of replaceable hydroxyl group present in one molecule of the base.



Hence, equivalent mass of the base = $\frac{\text{Molecular mass of the base}}{\text{Acidity of the base}}$

Table 2.6 Equivalent mass of some bases.

Base	Formula	Acidity	Molecular mass	Equivalent mass
Sodium hydroxide	NaOH	1	40	$\frac{40}{1} = 40$
Potassium hydroxide	KOH	1	56	$\frac{56}{1} = 56$
Calcium hydroxide	Ca(OH) ₂	2	74	$\frac{74}{2} = 37$
Barium hydroxide	Ba(OH) ₂	2	171	$\frac{171}{2} = 85.5$
Aluminium hydroxide	Al(OH) ₃	3	78	$\frac{78}{3} = 26$

- (c) **Equivalent mass of salt :-** Equivalent mass of a salt is a number which shows how many parts by mass of the salt contain one part by mass of hydrogen equivalent of an active element of a positive group.

NaCl is a salt whose molecular mass 58.5, 58.5 parts by mass of NaCl contain 23 parts by mass of Na which in turn is equivalent to one part by mass of hydrogen. So, 58.5 parts by mass of NaCl contain one equivalent mass of the metal and equivalent mass of NaCl is 58.5.

BaCl₂ is another salt whose molecular mass is 208. 208 parts by mass of BaCl₂ contain 137 parts by mass of barium which in turn is equivalent of two parts by mass of hydrogen. So, 208 parts by mass of BaCl₂ contain two equivalent mass of the metal and equivalent mass of BaCl₂ = $\frac{208}{2} = 104$.

In general, **Equivalent mass of the salt** = $\frac{\text{Molecular mass of the salt}}{\text{Total valency of the metal ion}}$.

Table : 2.7 Equivalent mass of some simple salts.

Salt	Formula	Mol. mass of the salt	Total Valency of the metal ion	Equivalent mass
Sodium sulphate	Na ₂ SO ₄	142	2	71
Ferrous chloride	FeCl ₂	127	2	63.5
Ferric chloride	FeCl ₃	162.5	3	54.16
Aluminium chloride	AlCl ₃	133.5	3	44.5

Gram-Equivalent Mass : Equivalent mass expressed in grams is called gram - equivalent mass, written as gm - equivalent. Thus, one gram - equivalent of HCl = 36.5g, one gram - equivalent of Na₂CO₃ is 53g, one gram - equivalent of H₂SO₄ is 49 g. and so on.

CHAPTER (2.8) AT A GLANCE

1. **Equivalent mass of acid :** How many parts by mass of the acid contain one part by mass of replaceable hydrogen. Number of replaceable hydrogen = Basicity.
2. **Equivalent mass of the base :** How many parts by mass of a base can just be neutralised by one equivalent mass of an acid. Number of moles of monobasic acid neutralising one mole of the base completely = Acidity = Number of replaceable hydroxyl group present in one molecule of the base.
3. **Equivalent mass of the salt :** How many parts by mass of the salt contain one part by mass of hydrogen equivalent of an active element of a positive group. Also molecular mass of the salt divided by the total valency of the metal ions.
4. **Gram - equivalent mass.** Equivalent mass expressed in grams.

2.9 PERCENTAGE COMPOSITION, MOLECULAR FORMULA AND EMPIRICAL FORMULA

Calculation of percentage composition

Percentage of composition is denoted as the number of parts by mass of each element present in hundred parts by mass of a compound.

$$\text{Percentage of the element} = \frac{\text{Number of parts by mass of the element}}{\text{Molecular mass}} \times 100$$

Example - 1

Calculate the percentage composition of calcium carbonate.

(At mass : Ca = 40, C = 12, O = 16)

Solution : Formula of calcium carbonate is CaCO₃

Therefore its molecular mass = $1 \times 40 + 12 + 3 \times 16 = 100$

$$\text{Hence, \% of Ca} = \frac{40}{100} \times 100 = 40$$

$$\% \text{ of C} = \frac{12}{100} \times 100 = 12$$

$$\% \text{ of O} = \frac{48}{100} \times 100 = 48$$

Example - 2

Calculate the percentage composition of ferrous sulphate crystal. (Fe = 56, S = 32, O = 16, H = 1)

Solution : Formula of ferrous sulphate crystal is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Therefore, its molecular mass

$$= 56 + 32 + 4 \times 16 + 7(1 \times 2 + 16)$$

$$= 56 + 32 + 64 + 126 = 278$$

$$\text{Hence , \% of Fe} = \frac{56}{278} \times 100 = 20.14$$

$$\% \text{ of S} = \frac{32}{278} \times 100 = 11.51$$

$$\% \text{ of O} = \frac{64}{278} \times 100 = 23.02$$

$$\% \text{ of H}_2\text{O} = \frac{126}{278} \times 100 = 45.33$$

Example - 3

Calculate the percentage of composition of sodium phosphate. (Na = 23, P = 31, O=16)

Solution : Formula of sodium phosphate is Na_3PO_4

Therefore its molecular mass is $3 \times 23 + 31 + 4 \times 16$

$$= 69 + 31 + 64 = 164$$

164 parts of Na_3PO_4 contains 69 parts of Na,

$$\text{Hence \% of Na} = \frac{69}{164} \times 100 = 42.07$$

$$\% \text{ of P} = \frac{31}{164} \times 100 = 18.90$$

$$\% \text{ of O} = \frac{64}{164} \times 100 = 39.02$$

Calculation of mass of element present in a given mass of substance :**Example - 1**

How many grams of sodium are present in 5.85 grams of sodium chloride ?

$$(\text{Na} = 23, \text{Cl} = 35.5)$$

Solution : Molecular mass of sodium chloride $\text{NaCl} = 23 + 35.5 = 58.5$

58.5g of NaCl contain 23g of sodium

$$\text{So } 5.85\text{gm of NaCl will contain } \frac{23}{58.5} \times 5.85 = 2.3\text{g of sodium}$$

Example - 2

How many grams of sulphur are present in 6.0 g of magnesium sulphate ? (Mg = 24, S = 32, O = 16)

Solution : Molecular mass of magnesium sulphate, $\text{MgSO}_4 = 24 + 32 + (4 \times 16) = 120$

120g of MgSO_4 Contain 32g of sulphur

Hence, 6.0g of MgSO_4 contain $\frac{32}{120} \times 6.0 = 1.6\text{g}$ of sulphur

MOLECULAR FORMULA AND EMPIRICAL FORMULA

A **formula** is a ratio of number of atoms of each element present in the compound.

Molecular formula : The molecular formula shows the exact number of atoms of each element present in one molecule of the compound.

Empirical formula : The empirical formula shows the simplest whole number ratio of atoms of each element present in one molecule of the compound.

It is the simplest formula which gives the atomic ratio in terms of smallest whole numbers of each type of atom present.

If the percentage composition of a compound is determined, then its simplest formula can be computed.

Relationship between molecular formula and empirical formula.

The molecular formula of hydrogen peroxide is H_2O_2 . Its empirical formula is HO.

The molecular formula of acetic acid is CH_3COOH or $\text{C}_2\text{H}_4\text{O}_2$ and its empirical formula is CH_2O .

The molecular formula of glucose is $\text{C}_6\text{H}_{12}\text{O}_6$ and its empirical formula is CH_2O . From the above examples, we arrive at a conclusion for a relationship between molecular formula and empirical formula and that is

Molecular formula = (Empirical formula)_n

Where, the value of n is a whole number.

For H_2O_2 the value of n = 2, for CH_3COOH , n = 2, and for glucose $\text{C}_6\text{H}_{12}\text{O}_6$, n = 6.

For some compounds the molecular formula is the same as its empirical formula. Both formulae for hydrogen chloride is HCl and have the value of n = 1.

Determination of empirical formula and molecular formula.

This is determined from percentage composition. The following steps are followed in determining the empirical formula.

1. The percentage composition of each element is divided by relative atomic mass to get the relative number of atoms present in the compound.
2. The quotients from (1) are divided by the smallest quotient to get the simplest ratio of atoms of different elements constituting the molecule of a compound.

If the above ratio of atoms is not a whole number ratio, then this ratio is multiplied by an integer to convert the same to a whole number ratio.

3. Once the whole number ratio is determined it is possible to write the empirical formula.

The molecular formula sometimes may be same as the empirical formula or it may be a simple multiple of the empirical formula.

Molecular formula = (Empirical formula)_n.

The value of n is a whole number and is determined by dividing the molecular mass of the compound by its empirical formula mass.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Example - 1

Calculate the empirical formula of a compound that contains 22.22% nitrogen, 1.59 % hydrogen and the rest oxygen.

Solution : The % of oxygen = [100 – (22.2 + 1.59)] = 76.19

Element	Percentage composition	Atomic mass	Relative number of atoms	Simplest ratio	Whole number ratio
H	1.59	1.008 or 1	1.59/1	1.59	1
N	22.22	14	22.22/14	1.59	1
O	76.0	16	76.19/16	4.76	3

So, the compound containing H, N, and O atoms with whole number ratio 1, 1 and 3 respectively, its empirical formula is HNO_3 .

As we know the molecular formula of nitric acid is HNO_3 , so here the value of n = 1 and the molecular formula and empirical formula of nitric acid is the same, that is HNO_3 .

Example - 2

A gaseous compound of carbon and nitrogen, containing 53.8% by weight of nitrogen was found to have vapour density of 25.8. What is the molecular formula of the compound ?

(IIT. 1971)

Solution :

Element	Percentage Composition	Atomic mass	Relative number of atoms	Simplest ratio
N	53.8	14	$\frac{53.8}{14} = 3.84$	$\frac{3.84}{3.84} = 1$
C	$100 - 53.8 = 46.2$	12	$\frac{46.2}{12} = 3.85$	$\frac{3.85}{3.84} = 1$

Hence the empirical formula of the gaseous compound is CN.

Now the empirical formula mass is $12 + 14 = 26$.

We shall learn later in this chapter that molecular mass of a compound is equal to twice its vapour density.

Since the vapour density of the above compound is 25.8, the molecular mass is $2 \times 25.8 = 51.6$.

$$\text{We Know, } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{51.6}{26} = 1.98 \approx 2$$

Thus the molecular formula of the gaseous compound is $(CN)_2$ or C_2N_2 .

Percentage of oxygen in an organic compound

In the analysis of elements of an organic compound, the elements carbon, hydrogen, nitrogen, sulphur and halogen can be estimated by chemical methods. But the element oxygen cannot be estimated directly. So the percentage of oxygen is obtained by subtracting the sum of percentage of other elements from 100.

Therefore, percentage of oxygen = $100 - (\text{Sum of percentage of other elements})$

Example - 3

An organic compound contains 40% carbon and 6.66% hydrogen and rest oxygen. The vapour density of the compound is 30. Calculate its empirical and molecular formula.

Solution :

Element	Percentage Composition	Atomic mass	Relative number of atoms	Simplest ratio
C	40	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$
H	6.66	1.008	$\frac{6.66}{1.008} = 6.61$	$\frac{6.61}{3.33} = 1.98 \approx 2$
O	$100 - (40 + 6.66)$ $= 53.34$	16	$\frac{53.34}{16} = 3.33$	$\frac{3.33}{3.33} = 1$

Hence the empirical formula is CH_2O . The molecular formula would be thus $(CH_2O)_n$.

The empirical formula mass = $12 + 2 \times 1.008 + 16 = 30.016 \approx 30$. Given the vapour density of the compound 30. So the molecular mass is $2 \times 30 = 60$

$$\text{Therefore, } n = \frac{60}{30} = 2$$

So the molecular formula of the compound is $(CH_2O)_2$ or $C_2H_4O_2$.

Example - 4

A compound on analysis was found to contain the following percentage composition Fe = 20.14% ; S = 11.51% ; O = 63.3% and H = 5.08%. The molecular mass of the substance is 278. Determine the molecular formula assuming that all the hydrogen atoms are present with oxygen as water of crystallisation. (At. mass Fe = 56, S = 32, O = 16, H = 1.008).

Element	Percentage Composition	Atomic mass	Relative number of atoms	Simplest ratio
Fe	20.14	56	$\frac{20.14}{56} = 0.36$	$\frac{0.36}{0.36} = 1$
S	11.51	32	$\frac{11.51}{32} = 0.36$	$\frac{0.36}{0.36} = 1$
O	63.30	16	$\frac{63.30}{16} = 3.96$	$\frac{3.96}{0.36} = 11$
H	5.08	1.008	$\frac{5.08}{1.008} = 5.03$	$\frac{5.03}{0.36} = 14$

Thus, the empirical formula of the compound is $\text{FeSO}_{11}\text{H}_{14}$

The empirical formula mass = $56 + 32 + (11 \times 16) + (14 \times 1) = 278$

Given, molecular mass = 278

$$\text{So } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{278}{278} = 1$$

Hence, the molecular formula is $\text{FeSO}_{11}\text{H}_{14}$

In this case we know, all the fourteen hydrogen atoms combine with seven oxygen atoms to form seven molecules of water. So, the molecular formula is to be written as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

CHAPTER (2.9) AT A GLANCE

- Percentage composition :** Percentage of composition is denoted as the number of parts of each element present in hundred parts by mass of a compound.
- Molecular formula :** The molecular formula shows the exact number of atoms of each element present in one molecule of the compound.
- Empirical formula :** The empirical formula shows the simplest whole number ratio of atoms of each element present in one molecule of the compound.

QUESTIONS

Long answer type

- What do you understand by empirical and molecular formula of a compound ? How are they related ?

An organic compound contains C = 62.15% and H = 10.34%. Its vapour density is 29. Find out the empirical and molecular formula of the compound. (Ans : CH_2 , C_4H_8)

- What do you understand by empirical and molecular formulae of a compound ? How are they related ?

A compound contains carbon, hydrogen and nitrogen in the ratio 18:2:7. Calculate its empirical formula. If the molecular mass of the compound is 108, what is its molecular formula ? (Ans : $\text{C}_3\text{H}_4\text{N}$, $\text{C}_6\text{H}_8\text{N}_2$)

NUMERICAL PROBLEMS

1. What is the molecular mass of :
 - (a) Hydrochloric acid (b) Sodium hydroxide (c) Sodium carbonate (d) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (e) Barium sulphate. (f) Aluminium oxide. (At mass, Cl = 35.5, Na = 23, C = 12, O = 16, Ba = 137, S = 32, Al = 27)
2. Calculate the percentage composition of :
 - (a) sodium chloride (b) Sodium sulphate
3. A given sample of chalk contains 55% by mass of calcium carbonate. Calculate the percentage of calcium, carbon and oxygen in the sample.
4. A compound on analysis gave the following percentage composition.
 $\text{Na} = 14.31\%$, $\text{S} = 9.97\%$, $\text{H} = 6.22\%$, $\text{O} = 69.5\%$. The molecular mass of the substance is 322. Find its molecular formula assuming that all the hydrogen atoms are present in combination with oxygen as water of crystallisation (At. mass Na = 23, H = 1, S = 32, O = 16)
5. An organic compound contains 52.18% carbon and 13.04% hydrogen, the remaining being oxygen. Vapour density of the compound is 23. Calculate the molecular formula.
6. In case of a hydrocarbon, it was found that the hydrogen content is $\frac{1}{12}$ of that of carbon by weight. What is the empirical formula of the compound ?
7. A compound with molecular weight 108, contained 88.89% C and 11.11% H. Calculate its molecular formula.

ANSWERS TO NUMERICAL PROBLEMS

1. (a) 36.5 (b) 40 (c) 106 (d) 244 (e) 233 (f) 102
2. (a) $\text{Na} = 39.3\%$, $\text{Cl} = 60.7\%$ (b) $\text{Na} = 32.4\%$, $\text{S} = 22.5\%$ $\text{O} = 45.1\%$
3. $\text{Ca} = 22\%$, $\text{C} = 6.6\%$, $\text{O} = 26.4\%$
4. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
5. $\text{C}_2\text{H}_6\text{O}$
6. CH
7. C_8H_{12}

2.10 AVOGADRO'S HYPOTHESIS AND THE MOLE CONCEPT

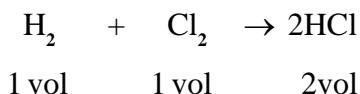
According to Dalton, **when elements combine, they do so in simple ratios by atoms**. We also know from Gay Lussac's law that **when gases combine, they do so in simple ratios by volume**.

J. J. Berzelius, a Swedish chemist attempted to correlate Dalton's atomic theory and Gay Lussac's law of gaseous volumes with the idea that there must be some relationship between the volume of a gas and the number of atoms present. Berzelius put forward a relationship called as Berzelius hypothesis.

Berzelius hypothesis : Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of atoms.

Berzelius hypothesis when applied to some gaseous reactions failed to explain Dalton's atomic theory.

Example : It was observed experimentally that for a reaction,



1 volume of hydrogen combines with 1 volume of chlorine to produce 2 volumes of hydrogen chloride, the volumes measured under similar conditions of temperature and pressure.

- Let 1 volume of a gas contain 'n' atoms and applying Berzelius hypothesis,
 n atoms of hydrogen combine with n atoms of chlorine to form
 2n atoms of hydrogen chloride.
 or 1 atom of hydrogen combines with 1 atom of chlorine to form 2 atoms of
 hydrogen chlorinde.
 or, 1 atom of hydrogen chloride contains $\frac{1}{2}$ atom of hydrogen and $\frac{1}{2}$ atom of
 chlorine.

The above statement contradicts Dallton's atomic theory that says atoms is indivisible. In 1811 Italian chemist, Amedeo Avogadro modified Berzelius hypothesis by distinguishing atoms and molecules.

Atom : An atom is the smallest particle of an element which takes part in a chemical change. An atom may or may not have independent existence.

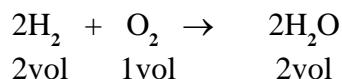
Molecule : A molecule is defined as the smallest particle of a compound which contains atoms of different kind. In case of an element, the smallest particle may be a molecule composed of atoms of the same kind. The molecule is capable of existing in the free state and retaining the properties of matter. In a chemical reaction between molecules reorganisation of atoms occurs.

The reactions between gases may be understood in terms of Avogadro's hypothesis.

AVOGADRO'S HYPOTHESIS

Equal volumes of all gases at the same temperature and pressure contain equal number of molecules.

Avogadro's hypothesis explains correctly the reaction between hydrogen and oxygen forming water vapour.



2 volumes of hydrogen gas combine with 1 volume of oxygen gas to form 2 volumes of water vapour measured **under same condition of temperature and pressure.**

Let there be **n** number of molecules present in 1 volume of hydrogen. Thus there are **2n** molecules present in 2 volumes of hydrogen.

According to Avogadro's hypothesis, there would be **n** molecules of oxygen in 1 volume of oxygen gas and **2n** molecules of water in 2 volumes of water vapour. Thus,

2n molecules of hydrogen combine with **n** molecules of oxygen to form **2n** molecules of water vapour.

2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water vapour.

Therefore, 1 molecule of hydrogen combines with 1/2 molecule of oxygen to form 1 molecule of water vapour.

According to Dalton's atomic theory atoms cannot be divided in a chemical reaction, but molecules are divisible.

If $\frac{1}{2}$ molecule of oxygen is regarded as 1 atom of oxygen making oxygen atom diatomic, then

1 molecule of hydrogen combines with 1 atom of oxygen to form 1 molecule of water vapour.

This deduction from Avogadro's hypothesis does not contradict Dalton's atomic theory.

Advantages of Avogadro's hypothesis

1. It could explain the difference between an atom and a molecule.
2. It proved that molecules are the ultimate particles of the elementary gases.
3. It explained correctly the law of gaseous volumes.

APPLICATIONS OF AVOGADRO'S HYPOTHESIS :

1. Explanation of Gay Lussac's law of gaseous volumes

In the chemical combination of gases A and B to form a gaseous compound AB,

Let 'a' molecules of gas A combine with 'b' molecules of gas B (a & b are simple integers).

Under the same condition of temperature and pressure,

If 1 cc of gas A contains n molecules then 1 cc of gas B would also contain the same number of n molecules. This is as per Avogadro's hypothesis.

Since 1 cc of the gas A contains n molecules then 'a' molecules of the gas A would be present in $(\frac{a}{n})$ cc.

And similarly 'b' molecules of the gas 'B' would be present in $(\frac{b}{n})$ cc.

Thus, the volumes of gases A and B will combine in the ratio : i.e. a : b (a simple ratio, since a and b are whole numbers), when the volumes are measured at the same temperature and pressure.

Avogadro's hypothesis thus, explains the law of gaseous volumes.

2. Determination of atomicity of elementary gases

Atomicity means the number of atoms present in a molecule.

(a) Atomicity of oxygen molecule

The fact that a molecule of oxygen is diatomic will be deduced from Avogadro's hypothesis.

It has been already stated that 2 volumes of hydrogen combine with 1 volume of oxygen to produce 2 volumes of water vapour at the same temperature and pressure.

It is also deduced by considering n molecules being present in 1 volume of hydrogen that

2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of water vapour.

And hence, 1 molecule of hydrogen combines with $\frac{1}{2}$ molecule of oxygen to form 1 molecule of water vapour.

Since water is a compound of hydrogen and oxygen only, each molecule of water must contain at least 1 atom of hydrogen and 1 atom of oxygen. This 1 atom of oxygen in water must have come from $\frac{1}{2}$ molecule of oxygen gas. Now since 1 atom of oxygen is present in $\frac{1}{2}$ molecule of oxygen, the oxygen molecule should be diatomic.

(b) Atomicity of hydrogen and chlorine molecules

Similarly from the gaseous combination of hydrogen and chlorine,

1 volume of hydrogen combines with 1 volume of chlorine to give

2 volumes of hydrogen chloride gas, volumes measured at the same temperature and pressure. It can be deduced with the help of Avogadro's hypothesis that hydrogen and chlorine molecules are diatomic.

(3) Determination of the relationship between molecular mass and vapour density

The vapour density of a gas or vapour is defined as the ratio of the mass of a definite volume of the gas or vapour to the mass of the same volume of hydrogen, both the volumes measured at the same temperature and pressure.

Vapour density of a gas or vapour

$$= \frac{\text{Mass of a definite volume of gas or vapour}}{\text{Mass of the same volume of hydrogen}} \quad (\text{at the same temperature and pressure})$$

The vapour density of a gas or vapour can be measured experimentally.

Let V_{cc} of a gas or vapour contain n molecules.

$$\text{Vapour density (V.D.)} = \frac{\text{Mass of Vcc of the gas or vapour}}{\text{Mass of Vcc of hydrogen}}$$

(at the same temperature and pressure)

According to Avogadro's hypothesis, Vcc of hydrogen gas under the same conditions of temperature and pressure would also contain **n** molecules of hydrogen.

Therefore,

$$\begin{aligned}\text{V. D.} &= \frac{\text{Mass of } \mathbf{n} \text{ molecules of the gas or vapour}}{\text{Mass of } \mathbf{n} \text{ molecules of hydrogen}} \\ &= \frac{\text{Mass of } \mathbf{1} \text{ molecule of the gas or vapour}}{\text{Mass of } \mathbf{1} \text{ molecule of hydrogen}}\end{aligned}$$

Since hydrogen molecule is diatomic (this fact has also been deduced from Avogadro's hypothesis),

$$\begin{aligned}\text{V. D.} &= \frac{\text{Mass of } \mathbf{1} \text{ molecule of the gas or vapour}}{\text{Mass of } \mathbf{2} \text{ atoms of hydrogen}} \\ \text{So, } \quad \text{V. D.} \times 2 &= \frac{\text{Mass of } \mathbf{1} \text{ molecule of the gas or vapour}}{\text{Mass of } \mathbf{1} \text{ atom of hydrogen}} \\ &= \text{Relative molecular mass of the gas or vapour.}\end{aligned}$$

Thus, **the relative molecular mass of a gas or vapour is twice its vapour density.**

The relative molecular mass of gas or vapour = $2 \times \text{V.D.}$

The atomic mass of hydrogen is 1.008 on the basis of atomic mass scale.

In order to calculate the exact relation,

the relative molecular mass of a gas or vapour is equal to **2.016** times its vapour density, i.e.,

$$\begin{aligned}&\text{Relative molecular mass of a gas or vapour} \\ &= \mathbf{2.016} \times \text{Vapour density of the gas or vapour.}\end{aligned}$$

4. Determination of Gram molecular mass or Molar mass and Gram molecular volume or Molar volume.

Gram molecular mass of any substance is the molecular mass expressed in grams.
According to Avogadro's hypothesis,

$$\begin{aligned}\text{Vapour density} &= \frac{\text{Mass of 1 litre of gas at NTP}}{\text{Mass of 1 litre of hydrogen at NTP}} \\ &= \frac{\text{Mass of 1 litre of gas at NTP}}{0.089 \text{ gram}}\end{aligned}$$

(Since 1 litre of hydrogen weighs 0.089 gram)

$$\text{Now, Vapour density} = \frac{\text{Mass of 1 litre of gas at NTP}}{0.089 \text{ gram}}$$

$$\text{Since, molecular mass or gram molecular mass} = 2 \times \text{V.D.} = \frac{2 \times \text{mass of 1 litre of gas at NTP}}{0.089 \text{ gram}}$$

= Mass of 22.4 litres of the gas at NTP.

Thus, gram molecular mass of any gas or vapour occupies 22.4 litres at NTP which is called the gram molecular volume or molar volume.

5. Determination of molecular formulae of gases

Molecular formula of a gas can be determined from its volumetric composition.

For example, it has been found from experiment that. 1 volume of nitrous oxide contains 1 volume of nitrogen gas.

If **n** number of molecules occupy **1** volume of nitrous oxide, according to Avogadro's hypothesis,

1 volume of nitrogen will also contain **n** molecules.

Thus, **n** molecules of nitrous oxide contain **n** molecules of nitrogen. So, **1** molecule of nitrous oxide will contain **1** molecule of nitrogen. (It can be deduced from Avogadro's hypothesis that nitrogen molecule is diatomic and hence its atomicity is **2**)

Therefore, **1** molecule of nitrous oxide contains **2** atoms of nitrogen.

Thus, its formula may be written as N_2O_x , x being the number of oxygen atoms present in a molecule of nitrous oxide.

The vapour density of nitrous oxide has been determined from experiment to be 22.

Again from Avogadro's hypothesis, the relative molecular mass of a gas or vapour = $2 \times$ Vapour density

Hence, the relative molecular mass of nitrous oxide gas is $2 \times 22 = 44$.

Again, the relative molecular mass of a compound is the sum of the relative atomic masses of all constituent elements.

So, $(2 \times 14 + 16x) = 44$ (The relative atomic masses of nitrogen and oxygen are 14 and 16 respectively)

Therefore, $x = 1$ and the molecular formula of nitrous oxide is N_2O .

6. Determination of atomic mass of elementary gases

Avogadro's hypothesis can be applied to determine the atomic mass of elementary gases

Molecular mass = $2 \times$ Vapour density

Again , Molecular mass = atomic mass \times atomicity

Therefore, atomic mass \times atomicity = $2 \times$ Vapour density

$$\text{and hence, atomic mass} = \frac{2 \times \text{Vapour density}}{\text{atomicity}}$$

7. Explanation of Dalton's atomic theory

According to Avogadro's hypothesis molecules are divisible whereas atoms are not. This distinguishes between atoms and molecules and explains Dalton's atomic theory.

AVOGADRO'S NUMBER AND MOLE CONCEPT

The basic unit of substances in different types of chemical problems is an atom, ion or a molecule. While dealing with a definite and macroscopic quantity of substance the number of atoms, ions or molecules which compose the substance will have to be counted.

Chemists have devised the unit **mole** to express the number of atoms, ions or molecules.

A mole is the quantity of a substance that contains the same number of atoms, ions or molecules as are contained in 12g of carbon - 12 (^{12}C). The number of atoms of carbon in 12g of carbon -12 has been found to be 6.023×10^{23} .

Thus, **1 mole of any substance is that quantity of the substance which contains 6.023×10^{23} particles or units of that substance. This number is called Avogadro's number (N) or (L).**

One gram-atom of an element is the mass of 6.023×10^{23} atoms of the element. For example, the gram-atomic mass of sodium is 22.9898 g. The mass of Avogadro number of sodium atoms is 22.9898g.

Hence, the mass of 1 atom of sodium

$$= \frac{22.9898}{6.023 \times 10^{23}} = 3.82 \times 10^{-23}\text{g}$$

Thus, **mass of one atom of the element = $\frac{\text{Gram-atomic mass}}{N}$**

Similarly, the gram-molecular mass of hydrogen is 2.016 g.

The mass of 1 mole of hydrogen molecule is 2.016g and

that contains Avogadro number of hydrogen molecules.

$$\text{Hence, the mass of 1 molecule of hydrogen} = \frac{2.016}{6.023 \times 10^{23}} = 3.85 \times 10^{-24}\text{g}$$

Thus, **mass of one molecule of the substance = $\frac{\text{Gram molecular mass}}{N}$**

The quantity 'mole' is written in an abbreviated form as 'mol'.

Again, the number atoms and number molecules in a given mass of element can be calculated.

$$\text{Number of atoms} = \frac{\text{Mass of substance} \times N}{\text{Gram atomic mass}}$$

$$\text{Number of molecules} = \frac{\text{Mass of substance} \times N}{\text{Gram molecular mass}}$$

Molar Volume

The gram-molecular volume or molar volume of all gases is the same at the same temperature and pressure and is 22.4 litres at NTP. (1 litre = 1000 cm³ = (10cm)³ = 1 dm³)

It is known from experiment that 1 litre of hydrogen gas at NTP weighs 0.089g, the molar mass of hydrogen being 2.016g,

2.016 g of hydrogen occupy $\frac{2.016}{0.0899} = 22.4$ litres at NTP. This volume is called gram – molecular volume or molar volume of hydrogen. This means that one mole of hydrogen molecules occupies 22.4 litres at NTP.

According to Avogadro's hypothesis , if we consider any other gas such as oxygen or carbon dioxide, 22.4 litres at NTP of any gas would contain the same number of molecules as are present in 22.4 litres of hydrogen gas at NTP.

Now we know that one mole of molecules of hydrogen occupy 22.4 litres at NTP. Hence 1 mole of molecules of any gas occupies 22.4 litres at NTP. Again the molar volume of any gas weighs its molar mass.

Thus, the molar volume or gram - molecular volume of any gas is the volume occupied by 1 mole of molecules of the gas at NTP and equals to 22.4 litres. The molar volume weighs the molar mass.

Hence,	O ₂	N ₂	CO ₂	Cl ₂
Molar mass (g)	32	28	44	71
Molar volume (litres at NTP)	22.4	22.4	22.4	22.4

NUMERICAL PROBLEMS

Example 1

Calculate the number of molecules of carbon dioxide present in 500 ml at NTP.

Solution The number of molecules present in a given volume of a gas at NTP

$$= \frac{\text{Volume of gas in litres} \times N}{22.4 \text{ litres}}$$

$$\text{Volume of gas} = 500 \text{ ml.} = 0.5l$$

Therefore, the number of molecules = $\frac{0.5l \times 6.023 \times 10^{23}}{22.4l} = 1.344 \times 10^{22}$ molecules.

Example 2

2.8 litres of a gas at NTP weighs 4 grams. Calculate the molecular mass of the gas.

Solution Molecular mass of the gas = $\frac{\text{Mass of the gas in g (W)}}{\text{Volume of gas in litres (V)}} \times 22.4l = \frac{W}{V} \times 22.4$

$$\text{Hence, The molecular mass} = \frac{W}{V} \times 22.4 = \frac{4}{2.8} \times 22.4 = 32$$

Example 3

Calculate the density of chlorine gas at NTP.

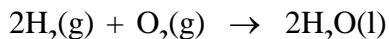
Solution Density of the gas = $\frac{\text{Gram molecular mass of the gas}}{\text{Molar volume (22.4l)}}$

Gram molecular mass of chlorine = 71 g.

$$\text{Hence, Density of chlorine gas} = \frac{71}{22.4} = 3.17 \text{ gm/litre} = 0.00317 \text{ gm/ml.}$$

Mole concept and chemical equations

The chemical equation for the reaction of hydrogen and oxygen forming water may also be interpreted in terms of moles of reactants and products.



This equation also represents that 2 moles of hydrogen react with 1 mole of oxygen to form 2 moles of water, i.e., $2(6.023 \times 10^{23})$ molecules of hydrogen combine with (6.023×10^{23}) molecules of oxygen to produce $2(6.023 \times 10^{23})$ molecules of water.

Since the weight of 1 mole in grams is the molar mass, the above fact implies that 4g of hydrogen reacts with 32g of oxygen to produce 36g of water.

$2\text{H}_2(\text{g})$	+	$\text{O}_2(\text{g}) \rightarrow$	$2\text{H}_2\text{O}(\text{l})$
2mol		1mol	2mol
$2(6.023 \times 10^{23})$		6.023×10^{23}	$2(6.023 \times 10^{23})$
Molecules		Molecules	Molecules
$2 \times 2\text{g}$		32g	$2 \times 18\text{g}$

The chemical equation for the preparation of carbon dioxide gas in the laboratory is as follows.

$\text{CaCO}_3(\text{s})$	+	$2\text{HCl} \rightarrow$	$\text{CaCl}_2(\text{aq})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
1mol		2mol	1Mol	1mol	1mol
100g		$2 \times 36.5\text{g}$	111g	44g	18g

The above equation represents that 1 mole of calcium carbonate reacts with 2 moles of hydrochloric acid to produce 1 mole of carbon dioxide gas, 1 mole of calcium chloride and 1 mole of water. Here, we are mainly concerned with calcium carbonate, hydrochloric acid and carbon dioxide gas. The relative molecular mass of calcium carbonate is 100. That is the sum of relative atomic masses of calcium, carbon and oxygen.

$$\text{Relative molecular mass of } \text{CaCO}_3 = (40 + 12 + 3 \times 16) = 100$$

Now 1 Mole of carbon dioxide gas occupies $22.4l$ at NTP.

Thus, 100g of CaCO_3 reacts with 1 mole of HCl to liberate $22.4l$ of carbon dioxide at NTP.

From the above examples it is evident that mole concept is very useful in the calculations involving stoichiometric relationship.

NUMERICAL PROBLEM

Example :

Calculate the volume of oxygen gas at NTP that can be produced by heating 4.9 grams of potassium chlorate ($K = 39$, $\text{Cl} = 35.5$, $O = 16$)

Solution :

The chemical equation for this reaction is



Thus, 2 moles of KClO_3 liberate three moles of oxygen. The relative molecular mass of $\text{KClO}_3 = 39 + 35.5 + (3 \times 16) = 122.5$ and 1 mole of oxygen gas occupies 22.4 litres at NTP.

Hence, from the equation

$2 \times 122.5 = 245$ g of KClO_3 produce $3 \times 22.4l = 67.2l$ of oxygen gas at NTP.

Therefore, 4.9g of KClO_3 will produce $\frac{67.2 \times 4.9}{245} = 1.344 l$ of oxygen at NTP.

CHAPTER (2.10) AT A GLANCE

Atom

An atom is the smallest particle of an element which takes part in a chemical change. An atom may or may not have independent existence.

Molecule

A molecule is the smallest particle of a compound that contains atoms of different kinds. In case of an element, the smallest particle may be a molecule composed of atoms of the same kind. The molecule is capable of existing in the free state and retaining the properties of matter.

Berzelius hypothesis

Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of atoms.

Avogadro's hypothesis

Equal volumes of all gases at the same temperature and pressure contain equal number of molecules.

Atomicity of elementary gases

Atomicity means the number of atoms in elementary gases present in a molecule.

Relation between molecular mass and vapour density

The relative molecular mass of a gas or vapour is twice its vapour density.

$$\text{Relative Molecular mass} = 2 \times \text{V. D.}$$

Mole and Avogadro's number

One mole of any substance is that quantity of substance which contains 6.023×10^{23} particles or units of that substance. This number is Avogadro's number (N).

Gram-atom and Gram atomic mass

One gram -atom or one mole-atom of an element contains 6.023×10^{23} atoms of the element. Gram-atomic mass of an element is the atomic mass expressed in grams.

Gram-molecule and Gram molecular mass

One gram-molecule or one mole-molecule of a substance contains 6.023×10^{23} molecules of that substance. Gram molecular mass of any substance is the molecular mass expressed in grams.

Molar volume or Gram molecular volume

Molar volume or Gram molecular volume is the volume occupied by one gram molecular mass of any gas or vapour at NTP. **Molar volume of any gas or vapour occupies 22.4 litres at NTP.** Molar volume of all gases is the same at the same temperature and pressure and is 22.4 litres at NTP.

Solved problems

Problem 1

Calculate the mass of 1 atom of carbon –12 isotope and hence find out the value of 1 amu in grams. Evaluate the mass of one molecule of oxygen.

Solution

$$\begin{aligned}\text{Mass of 1 atom of C - 12} &= \frac{\text{gram atomic mass of C -12}}{N} \\ &= \frac{12}{6.023 \times 10^{23}} = 2 \times 10^{-23} \text{ g.}\end{aligned}$$

$$\begin{aligned}1 \text{ atomic mass unit (amu)} &= \frac{1}{12} \text{ th of mass of one atom of carbon - 12} \\ &= \frac{1}{12} \times 2 \times 10^{-23} = 1.66 \times 10^{-24} \text{ g}\end{aligned}$$

The relative molecular mass of oxygen is 32.

Therefore, the mass of an oxygen molecule is 32 amu which is equal to $32 \times 1.66 \times 10^{-24}$
 $= 5.31 \times 10^{-23}$ g.

Problem 2 What is the mass of half mole of oxygen atom ? (C.H.S.E. 1991(A))

Solution Number of moles = $\frac{\text{Mass of atoms}}{\text{gram atomic mass}}$
 or, mass of atoms = number of moles \times gram.. atomic mass
 So, mass of oxygen atom = $0.5 \times 16 = 8\text{g.}$

Problem 3 Calculate the number of moles in 25 gm. of CaCO_3 . (C.H.S.E. 1989(S))

Solution Number of moles = $\frac{\text{Mass of substance}}{\text{gram molecular mass of substance}}$
 Here, Number of moles = $\frac{25}{100} = 0.25$ mole (since molecular mass of $\text{CaCO}_3 = 100$)

Problem 4 Calculate the number of molecules present in 1.6 gm of methane.
 (C.H.S.E. 1994(S))

Solution Number of molecules = $\frac{\text{Mass of substance} \times N}{\text{gm. molecular mass of the substance}}$
 Here, molecular mass of methane, $\text{CH}_4 = 16$
 and number of molecules = $\frac{1.6 \times 6.023 \times 10^{23}}{16} = 6.023 \times 10^{22}$ molecules.

Problem 5 Calculate the number of molecules of sodium hydroxide present in 4 gms of the sample.
 (C.H.S.E. 1991(S))

Solution Number of molecules of $\text{NaOH} = \frac{\text{Mass of NaOH} \times N}{\text{gm. molecular mass of NaOH}}$
 $= \frac{4 \times 6.023 \times 10^{23}}{40} = 6.023 \times 10^{22}$ molecules.

Problem 6 Write the number of atoms present in 1 mole of sulphuric acid.(O. J. E. E 1993)

Solution Total number of atoms in the substance =Number of moles \times total number of atoms $\times N$
 Here, number atoms in one molecule of $\text{H}_2\text{SO}_4 = 7$
 and therefore total number of atoms present
 $= 1 \times 7 \times 6.023 \times 10^{23} = 4.216 \times 10^{23}$ atoms

Problem 7 In 93 g of phosphorus calculate the number of molecules.

Solution Phosphorus molecule is tetra atomic, P_4
 Hence its molecular mass = 124 g

Number of molecules = $\frac{\text{Mass of substance} \times N}{\text{gram molecular mass}}$
 $= \frac{93 \times 6.023 \times 10^{23}}{124} = 4.517 \times 10^{23}$ molecules.

Problem 8 Calculate the total number of electrons present in 1.6 gms of methane.

Solution Molecular formula of methane = CH_4
 and hence, Molecular mass of methane = 16

So, number of molecules = $\frac{\text{Mass of substance} \times N}{\text{gram molecular mass}}$

$$= \frac{1.6 \times 6.023 \times 10^{23}}{16} = 6.023 \times 10^{22} \text{ molecules}$$

One molecule of methane contains 10 electrons.

Hence 6.023×10^{22} molecules of methane contain $6.023 \times 10^{22} \times 10 = 6.023 \times 10^{23}$ electrons.

Problem 9 How many atoms of each of the constituent elements are there in 25g. of CaCO_3 ?
(Ca = 40, C = 12, O = 16).

Solution Gram molecular mass of $\text{CaCO}_3 = 40 + 12 + 3 \times 16 = 100\text{g.}$

$$\text{Thus, } 25 \text{ g of } \text{CaCO}_3 = \frac{25}{100} = 0.25 \text{ moles of } \text{CaCO}_3.$$

Now, 1 mole of CaCO_3 contains 6.023×10^{23} atoms of Ca,

6.023×10^{23} atoms of C and $3 \times 6.023 \times 10^{23}$ atoms of O.

Hence, the number of atoms of the constituent elements in 25g i.e. 0.25 moles of CaCO_3 is equal to

$$\text{Ca} = 0.25 \times 6.023 \times 10^{23} = 1.506 \times 10^{23} \text{ atoms}$$

$$\text{C} = 0.25 \times 6.023 \times 10^{23} = 1.506 \times 10^{23} \text{ atoms}$$

$$\text{O} = 0.25 \times 3 \times 6.023 \times 10^{23} = 4.517 \times 10^{23} \text{ atoms}$$

Problem 10 How many gram atoms of oxygen and hydrogen are there in 0.2 moles of water ? What are the number of atoms of each element present in this quantity of water ?

Solution 1 mole of H_2O or 18g of H_2O contains 2 gram atomic mass of hydrogen and 1 gram atomic mass of oxygen.

So, 0.2 moles of water will contain

$2 \times 0.2 = 0.40$ gram atomic mass of hydrogen

and $1 \times 0.2 = 0.20$ gram atomic mass of oxygen

Now, the number of hydrogen atoms = $0.40 \times 6.023 \times 10^{23} = 2.409 \times 10^{23}$ atoms

and the number of oxygen atoms = $0.20 \times 6.023 \times 10^{23} = 1.205 \times 10^{23}$ atoms

Problem 11 What will be number of molecules of a gas occupying 280 ml at NTP ?

(C.H.S.E 1987 (A))

Solution 280 ml of the gas = 0.28 litres of the gas

$$\text{So number of molecules} = \frac{0.28 \times 6.023 \times 10^{23}}{22.4} = 7.529 \times 10^{21} \text{ molecules}$$

Problem 12 A tetra-atomic gas occupies 1.4 litres at 0°C and 760 mm pressure. Find the number of atoms in the gas.

Solution Number of molecules of the gas present = $\frac{1.4}{22.4} \times 6.023 \times 10^{23}$ molecules.

Since the gas is tetra-atomic, one molecule contains 4 atoms.

$$\begin{aligned} \text{Therefore, the number of atoms present in the gas} &= \frac{1.4}{22.4} \times 6.023 \times 10^{23} \times 4 \\ &= 1.505 \times 10^{23} \text{ atoms.} \end{aligned}$$

Problem 13 Density of water at room temperature is 1.0 g./ml. How many molecules are there in a drop of water if the volume is about 0.05 ml ?

Solution Weight of 1 drop or 0.05 ml of H_2O = $\frac{0.05}{1} = 0.05$ g

Since molecular mass of water is 18,

number of moles of H_2O in 0.05g of it = $\frac{0.05}{18}$

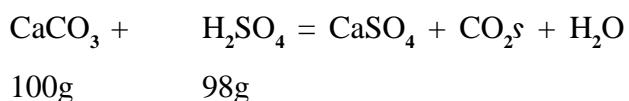
Each mole of water contain 6.023×10^{23} molecules.

Hence, The number of water molecules in one drop

$$= \frac{0.05}{18} \times 6.023 \times 10^{23} = 1.673 \times 10^{21} \text{ molecules.}$$

Problem 14 Calculate the weight of 60% sulphuric acid required to decompose 25 g of chalk, calcium carbonate. (Ca = 40, C = 12, O = 16, S = 32)

Solution Chemical reaction :



From the above equation it is known that 98g of H_2SO_4 required to decompose 100g of chalk (CaCO_3).

So, weight of H_2SO_4 required to decompose 25g of chalk

$$= \frac{98 \times 25}{100} = 24.5\text{g.}$$

Since, 60g of H_2SO_4 are contained in 100 gm of 60% H_2SO_4 ,

$$\begin{aligned} & 24.5 \text{ g of } 100\% \text{ H}_2\text{SO}_4 \\ & = \frac{100 \times 24.5}{60} = 40.83\text{g of } 60\% \text{ H}_2\text{SO}_4. \end{aligned}$$

QUESTIONS

A. Very short answer type (1 mark each)

State true or false :

1. Avogadro number has value 6.023×10^{23} .
2. Equal volumes of all gases contain equal number of molecules at all temperature and pressure.
3. Half a molecule of oxygen is equal to one atom of oxygen.
4. Avogadro's hypothesis explains the law of gaseous volume.
5. Atomicity is equal to valency of an element.
6. One mole of hydrogen contains 6.023×10^{23} atoms.
7. 6.023 molecules of hydrogen weigh 1 gram.

8. 2 grams molecular mass of a substance contain 2 moles.
9. 1 mole of chlorine occupies 22.4 ml at NTP.
10. 1 mole of electrons contains 6.023×10^{22} electrons.
11. One mole of KClO_3 contains 18.069×10^{23} atoms of oxygen.
12. Molecular mass = 22.4 litres at 27°C .
13. Gram molecular volume of any substance at NTP is 22.4 litres.
14. One mole of oxygen contains 2 gm atoms.

B. Short answer type (1 mark)

1. How many atoms are present in 10 gms of calcium carbonate ?
2. What is the mass of 224ml of oxygen at NTP ?
3. What is the volume of 17.75 g of chlorine at NTP ?
4. What is the mass of 2.8 litres of CO_2 at NTP ?
5. How many electrons are there in ammonium ion ?
6. How many atoms of oxygen are present in 4.4 gms of CO_2 at NTP ?
7. How many gms of H_2O_2 are present in 1 litre of 20 volumes of H_2O_2 solution ?

C. Short answer type (2marks each)

1. What is Avogadro's number ?
2. State Berzelius hypothesis
3. State Avogadro's law.
4. What is meant by atomicity of a gas ?
5. What is vapour density ?
6. What is the relationship between vapour density and molecular mass ?
7. Define gram molecular volume.
8. Define gram molecular mass.
9. Write the merits of Avogadro's hypothesis.

D. Long Answer Type (7 marks each)

1. State Avogadro's hypothesis. What are its applications ? The vapour density of a gas is 11.2. Calculate the volume occupied by 1.6 grams of the gas at STP.
2. State and explain Avogadro's hypothesis. Derive the relations between molecular mass and vapour density of a gas.
3. (i) Determine the atomicity of oxygen by applying Avogadro's law,
(ii) Derive from the Avogadro's law that molecular mass is equal to mass of 22.4 litres of gas or vapour at NTP.
4. State and explain Avogadro's law. How does it explain Gay-Lussac's law of gaseous volumes. How it could discard Berzelius hypothesis ?
5. State and explain Avogadro's hypothesis. How is the hypothesis applied to determine the gram molecular mass and molecular formulae of gases ?

6. Derive the relationship between molecular mass and vapour density of a gas from Avogadro's hypothesis. 0.796 g of a metal oxide was heated in a current of dry hydrogen when 0.18g of water was formed. Calculate the equivalent mass of the metal.
7. What is Avogadro's hypothesis ? How can it be derived from combined gas equation ? 1.40 litre of a gas at 27°C and 900 mm pressure weighs 3.5g. Calculate the molecular mass of this gas.

E. Numerical Problems : (3 marks)

1. (a) How many molecules will be present in one gram molecular mass of hydrogen gas ?
 (b) How many atoms of hydrogen are present in two moles of H_3PO_4 ?
2. How many atoms of oxygen are present in one gram of oxygen ?
3. How many calcium atoms are present in 10 g of CaCO_3 ?
4. (a) How many moles of hydrogen molecules are present in one mole of hydrogen peroxide ?
 (b) How many molecules of oxygen are present in one mole of sulphuric acid ?
5. How many molecules are there in 90 gms of H_2O ?
6. How many atoms are present in 49 gms of sulphuric acid ?
7. What is mass of half mole of nitrogen atom ?
8. Avogadro's number of helium atoms weigh how many grams ?
9. How many moles do 3g of water represent ?
10. How many moles do 2×10^{22} molecules of hydrogen represent ?
11. A piece of copper weighs 0.635 g. How many atoms of copper does it contain ?
12. Between 1 gram of water and 1 gram of methanol, which has more number of molecules ?
13. What will be the weight of 1×10^{22} molecules of ammonia ?
14. What is the mass of 2.5×10^{23} atoms of nitrogen ?
15. What is the mass of a carbon dioxide molecule ?
16. Calculate the number of molecules present in carbon dioxide gas weighing 4.4g.
17. Calculate the number of moles in 30 gms of sodium hydroxide.
18. Calculate the mass of 1 ml. of hydrogen at NTP.
19. Find the volume occupied by 6.023×10^{23} molecules of oxygen at NTP.
20. 5.6 litres of gas at NTP weighs 8.25 gms. Calculate its vapour density.
21. Calculate the density of nitrogen at NTP.
22. Calculate the number of electrons present in 0.3 mole of electrons.
23. How many moles of water should be electrolysed to produce 80g of oxygen ?
24. Find out the amounts of magnesium and oxygen consumed to prepare 60g of magnesium oxide.
25. What would be the volume of 44 grams of CO_2 at NTP ?
26. What volume of CO_2 is liberated at NTP from 0.1 mole of CaCO_3 ?

27. What weight of water will be formed by the combination of 11.2 litres of oxygen at NTP with excess of hydrogen ?
28. 6 gms of carbon was completely burnt in oxygen. What would be the volume of carbon dioxide produced at NTP and how many molecules will be present in that gas ?
29. Calculate the volume of oxygen at STP required to completely burn 30ml of acetylene at STP.
30. Calculate the total number of electrons present in 2.24 litres of methane at NTP.
31. What is the mass of one mole of electrons ?
32. How many atoms of fluorine are there in 1.9×10^{-6} gms of Fluorine ? ($F = 19$ amu)

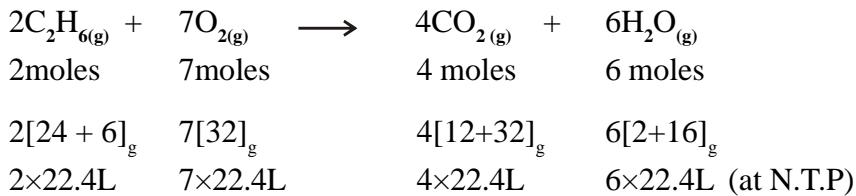
ANSWERS

- A. 1. True 2. False 3. True 4. True 5. False 6. False 7. False 8. True. 9. False 10. False
11. True **12.** False **13.** True. **14.** True.
- C. 1. 1.6 litres.
- E. 1. (a) 6.023×10^{23} molecules (b) $3 \times 2 \times 6.023 \times 10^{23}$ atoms 2. 3.76×10^{23} atoms
3. 6×10^{22} atoms **4.** (a) 1 mole (b) $2 \times 6.023 \times 10^{23}$ molecules **5.** 3.0115×10^{24} molecules **6.** 2.108×10^{24} atoms **7.** 7g **8.** 4g **9.** 0.167 mole **10.** 0.333 mole **11.** 6.023×10^{21} atoms. **12.** 1g of water **13.** 0.282 g **14.** 5.81g **15.** 7.3×10^{-23} g **16.** 6.023×10^{22} molecules **17.** 0.75 mole **18.** 0.00009g **19.** 22.4 litres **20.** 16.5 **21.** 0.00125 gm/ml **22.** 1.807×10^{23} electrons **23.** 5moles **24.** Mg 36g & oxygen 24g **25.** 22.4 litres **26.** 2.24 litres **27.** 18g **28.** 11.2 litres, 3.01×10^{23} molecules **29.** 75 ml.
30. 6.023×10^{23} electrons. **31.** $9.1 \times 6.023 \times 10^{-5}$ g. **32.** 6.023×10^{16} atoms.

2.11 STOICHIOMETRY (CALCULATIONS BASED ON CHEMICAL EQUATION)

A chemical change is represented both qualitatively and quantitatively by a chemical equation. Since a symbol or a formula has a quantitative meaning, a balanced chemical equation gives quantitative informations regarding reactants and products. Calculations based on chemical equations are known as **stoichiometric calculations**. They take into account the molecule, molecular mass, mole concept, gram molar volume etc. in their calculation.

Let us consider the combustion of ethane (C_2H_6). The balanced equation of the chemical change is represented by



The above chemical equation means-

2moles of $\text{C}_2\text{H}_{6(\text{g})}$ reacts with 7 moles of $\text{O}_{2(\text{g})}$ to give

4 moles of $\text{CO}_{2(\text{g})}$ and 6 moles of $\text{H}_2\text{O}_{(\text{g})}$

60g of $\text{C}_2\text{H}_{6(\text{g})}$ reacts with 224g of $\text{O}_{2(\text{g})}$ to gives

176g of CO_2 and 108 g of $\text{H}_2\text{O}_{(\text{g})}$

44.8L of $\text{C}_2\text{H}_{6(\text{g})}$ reacts with 156.8 L of $\text{O}_{2(\text{g})}$ to give

89.6L of $\text{CO}_{2(\text{g})}$ and 134.4L of $\text{H}_2\text{O}_{(\text{g})}$ (all measured under N.T.P)

From this, it is evident that mole, molecular mass and volume are all correlated.

The calculations based on chemical equations are of three types :

- (i) calculations based on mass-mass relationship
- (ii) calculations based on mass-volume relationship
- (iii) calculations based on volume-volume relationship

Calculations based on mass-mass relationship

In general, the following steps are followed for the calculation.

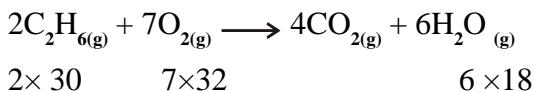
- (a) First write down the balanced chemical equation.
- (b) Write down the molecular masses along with their respective coefficients multiplied with molecular masses (written below the respective species). These represent the theoretical amount of the reactants and products.
- (c) Then establish the mass-mass relationship and find out the mass of the required species by unitary method.

Example -1.

Calculate the mass of O_2 required for completely burning 30g of ethane to produce CO_2 . Also calculate the mass of H_2O produced during the reaction.

Solution :

The balanced chemical equation is



For burning 60g of ethane, O_2 required in 224g

Thus, for burning 30g of ethane, O_2 required will be $\frac{224 \times 30}{60} \text{g} = 112\text{g}$

On burning 60g of ethane, H_2O produced is 108g

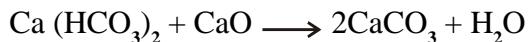
Thus, on burning 30g of ethane, H₂O produced will be $\frac{108}{60} \times 30\text{g} = 54\text{g}$

Example -2

Calculate the mass of lime required to remove the hardness of 10,00,000 L of water containing 16.2g of calcium bicarbonate per litre.

Solution :

Ca(HCO₃)₂ in water causes hardness. Lime (CaO) reacts with Ca(HCO₃)₂ present in hard water precipitating CaCO₃ and thus removes hardness.



162 56

Total amount of Ca(HCO₃)₂ present in 10,00,000 L of water

$$= 16.2\text{g L}^{-1} \times 10,00,000\text{L} = 16200 \text{ kg}$$

162 g of Ca(HCO₃)₂ requires 56g of lime (as per equation)

$$16200 \text{ kg of Ca}(\text{HCO}_3)_2 \text{ will require } \frac{56\text{g}}{162\text{g}} \times 16200 \text{ kg} = 5600 \text{ kg of lime.}$$

Hence, 5600 kg of lime will be required for removing hardness.

Limiting reagent : Often, reactions are carried out when the reactants are not present in the amounts required by a balanced chemical reaction. The reactant which is present in the lesser amount gets consumed and no further reaction takes place even though the other reactant is present. Thus, the reactant present in lesser amount limits the amount of product formed and is, therefore named as **limiting reagent**.

In stoichiometric calculations, this fact should be borne in mind.

Example - 3

100g sample of calcium carbonate is allowed to react with 75g of orthophosphoric acid.

Calculate the mass of calcium phosphate that could be produced and the mass of excess reagent that will remain unreacted.

Solution :

The balanced equation is represented as



3 mole 2mole 1 mole

$$3[40 + 12 + 48] \quad 2[3 + 31 + 64] \quad [3 \times 40 + 2 \times 95]$$

300g 196g 310g

300g of CaCO₃ produce Ca₃(PO₄)₂ = 310 g or 1 mole

$$100\text{g of CaCO}_3 \text{ will produce } \frac{310}{300} \times 100 = 103 \text{ g or } 0.33 \text{ mole of Ca}_3(\text{PO}_4)_2$$

or, 196g of H₃PO₄ produce Ca₃(PO₄)₂ = 310g or 1 mole

$$75\text{g of H}_3\text{PO}_4 \text{ will produce Ca}_3(\text{PO}_4)_2 = \frac{310}{196} \times 75 = 118.6\text{g or } 0.38 \text{ mole}$$

The values show that CaCO_3 is the limiting reagent.

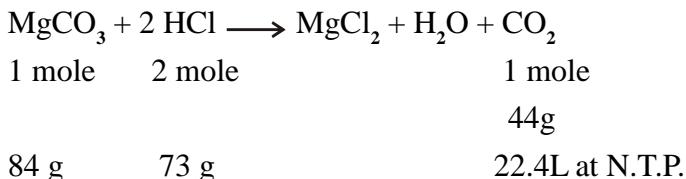
Therefore, $\text{Ca}_3(\text{PO}_4)_2$ formed is 0.33 mole or 103 g.

For producing 103g of $\text{Ca}_3(\text{PO}_4)_2$, H_3PO_4 required will be $= \frac{196}{310} \times 103 = 65.12\text{g}$

Therefore, mass of remaining $\text{H}_3\text{PO}_4 = (75 - 65.12)\text{g} = 9.88\text{g}$

Calculations based on mass-volume relationship

These calculations are based on the fact that 1 mole or 1 gram molecular mass of the substance occupies 22.4 litres or 22400 mL at N.T.P. The following example shows the mass-volume relationship.



Volume of a gas at any temperature and pressure can be converted to mass or vice-versa using the equation

$$PV = \frac{W}{M} RT$$

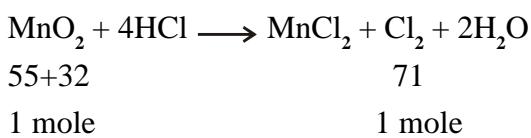
where W = mass of the gas with molecular mass M and R is molar gas constant. P, V & T have their usual meaning.

Example -1

What volume of chlorine gas at N.T.P. will be produced when 8.7g of MnO_2 reacts with excess of conc. HCl ? (Mn = 55, O = 16, Cl = 35.5)

Solution :

The balanced reaction is



One mole i.e. 87g of MnO_2 produce 22.4L of Cl_2 at N.T.P.

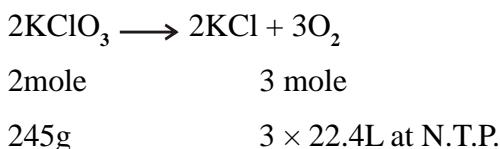
Hence, 8.7g of MnO_2 will produce 2.24L of Cl_2 at N.T.P.

Example -2

10g of an impure sample of potassium chlorate on complete decomposition gave 1.12 litre of oxygen at N.T.P. What is the percentage purity of the sample of potassium chlorate ?

Solution :

The balanced equation for decomposition is



$3 \times 22.4\text{L}$ of O_2 is obtained from $\text{KClO}_3 = 245\text{g}$
 1.12 L of O_2 will be obtained from $\text{KClO}_3 = \frac{245\text{g}}{3 \times 22.4\text{L}} \times 1.12\text{ L} = 4.08\text{g}$

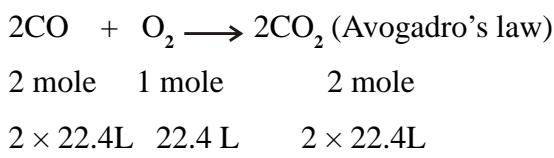
10g of sample contains $\text{KClO}_3 = 4.08\text{g}$
Percentage purity of the sample = $\frac{\text{Amount of pure sample}}{\text{Amount of impure sample}} \times 100$
 $= \frac{4.08\text{g}}{10\text{g}} \times 100 = 40.8$

Calculations based on volume - volume relationship

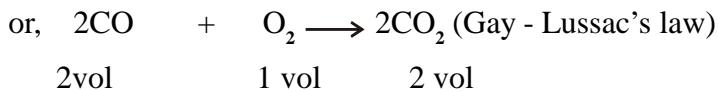
These calculations are based on two laws :

(i) Avogadro's law & (ii) Gay-Lussac's law

For example,



(Under similar conditions of temperature and pressure, equal moles of gases occupy equal volumes)



(Under similar conditions, gases react in simple ratio of their volumes)

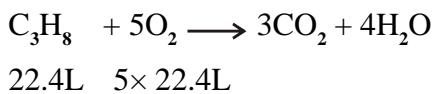
It may be remembered that the law holds good only for gaseous reactants & products, which do not liquify on cooling.

Example -1

What volume of oxygen at N.T.P. is necessary for complete combustion of propane (C_3H_8) measured at 27°C and 760 mm of Hg.

Solution :

The balanced chemical equation is



Since the volume of propane is at 27°C & 760 mm of Hg pressure, it has to be converted to N.T.P. condition applying gas law. Pressure remains constant at 760 mm of Hg. Therefore, according to Charle's law,

$$\text{Volume at NTP} = \text{Given volume} \times \frac{273\text{K}}{(27+273)\text{K}} = 20\text{ L} \times \frac{273}{300} = 18.2\text{ L}$$

Hence, 18.2 L of propane will undergo combustion at N.T.P.

$$22.4\text{ L of C}_3\text{H}_8 \text{ requires O}_2 = 5 \times 22.4\text{L} = 112\text{L}$$

$$18.2\text{ L of C}_3\text{H}_8 \text{ will require } \frac{112\text{L}}{22.4\text{L}} \times 18.2\text{L} = 91.0\text{ L}$$

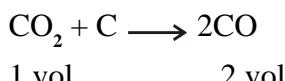
Therefore, 91 L of O_2 at N.T.P. is necessary for complete combustion of C_3H_8

Example -2

One litre of a mixture of carbon monoxide and carbondioxide is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. Volumes are measured under similar conditions. Find the composition of gaseous mixture. [I.I.T. 1980]

Solution :

When the mixture is passed through red hot charcoal, only CO_2 is reduced to carbon monoxide resulting in the increase in volume according to the equation



Let the volume of CO_2 in the mixture = x L

volume of CO in the mixture will be = $(1 - x)$ L

x vol. of CO_2 produce $2x$ vol. of CO

Total volume of CO = $2x + 1 - x$

$$= (1 + x) \text{ vol} = 1.6 \text{ L} \text{ (Given)}$$

Therefore, $x = 0.6 \text{ L}$ = volume of CO_2 in the mixture.

and volume of CO in the mixture = $(1 - 0.6) \text{ L} = 0.4 \text{ L}$

Example -3

A gas mixture of 3 litres of propane (C_3H_8) and butane (C_4H_{10}) on complete combustion of gas at 25°C produced 10 litres of CO_2 . Find out the composition of the mixture.

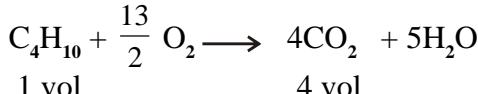
Solution :

Let x litre of C_3H_8 and y litre of C_4H_{10} be present in the mixture.

$$x + y = 3 \text{ (given)} \dots \text{(i)}$$



1 vol	3 vol
-------	-------



CO_2 formed by $\text{C}_3\text{H}_8 = 3x$

CO_2 formed by $\text{C}_4\text{H}_{10} = 4y$

$$3x + 4y = 10 \text{ (given)} \dots \text{(ii)}$$

Solving equations (i) and (ii)

$$x = 2 \text{ litre} = \text{volume of } \text{C}_3\text{H}_8$$

$$y = 1 \text{ litre} = \text{volume of } \text{C}_4\text{H}_{10}$$

QUESTIONS

(Stoichiometric Calculations)

1. 1.5g of an impure sample of Na_2CO_3 is dissolved in water. On adding excess amount of CaCl_2 solution, a white precipitate was obtained which was filtered, dried and found to weigh 1g. Calculate the percentage purity of the Na_2CO_3 sample.
2. Find out the amount of litharge (PbO) produced by heating 132.4g of lead nitrate of 50% purity. ($\text{Pb} = 207.2$) (Ans. 44.6g)
3. A 2g sample containing Na_2CO_3 and NaHCO_3 loses 0.248g when heated to 300°C , the temperature at which NaHCO_3 decomposes to Na_2CO_3 , CO_2 and H_2O . What is the percentage of Na_2CO_3 in the mixture ? [Ans. 66.4%]
4. 2g of a mixture of NaCl and KCl was dissolved in water and the resulting solution was treated with excess of AgNO_3 solution. AgCl when weighed after drying was found to be 4.483g. Calculate the percentage composition of the mixture. [Ans. $\text{NaCl} = 59.85\%$, $\text{KCl} = 40.15\%$]
5. How many litres of oxygen at NTP is required to burn completely 2.2 g of propane (C_3H_8) ? [Ans. 5.6L]
6. How much KClO_3 is needed to produce oxygen enough for burning 10g of coke ? (Ans. 68.05g)
7. 1.84 g of a mixture of CaCO_3 and MgCO_3 is strongly heated till no further loss of weight takes place. The residue weighs 0.96g. Calculate the percentage composition of the mixture. ($\text{Ca}=40$, $\text{Mg} = 24$) [Ans. 54.3% : 45.7%]
8. What volume of CO_2 at STP can be obtained from 500 g of marble containing 80% CaCO_3 ? [Ans : 89.6L]
9. 8.7g pure MnO_2 is heated with excess of HCl and the gas evolved is passed through a solution of KI. Calculate the mass of iodine liberated ($\text{Mn} = 55$, $\text{Cl} = 35.5$, & $\text{I} = 127$) [Ans. 25.4g]
10. How many grams of potassium permanganate completely oxidise 4.5g of oxalic acid present in an acid solution ? ($\text{K} = 39$, $\text{Mn} = 54.94$, $\text{C} = 12$) [Ans. 3.16g]
11. 5g of a natural gas consisting of methane and ethylene was burnt in excess of oxygen producing 14.5g of carbon dioxide and some amount of water as products. Find out the percentage of ethylene in the natural gas. (Ans. 40.4%)

Multiple choice questions

Select the correct answer for the following.

1. The number of grams of oxygen which will completely react with 27g of aluminium is
 (a) 8 g (b) 16g (c) 24 g (d) 32g [Ans. (c)]

2. 2.76 g of silver carbonate on being strongly heated yield a residue weighing
(a) 2.48g (b) 2.16g (c) 2.32g (d) 2.64g [Ans. (b)]
3. The mass of CO_2 produced by heating 21g of NaHCO_3 is
(a) 5.5g (b) 11.0g (c) 7.5g (d) 5.9g [Ans. (a)]
4. The amount of zinc (65) required to produce 224 mL of H_2 at S.T.P on treatment with dil. H_2SO_4 will be
(a) 0.65g (b) 6.5g (c) 65g (d) 0.065g [Ans. (a)]
5. 56g of CaO has been mixed with 63g of HNO_3 . The amount of calcium nitrate formed will be
(a) 4g (b) 3.28g (c) 164 g (d) 82g [Ans.(d)]
6. 10mL of gaseous hydrocarbon on combustion gives 40mL of $\text{CO}_2(\text{g})$ and 50mL of H_2O (vap). The hydrocarbon is
(a) C_4H_5 (b) C_8H_{10} (c) C_4H_8 (d) C_4H_{10} [Ans. (d)]
7. 4L of CO at NTP will require for complete oxidation, the volume of O_2 at NTP
(a) 4L (b) 8L (c) 2L (d) 1L [Ans (c)]
8. The minimum quantity of H_2S needed (in g) to precipitate 63.5g of Cu^{2+} will be nearly
(a) 63.5g (b) 31.75g (c) 34g (d) 20g [Ans. (c)]
9. Which of the following will have largest number of atoms ?
(a) 1gAu(s) (b) 1gNa(s) (c) 1gLi(s) (d) 1g of $\text{Cl}_2(\text{g})$ [Ans. (b)]

□□□

UNIT - II

CHAPTER - 3

STRUCTURE OF ATOM

3.1 FUNDAMENTAL PARTICLES AND THEIR PROPERTIES

John Dalton (1809) developed famous "atomic theory". He considered the atom as a hard, dense and **smallest indivisible particle of matter**. According to the theory each element consists of a particular kind of atoms differing in mass. But the mass difference of atoms of different elements could not be explained by him. Subsequent investigators were of the opinion that there should be some material difference for making atoms of different elements. But the experimental evidence in support of it was obtained during the last part of nineteenth century. The passage of electricity through gases at very low pressure and discovery of radioactivity showed the presence of three fundamental particles i.e. **electron, proton and neutron** in the atoms.

CONDUCTION OF ELECTRICITY THROUGH GASES - CATHODE RAYS DISCOVERY OF ELECTRON

Normally gases are poor conductors of electricity. But under the influence of high voltage (20,000 - 30,000 volts) gases conduct electricity. Even very interesting results are obtained at low pressure. Experiments were conducted in discharge tubes of hard glass of 60 cm length and 4 cm in diameter closed at both ends. (Fig. 3.1) Two metal electrodes 'C' and 'A' were fused into the tube and a side tube was connected to the vacuum pump 'V'.

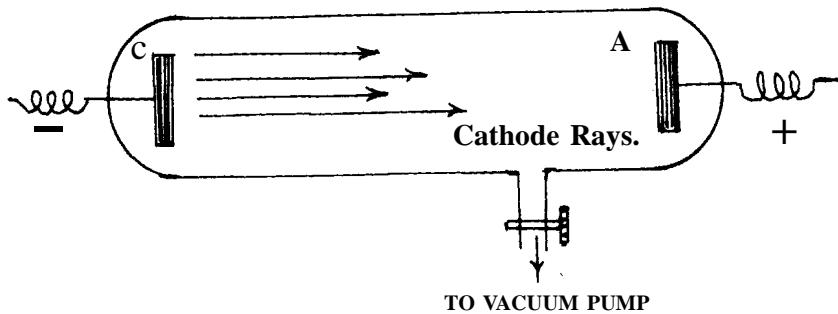


Fig. 3.1 Production of Cathode Rays.

When pressure was reduced inside the tube to 0.06 - 0.03 mm by operating the vacuum pump and a high potential of 20,000 volts was applied across the terminals of the tube, the tube began to glow and a stream of faint greenish light was seen to travel from Cathode. These were known as **Cathode rays**.

Properties of Cathode Rays :

1. These rays travel in straight lines with velocity approaching the velocity of light and cast shadows of objects placed in their path.
2. These are considered to be possessing energy as they rotate a small paddle wheel placed in their path.
3. These rays penetrate through, thin metal sheets, produce phosphorescence, affect photographic plates, ionise gases and produce X-rays on striking a metal target.
4. These rays are deflected in electric and magnetic fields and consist of negatively charged particles as found by its deflection in an electric field (Fig 3.2). On applying electric field across the tube, the rays are bent towards the positive plate.

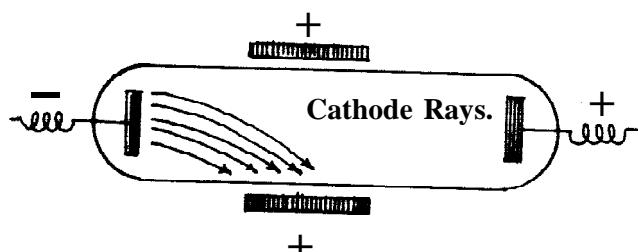


Fig 3.2 Deflection of cathode rays in electric field.

Therefore, Cathode rays consist of negatively charged particles. These negatively charged particles are called **electrons**.

J. J. Thompson carried out a number of experiments to find out charge and mass of the electron. Charge of the electron was found to be 1.602×10^{-19} coulomb. Mass of the electron was found to be 9.1×10^{-28} g.

$$\frac{\text{charge}}{\text{mass}} \text{ of electron } (\frac{e}{m}) = 1.7599 \times 10^8 \text{ coulombs per gram.}$$

Thompson carried out a number of measurements on the value of e/m of Cathode rays in which he varied the metal forming the Cathode as well as the gas in the vacuum tube. In every case the ratio of charge to mass (e/m) was the same. Millikan found that charge (e) on each electron was 1.602×10^{-19} coulomb, irrespective of the gas taken inside the tube. From these observations, it was concluded that **electrons are universal constituent of matter**.

Discovery of Protons :

Positive Rays : Since electron is an essential constituent of atom and atom as a whole is electrically neutral, it follows that an equal magnitude of positive electricity must also be present in the atom.

In 1886, M. Goldstein experimented with discharge tubes containing perforated cathode and showed the presence of another type of radiation that passed through the holes in the cathode and carried positive charge. These rays were called **positive rays or anode rays**. (Fig. 3.3)

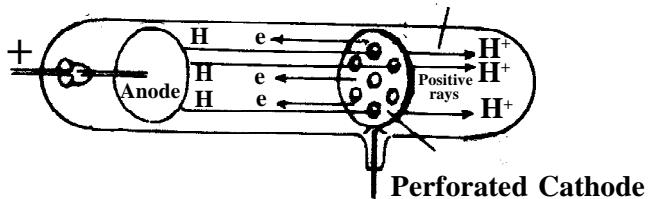


Fig. 3.3 Positive Rays or Anode Rays.

Properties of Anode Rays :

1. These travel in a straight line.
2. These rays cause phosphorescence, affect photographic plate, and penetrate through very thin aluminium foils.
3. These rays are deflected by electric and magnetic field, but deflection takes place in opposite direction to that of the electrons. Thus, these rays are found to be positively charged.

The ratio of charge to mass (e/m) of positive rays was determined by taking different gases in the discharge tube. Hydrogen gave the highest value for e/m . This shows that if charge (e) is the same in the case of each gas, the mass (m) of positive ray particle produced in the hydrogen tube is the lowest. It was concluded that the positive particle given out by hydrogen is one of the fundamental particles of matter. Its **charge was found to be equal in magnitude but opposite in sign to that of the electron. Mass was found to be 1.672×10^{-24} gm. This lightest positive particle is known as proton.**

Existence of charges on cathode and anode rays indicates that atom consists of one or more electrons and a positive residue. Since electrons have negligible mass, it follows that **almost the entire mass of atom is associated with the positive residue.**

Discovery of Neutron : In 1932, James Chadwick bombarded thin sheets of light elements such as Beryllium, Boron etc with α -particles. It was observed that a stream of highly penetrating rays were produced. These rays were found to consist of neutral particles. These neutral particles were found to have a mass of 1.675×10^{-24} gm. **These particles were called neutrons.** Neutron is present in all atoms excepting hydrogen atom.

3.2 THOMSON'S MODEL FOR THE STRUCTURE OF ATOM

After the discovery of the sub-atomic particles, the electrons, protons and neutrons, several models for the structure of atom were proposed. The first model of the atom was proposed by Sir J.J. Thomson in 1898. He assumed that the basic body of an atom is a spherical object containing electrons confined in homogeneous jelly like but relatively massive positive charge distribution whose total charge cancels that of the number of electrons present. The schematic drawing of the model is shown in fig. Thomson's model is sometimes called a **plum pudding** model. This model was soon discarded and is only of historical importance.

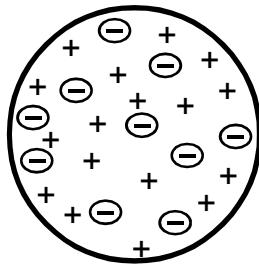


Fig. 3.4 Thomson's model of atom

Defects : Thomson's model of the atom could not explain the large angle scattering of α -particles. Further, it could not explain the experimental observations of the atomic spectra of elements.

3.3 RUTHERFORD'S EXPERIMENT - SCATTERING OF α - PARTICLES.

In 1911 E.Rutherford performed experiments with α -particles which gave insight into the structure of atom. A radioactive substance spontaneously emits radiations consisting of α -particles which are positively charged, β -particles which are negatively charged and γ -rays which are neutral. In fact α -particles are doubly charged helium nucleus. It carries two units of positive charge and has mass equal to four times that of hydrogen atom.

Rutherford produced α -particles from a radioactive source (polonium) and bombarded it with thin (0.00004 cm thick) sheet of silver or gold metal. After passing through the metal sheet, α -particles struck a zinc sulphide screen.

It was found that most of the α -particles passed through the metal sheet with no change in their path. Only very few were deflected from the original path through wider angles. Only 1 out of 20,000 α -particles was deflected backwards retracing the path. (Fig 3.5)

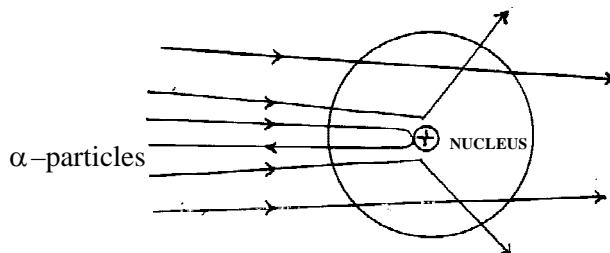


Fig 3.5 Scattering of α -particles by the atom.

Rutherford after carrying out a series of experiments concluded that

- (1) Since most of the α particles pass through the metal sheet, without being deflected, it is concluded that **the atom consists of empty space predominantly**.
- (2) Since a few of the α -particles (having appreciable mass and positive charge) get deflected through wide angles or even backwards, there must be present in the atom a heavy positively charged mass. For such large scattering of α -particles, these must have come close to even collide with the positively charged body of heavy mass.
- (3) Since only very few α -particles suffer such deflection, the volume occupied by this heavy positively charged mass is a very small fraction of the volume of the atom and present in the centre of the atom.

RUTHERFORD'S NUCLEAR MODEL

Based on his observations and conclusions derived from it Rutherford proposed a nuclear model of atom. According to this model, **the atom consists of a minute but heavy**

positively charged body at its centre, called the nucleus. Since atom is largely empty and electrons have negligible mass, the entire mass of the atom is due to the protons present in the nucleus. Positive charge of the nucleus is due to the presence of the protons. Electrons are referred as planetary electrons which move round the nucleus in different orbits or path just as planets move round the sun. Thus, atom was compared to a **mini solar system**.

Since the atom is electrically neutral, the number of planetary electrons is equal to the number of protons present in the nucleus.

From the Scattering experiments, Rutherford also calculated that the nucleus has a diameter of the order of 10^{-13}cm Where as the atom has a diameter of the order of 10^{-8}cm . To justify the revolving of the electrons around the nucleus without falling into the nucleus, Rutherford suggested that the attraction forces acting between the electrons and the nucleus acting towards the nucleus is balanced by the centrifugal force due to movement of electrons acting away from the nucleus.

MOSLEY'S EXPERIMENT AND CONCEPT OF ATOMIC NUMBER

In 1913, H.G.J. Mosley, a young British physicist working in Rutherford's laboratory, devised a method to find out the exact charge on the nucleus. He produced X-rays by bombarding different elements (used as anode in discharge tubes) with cathode rays. He suggested that the frequency of X-rays produced in this manner was related to the charge present in the nucleus of an atom of the element used as anode. Data obtained by him fitted to the equation.

$$\sqrt{v} = a(Z-b)$$

where 'v' is the frequency of X-ray, 'Z' is the nuclear charge and 'a' and 'b' are constants. Mosley found that the nuclear charge increases by one unit in passing from one element to the next arranged by Mendeleeff in the order of increasing atomic weight. Increase in positive charge on the nucleus was taken to imply an increase in the number of protons in the nucleus.

The number of unit positive charge carried by the nucleus of an atom is termed as the atomic number of the element.

Therefore, **atomic number** of an element (Z)

- = Number of unit positive charges present in the nucleus.
- = Number of protons present in the nucleus.
- = Number of electrons present outside the nucleus of the atom .

Thus, **atomic number** is taken as a **fundamental property** of an element. The elements are now arranged in the periodic table in the order of increasing atomic numbers.

Mass number : The sum of the number of protons and neutrons is called the mass number. Since each proton and each neutron has a mass approximately equal to 1, on the atomic weight scale, the **atomic weight of an element is approximatley equal to its mass number** (A). Knowing the atomic number (Z) and mass number (A) of an element, the number of protons, neutrons and electrons can be calculated.

If the mass number of an elements X is 'A' and its mass number is 'Z', then the element can be represented as ${}^A_Z\text{X}$. Then, the number of protons = Z, number of electrons = Z, and number of neutrons = A – Z

For example, in case of sodium atom, $Z = 11$, $A = 23$.

Then, number of protons = 11, number of electrons = 11
and number of neutrons = $23 - 11 = 12$.

ISOTOPES, ISOBARS AND ISOTONES :

Isotopes : Isotopes are defined as the atoms of the same element which has the same atomic number but different mass numbers. Isotopes have same physical and chemical properties, same atomic number, same position in the periodic table, but different number of neutron and different atomic weights, density, atomic volume, melting and boiling points.

For example, hydrogen has three isotopes.

Protium (ordinary hydrogen) ${}^1_1\text{H}$

Deuterium ${}^2_1\text{H}$ (mass number – 2)

Tritium ${}^3_1\text{H}$ (mass number – 3)

Isobars : Isobars are the atoms of different elements having the same mass number but differ in their atomic numbers. These have different physical and chemical properties, different atomic numbers, different position in the periodic table.

For example, Argon = ${}^{40}_{18}\text{Ar}$

Calcium = ${}^{40}_{20}\text{Ca}$

Isotones : Atoms of different elements which possess the same number of neutrons are called isotones.

For example, ${}^{76}_{32}\text{Ge}$ and ${}^{77}_{33}\text{As}$ (contain 44 neutrons each).

DEFECT OF RUTHERFORD'S MODEL

In view of Clark Maxwell's classical electromagnetic theory Niels Bohr pointed out that Rutherford's atom should be highly unstable. Clark Maxwell had shown that **whenever an electric charge is subjected to acceleration, it emits radiation and loses energy**. Bohr argued that an electron (charged particle) moving round the nucleus in an orbit will be subjected to acceleration due to continuous change in its direction of motion. Therefore, the electron will continuously emit radiation and lose energy, as a result of which the curvature of the path (orbit) of the electron will decrease and ultimately it will fall into the nucleus (Fig.6.6). Bohr modified the defect in the Rutherford's model and provided the Bohr's model of atom.

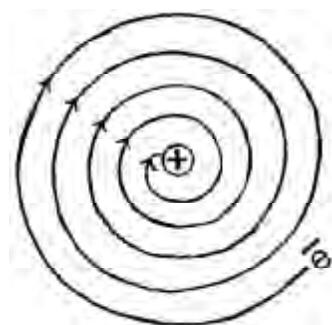


Fig 3.6 Decrease in path of the electron.

3.4 CHARACTERISTICS OF RADIATION AND PLANCK'S QUANTUM THEORY

Light, X - rays, infrared and ultraviolet rays are some examples of radiant energy. Clark Maxwell proposed that radiant energy has **wave character**. He called radiant energy as electromagnetic radiations or electromagnetic waves. The term electromagnetic was used because similar waves can be produced by moving a charged body or a magnet to and fro in an oscillating manner. Electromagnetic waves do not need any medium for propagation.

There are three fundamental characteristics of wave motion i.e.wavelength, frequency velocity and amplitude.

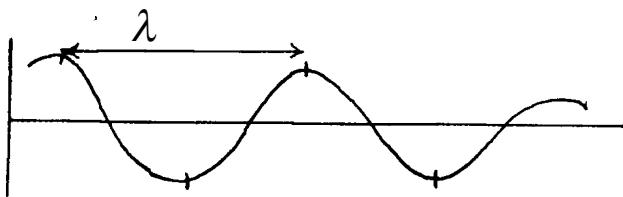


Fig 3.7 Wave motion

Wave length —The distance between two nearest crests or troughs. It is denoted by "λ" (lambda) and is expressed in centimetres or Angstrom (A^0) units $1 \text{ A}^0 = 10^{-8}\text{cm}$.

Amplitude – Height of crest or depth of trough of a wave

Frequency – The number of times a wave passes through a given point in one second. It is denoted by 'ν' (nu)

Velocity – The distance travelled by the wave in one second. It is denoted by 'C'.

The product of wavelength and frequency gives the velocity.

$$\text{Thus, } C = \nu \lambda \quad \text{or} \quad \nu = \frac{C}{\lambda}$$

All types of electromagnetic radiations travel with the same velocity but their wavelength and frequency are different.

Planck's quantum theory — In 1901, Max Planck studied the radiations from black (hot) bodies and proposed a theory which goes by the name of Planck's quantum theory. The postulates of his theory are :-

- (1) Radiant energy, such as light and heat is emitted or absorbed not continuously but discontinuously in the form of small packets or bundles.
- (2) The packet or bundle of energy is called **quantum** and in case of light the quantum is called **photon**. Photon is a massless bundle of energy.
- (3) The energy of the photon is given by the expression

$$E = h\nu$$

where 'ν' is the frequency of radiation and 'h' is the Planck's constant. Its value is equal to 6.62×10^{-27} erg. second.

- (4) A body can emit or absorb either one quantum of energy ($h\nu$) or any whole number multiples of this unit i.e. $2h\nu$, $3h\nu$ $nh\nu$. $E = nh\nu$, where $n = 1, 2, 3, \dots$

3.5 BOHR'S MODEL OF ATOM

Danish physicist Niels Bohr gave a model of atom in 1913. He accepted the provisions of Rutherford's model such as the positively charged nucleus at the centre contained the protons and neutrons. He also agreed to the fact that the electrons are revolving round the nucleus, but modified the model to meet the objections of Clark Maxwell's theory. On the basis of Planck's quantum theory Bohr gave a number of postulates.

- (1) **The electrons move round the nucleus in stationary orbits without losing energy, because energy in fractions of a quantum cannot be lost.**

This means that **energy of an electron remains constant as long as it remains in the same orbit**. Thus, **electron in each orbit is associated with definite amount of energy or a definite whole number quantum of energy**. The orbits are therefore, called as **energy levels** or **energy shells** and are given numbers 1, 2, 3, 4 etc. starting with the nearest orbit to the nucleus. These numbers are now called **principal quantum numbers** and the orbits are designated as K, L, M, N etc. (Fig 3.8) Nearest orbit to the nucleus has the least energy and increases on going away from the nucleus. As long as the electron is in a particular energy level, it neither emits nor absorbs energy.

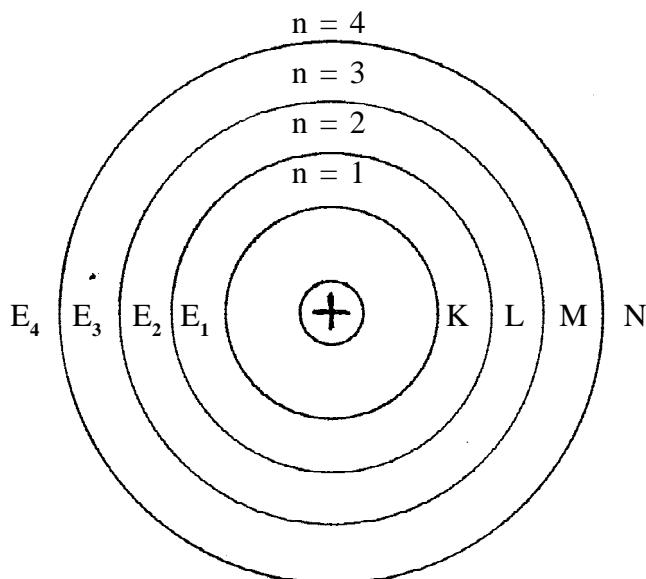


Fig. 3.8 Energy levels of the electron

- (2) **The angular momentum of the electron moving round the nucleus is quantised.**

An electron moving in a circular orbit has an angular momentum given by ' mvr ' where 'm' is the mass, 'v' is the velocity of the electron and 'r' is the radius of the orbit. According to Bohr, angular momentum of the electron is quantised or has definite values given by the following expression :

Angular momentum = $mvr = n\frac{h}{2\pi}$, where $n = 1, 2, 3 \dots$ etc. Thus, the angular momentum of an electron can be $\frac{h}{2\pi}$ or whole number multiples of $\frac{h}{2\pi}$, such as $\frac{2h}{2\pi}, \frac{3h}{2\pi}, \dots, \frac{nh}{2\pi}$. This is termed as **quantisation** of angular momentum.

(3) Energy is emitted or absorbed by an atom when electron moves from one energy level to another.

Thus, if energy associated with the electron in orbits 1, 2, 3, 4 etc. are E_1, E_2, E_3, E_4 etc. respectively, where $E_1 < E_2 < E_3 < E_4$, the change in energy on movement of electron from one orbit to the other is given by ΔE .

When electron jumps from a lower energy orbit (E_1) to a higher energy orbit (E_2), the amount of energy absorbed is given by $\Delta E = E_2 - E_1$. Similarly, this amount of energy is emitted when electron jumps from a higher energy orbit (E_2) to a lower energy orbit (E_1).

3.6 BOHR'S EQUATION FOR ENERGY OF ELECTRON IN HYDROGEN ATOM

The expression for energy of an electron in hydrogen atom or hydrogen like atom was calculated by Bohr basing on his postulates. According to Bohr the electron continues to stay in a particular orbit so long as it is associated with a definite amount of energy. The electrostatic force of attraction exerted by the nucleus is exactly balanced by the centrifugal force resulting from its circular motion.

A hydrogen atom has one proton in the nucleus and one electron in the extra nuclear part of the atom.

Let Z = Atomic number of hydrogen like species (one electron system)

e = charge in the electron revolving round the nucleus.

For hydrogen atom $Z = 1$

For hydrogen like atoms such as He^+ , Li^{2+} , $Z = 2$ and 3 respectively

Hence, the charge on the nucleus = Ze

Suppose, $r \rightarrow$ Distance between the revolving electron and the nucleus i.e. the radius of the orbit in which the electron is revolving.

$m \rightarrow$ mass of the electron

$v \rightarrow$ Tangential velocity of the revolving electron.

Now two types of forces are seen to play simultaneously.

(i) Electrostatic force of attraction (Centripetal force)

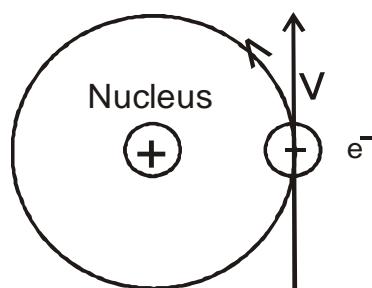
This force exists between the revolving electron and the nucleus. It tends to attract the electron towards the nucleus.

$$\text{The centripetal force} = Ze \times \frac{e}{r^2} = \frac{Ze^2}{r^2}$$

(ii) Repulsive force (Centrifugal force)

This force tends to keep the electron away from the nucleus

$$\text{The centrifugal force acting on the electron} = \frac{mv^2}{r}$$



Both the above forces act in opposite direction. In order to keep the electron revolving round the nucleus in its orbit, Bohr assumed that these forces must be equal.

$$\text{Hence } \frac{Ze^2}{r^2} = \frac{mv^2}{r} \dots\dots\dots (1)$$

$$\text{or } v^2 = \frac{Ze^2}{mr} \dots\dots\dots(2)$$

According to Bohr's postulate the angular momentum is an integral multiple of $\frac{h}{2\pi}$

$$\text{or } v = \frac{nh}{2\pi mr} \dots\dots\dots(4)$$

$$\text{Squaring equation (4), } v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \dots \quad (5)$$

From equation (2) and (5)

For hydrogen atom, $Z = 1$, hence

In the ground state $n = 1$

$$\text{So, } r_1 = \text{Bohr's radius} = a_0 = \frac{h^2}{4\pi^2 m e^2} \dots \quad (10)$$

The total energy ‘E’ of the electron revolving in the n^{th} orbit is given by the sum of kinetic energy and potential energy.

$$\text{Kinetic energy} = \frac{1}{2} mv^2 \dots\dots\dots (11)$$

$$\text{Potential energy} = \frac{-Ze^2}{r} \dots\dots\dots(12)$$

From equation (2), $mv^2 = \frac{Ze^2}{r}$ (14)

Substituting the value of mv^2 from equation (14) in equation (13), we have

$$E = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = \frac{-Ze^2}{2r} \dots\dots\dots (15)$$

Substituting the value of r_s from equation (8) in equation (15), we have

$$E = \frac{-Ze^2}{2} \times \frac{1}{r_n} = \frac{-Ze^2}{2} \times \frac{1}{\frac{n^2 h^2}{4\pi^2 Z me^2}}$$

$$\begin{aligned} &= \frac{-Ze^2}{2} \times \frac{4\pi^2 Z me^2}{n^2 h^2} \\ &= \frac{-2\pi^2 Z^2 me^4}{n^2 h^2} \end{aligned}$$

So, energy of electron in the n^{th} orbit E_n is given by

$$E_n = \frac{-2\pi^2 Z^2 me^4}{n^2 h^2} \dots \quad (16)$$

Equation (16) is the Bohr's equation for energy of electron in n^{th} orbit. This equation is applicable to both hydrogen and hydrogen like atoms (He^+ , Li^{2+} , Be^{3+} , etc)

Calculation of r_n is CGS unit

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2 Z}$$

Here, $h = 6.624 \times 10^{-27}$ ergs.sec

$\pi = 3.14$

$m = 9.108 \times 10^{-28}$ g

$e = 4.8 \times 10^{-10}$ esu.

$$r_n = \frac{n^2 \times (6.624 \times 10^{-27} \text{ erg} \cdot \text{sec})^2}{4 \times (3.14)^2 \times (9.108 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{-10} \text{ esu})^2 \times Z}$$

$$= \frac{n^2 \times (6.624 \times 10^{-27})^2 \text{ erg}^2 \cdot \text{s}^2}{4 \times (3.14)^2 \times (9.108 \times 10^{-28}) \times (4.8 \times 10^{-10})^2 \text{ g} \cdot \text{esu}^2 \times Z}$$

Use the relation

$\text{erg} = \text{g cm}^2 \text{s}^{-2}$

$\text{esu} = \text{g}^{\frac{1}{2}} \text{cm}^{\frac{3}{2}} \text{s}^{-1}$

$$r_n = \frac{0.529 \times 10^{-8} \times n^2}{Z} \times \frac{(\text{g cm}^2 \text{s}^{-2}) \text{s}^2}{\text{g} \cdot (\text{g}^{\frac{1}{2}} \text{cm}^{\frac{3}{2}} \text{s}^{-1})^2}$$

$$= \frac{0.529 \times 10^{-8} \times n^2}{Z} \times \frac{\text{g}^2 \text{ cm}^4 \text{s}^{-4} \cdot \text{s}^2}{\text{g} \cdot \text{g} \cdot \text{cm}^3 \cdot \text{s}^{-2}}$$

$$= \frac{0.529 \times 10^{-8} \times n^2}{Z} = \frac{0.529 \times n^2}{Z} \text{ A}^0$$

Calculation of r_n is SI units

$$r_n = \frac{n^2 h^2 (4\pi \epsilon_0)}{4\pi^2 Z me^2}$$

The factor $4\pi\epsilon_0$ is known as Permittivity factor

$$h = 6.624 \times 10^{-34} \text{ Js}$$

$$\in_0 = 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$$

$$\pi = 3.14$$

$$m = 9.108 \times 10^{-31} \text{ kg}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

Use the relation $J = kg \cdot m^2 s^{-2}$

$$r_n = \frac{n^2 \times (6.624 \times 10^{-34} \text{ Js})^2 \times 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}}{3.14 \times (9.108 \times 10^{-31} \text{ Kg}) \times (1.602 \times 10^{-19} \text{ C})^2 \times Z}$$

$$= \frac{n^2 \times 5.29 \times 10^{-11} \times J^2 s^2 J^{-1} C^2 m^{-1}}{Kg \cdot C^2 \times Z}$$

$$= \frac{n^2 \times 5.29 \times 10^{-11} \times J s^2 m^{-1}}{Kg \times Z}$$

$$= \frac{5.29 \times 10^{-11} \times n^2 \times Kg \cdot m^2 s^{-2} s^2 m^{-1}}{Kg \times Z}$$

$$= \frac{0.529 \times 10^{-10} \times n^2}{Z} \text{ m}$$

Bohr's radius (r_1)_H or r_H or a_0

$$(i) \text{ in CGS unit } r_H = 0.529 \text{ A}^{\circ}$$

$$(ii) \text{ in SI unit } r_H = 0.529 \times 10^{-10} \text{ m}$$

Calculation of E_n in CGS unit

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

Putting the values of π , m , e and h

$$\pi = 3.14$$

$$m = 9.108 \times 10^{-28} \text{ g}$$

$$e = 4.8 \times 10^{-10} \text{ esu}$$

$$h = 6.624 \times 10^{-27} \text{ erg} \cdot \text{s}$$

$$E_n = \frac{-2 \times (3.14)^2 \times (9.108 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{10} \text{ esu})^4 Z^2}{n^2 \times (6.624 \times 10^{-27} \text{ erg} \cdot \text{s})^2}$$

$$= \frac{-2.18 \times 10^{-11} \times Z^2}{n^2} \times \frac{g(\text{esu})^4}{(\text{erg} \cdot \text{s})^2}$$

Utilising the relations

$$\text{erg} = \text{g cm}^2 \text{s}^{-2}$$

$$\text{esu} = \text{g}^{1/2} \text{ cm}^{3/2} \text{ s}^{-1}$$

We have,

$$E_n = -\frac{2.18 \times 10^{-11} \times Z^2}{n^2} \times \frac{g(g^{1/2} \text{ cm}^{3/2} \text{ s}^{-1})^4}{(g \text{ cm}^2 \text{ s}^{-2})^2}$$

$$\begin{aligned}
 &= -\frac{2.18 \times 10^{-11} \times Z^2}{n^2} \times \frac{g \times g^2 cm^6 s^{-4}}{g^2 cm^4 s^{-2}} \\
 &= -\frac{2.18 \times 10^{-11} \times Z^2}{n^2} g cm^2 s^{-2} \\
 &= -2.18 \times 10^{-11} \times \frac{Z^2}{n^2} erg \text{ atom}^{-1}
 \end{aligned}$$

Value of E_n in ev. atom $^{-1}$ Since $1 \text{ erg} = 6.2419 \times 10^{11} \text{ ev}$

$$\begin{aligned}
 E_n &= -2.18 \times 10^{-11} \times 6.2419 \times 10^{11} \times \frac{Z^2}{n^2} \text{ ev . atom}^{-1} \\
 &= -13.6 \times \frac{Z^2}{n^2} \text{ ev . atom}^{-1}
 \end{aligned}$$

Calculation of E_n in SI units

$$E_n = \frac{-2\pi^2 Z^2 me^4}{(4\pi \epsilon_0)^2 n^2 h^2}$$

where $4\pi \epsilon_0$ is the permittivity factor.

$$\begin{aligned}
 \text{or, } E_n &= \frac{-me^4 Z^2}{8 \epsilon_0^2 n^2 h^2} \\
 \text{Putting } m &= 9.109 \times 10^{-31} \text{ kg} \\
 e &= 1.602 \times 10^{-19} \text{ C} \\
 \epsilon_0 &= 8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \\
 h &= 6.626 \times 10^{-34} \text{ Js}
 \end{aligned}$$

$$\begin{aligned}
 E_n &= -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J atom}^{-1} \\
 &= -13.1279 \times 10^5 \times \frac{Z^2}{n^2} \text{ J mole}^{-1} \\
 &= -13.1279 \times 10^2 \times \frac{Z^2}{n^2} \text{ kJ mole}^{-1}
 \end{aligned}$$

Energy of an Electron in the 1st orbit of H - atom (E_1)_HHere $n = 1, Z = 1$

(i) In CGS unit

$$\begin{aligned}
 (E_1)_H &= \frac{2\pi^2 me^4}{h^2} \times \frac{Z^2}{n^2} \\
 &= -2.18 \times 10^{11} \text{ erg atom}^{-1} \\
 &= -13.1279 \times 10^{10} \text{ erg mol}^{-1} \\
 &= -13.6 \text{ ev. atom}^{-1}
 \end{aligned}$$

(ii) **In SI units**

$$\begin{aligned}(E_1)_H &= -\frac{me^4}{8 \times 0 h^2} \times \frac{Z^2}{n^2} \\ &= -2.18 \times 10^{-18} \text{ J atom}^{-1} \\ &= -13.1279 \times 10^2 \text{ kJ mol}^{-1}\end{aligned}$$

To find out the value of $(E_1)_H$, $(E_2)_H$, $(E_3)_H$ etc

$(E_1)_H$, $(E_2)_H$, $(E_3)_H$ are the values of energy of H atom moving in 1st, 2nd and 3rd orbit respectively.

$$(E_1)_H = -2.18 \times 10^{-11} \times \frac{(1)^2}{(1)^2} \text{ erg} = -2.18 \times 10^{-11} \text{ erg}$$

$$(E_2)_H = -2.18 \times 10^{-11} \times \frac{(1)^2}{(2)^2} \text{ erg} = -0.5448 \times 10^{-11} \text{ erg}$$

$$(E_3)_H = -2.18 \times 10^{-11} \times \frac{(1)^2}{(3)^2} \text{ erg} = -0.2421 \times 10^{-11} \text{ erg}$$

Thus, $(E_1)_H < (E_2)_H < (E_3)_H$

Thus the energy of electrons goes on increasing as it moves away from the nucleus.

Why is Energy of an electron negative ?

Consider an electron situated at infinite distance from the nucleus. There is no interaction between the electron and the nucleus. As the electron approaches the nucleus, it does some work and some energy is released due to attractive forces existing between the nucleus and the electron. Thus the energy of the electron decreases. The energy of electron increases i.e (becomes less and less -ve) as it moves away from the nucleus.

Expression for velocity of an electron

$$\text{From eqn (2), } v^2 = \frac{Ze^2}{mr}$$

$$\text{From eqn (4), } v = \frac{nh}{2\pi mr}$$

On dividing eqn (2) by eqn (4) we have

$$\frac{v^2}{v} = \frac{Ze^2}{mr} \times \frac{2\pi mr}{nh} = \frac{2\pi Ze^2}{nh} \text{ or } v_n = \frac{2\pi Ze^2}{nh}$$

(i) Value in CGS unit

Putting $\pi = 3.14$

$e = 4.8 \times 10^{-10}$ esu

$h = 6.624 \times 10^{-27}$ erg.s

and using the relation

erg = g cm²s²

esu = g^{1/2} cm^{3/2}s⁻¹

We get,

v_n = Velocity of electron in n^{th} orbit of H atom

$$= \frac{2 \times 3.14 \times Z \times (4.8 \times 10^{-10})^2}{n \times 6.624 \times 10^{-27}} \text{ cm s}^{-1}$$

$$= \frac{21.8368 \times 10^7 \times Z}{n} \text{ cm s}^{-1}$$

$$= \frac{2.1836 \times 10^8 \times Z}{n} \text{ cm s}^{-1}$$

$$= \frac{0.2136 \times 10^9 \times Z}{n} \text{ cm s}^{-1}$$

(ii) Value of SI unit

$$v_n = \frac{2\pi Ze^2}{4\pi \epsilon_0 \cdot nh}, \text{ where } 4\pi \epsilon_0 \longrightarrow \text{Permittivity factor.}$$

$$= \frac{Ze^2}{2\epsilon_0 \cdot nh}$$

Putting the value of e , ϵ_0 , h etc.

$$v_n = \frac{0.2185 \times 10^7 \times Z}{n} \text{ ms}^{-1}$$

Number of revolutions made by an electron moving with a velocity v_n in n^{th} orbit is given

$$\text{by } \frac{v_n}{2\pi r_n}$$

Substituting the value of v_n & r_n in the above expression,

$$\text{Number of revolutions} = \frac{65.711 \times 10^{14} \times Z^2}{n^3} s^{-1}$$

Problems

(i) Find the expression for energy of an electron in n^{th} orbit of He^+ , Li^{2+} and Be^{3+} ions.

Solution

For He^+ , Li^{2+} and Be^{3+} , $Z = 2, 3$ and 4 respectively. And all are 1 electron species.

$$E_{\text{He}^+} = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2} = \frac{-2\pi^2 me^4 (2)^2}{n^2 h^2} = \frac{-8\pi^2 me^4}{n^2 h^2}$$

$$E_{\text{Li}^{2+}} = \frac{-2\pi^2 me^4 (3)^2}{n^2 h^2} = \frac{-18\pi^2 me^4}{n^2 h^2}$$

$$E_{\text{Be}^{3+}} = \frac{-2\pi^2 me^4 (4)^2}{n^2 h^2} = \frac{-32\pi^2 me^4}{n^2 h^2}$$

(ii) Compare the frequencies and wavelengths of radiation emitted by H atom with those emitted by He^+ , Li^{2+} and Be^{3+} ions.

Solution

We know that $E = hv$

$$\text{or } v_n = \frac{E_n}{n}$$

$$\text{Again } \Theta \ E_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^2}, \ v_n = \frac{-2\pi^2 me^4 Z^2}{n^2 h^3}$$

$$\text{For H atom, } Z = 1, \text{ so } v_H = \frac{-2\pi^2 me^4}{n^2 h^3}$$

$$v_{He^+} = -\frac{8\pi^2 me^4}{n^2 h^3}, \quad v_{Li^+} = \frac{-18\pi^2 me^4}{n^2 h^3}, \quad v_{Be^{3+}} = \frac{-32\pi^2 me^4}{n^2 h^3}$$

$$\text{So, } \frac{v_H}{v_{He^+}} = \frac{-2\pi^2 me^4}{n^2 h^3} \times \frac{n^2 h^3}{8\pi^2 me^4} = \frac{1}{4}$$

$$\frac{v_H}{v_{Li^{2+}}} = \frac{-2\pi^2 me^4}{n^2 h^3} \times \frac{n^2 h^3}{18\pi^2 me^4} = \frac{1}{9}$$

$$\frac{v_H}{v_{Be^{3+}}} = \frac{-2\pi^2 me^4}{n^2 h^3} \times \frac{n^2 h^3}{-32\pi^2 me^4} = \frac{1}{16}$$

Comparison of wave length

$$\text{We know that, } E = h\nu = \frac{hc}{\lambda}$$

$$\text{So, } \lambda = \frac{hc}{E}$$

$$\lambda_H = \frac{hc}{E} = \frac{hc}{\cancel{2\pi^2 me^4} / n^2 h^2} = \frac{n^2 h^3 c}{-2\pi^2 me^4}$$

$$\lambda_{He^+} = \frac{n^2 h^3 c}{-8\pi^2 me^4}, \quad \lambda_{Li^+} = \frac{n^2 h^3 c}{-18\pi^2 me^4}$$

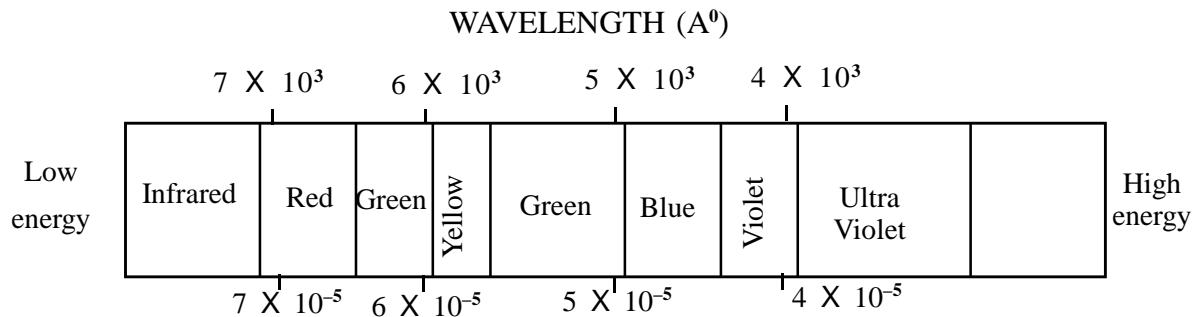
$$\lambda_{Be^{3+}} = \frac{n^2 h^3 c}{-32\pi^2 me^4}$$

$$\text{Thus, } \frac{\lambda_H}{\lambda_{He^+}} = \frac{4}{1}, \quad \frac{\lambda_H}{\lambda_{Li^{2+}}} = \frac{9}{1}, \quad \frac{\lambda_H}{\lambda_{Be^{3+}}} = \frac{16}{1}$$

3.7

SOLAR SPECTRUM

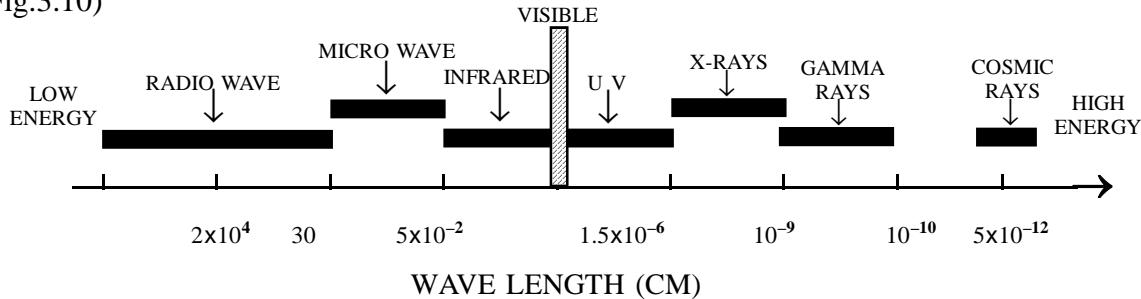
When sunlight or any other white light is passed through a prism, it is separated into different colours. Assembly of these colours is called **spectrum**. Different colours correspond to waves of different frequencies and wavelengths. The wavelengths of various radiations constituting the **visible spectrum** are shown below.



WAVE LENGTH (CM)

Fig. 3.9 Wavelengths of visible spectrum

The wavelengths of some important electromagnetic radiations are given below. (Fig.3.10)

**Fig. 3.10 Wavelengths of electromagnetic radiations.**

ATOMIC SPECTRA

If sunlight is passed through a prism, it gets separated into a **continuous spectrum** extending from red at one end to violet at the other.

But when a crystal of sodium chloride or any other sodium salt is shown to the bunsen flame, a bright yellow light is produced. If this light is passed through a prism and then allowed to fall on a photographic plate (or examined through a spectroscope) it is seen to consist of two isolated yellow lines separated by dark space. The wavelengths of these two lines are 5890 (D_1) and 5896 A° (D_2). Such a spectrum is known as **line spectrum**. It has been found that each element emits its own characteristic line spectrum which is different from that of any other element. Therefore, the atoms of the elements produce line spectra. Hence, line spectra is called **atomic spectra**.

Absorption and Emission spectrum — When an element is exposed to a strong source of light (light from arc lamp), one of the electrons present in the atom of the element may absorb energy and pass from a lower energy level to a higher energy level. This is in accordance with Bohr's theory. If the electron jumps from energy level ' E_1 ' to a level of energy ' E_2 ' then $E_2 - E_1 = \Delta E$ will be absorbed. As a result of this the spectral line of frequency corresponding to energy $E_2 - E_1$ will be missing and consequently a **dark line will appear in the spectrum**. This dark line constitutes **absorption spectrum**. When an atom loses energy so that the spectral line corresponding to $E_2 - E_1 = \Delta E$ of specific wavelenght will be emitted. This will appear as a bright line which constitutes the **emission spectrum**. For example, in case of sodium, the two lines corresponding to wavelengths of D_1 and D_2 are found missing. Two dark lines appear in their place. These two dark lines constitute the absorption spectrum of sodium.

3.8 BOHR'S THEORY AND HYDROGEN SPECTRUM

In the hydrogen atom, where there is one proton and one electron, the energy of the electron is given by the expression : $\frac{-2\pi^2 me^4}{n^2 h^2} = -\frac{313.5}{n^2}$ k.cal per mole..... (1)

where m = mass of the electron, e = charge of electron, h = planck's constant = 6.624×10^{-27} erg.sec. and n = 1, 2, 3, 4 etc. Substituting the value of 'n', energy of electron in various energy levels can be easily calculated .

Negative value of energy of electron is accounted for by the following explanation. When the electron is at infinite distance from the nucleus, there is no electrical interaction between the two and energy of the electron is taken as zero. When electron moves closer to the nucleus, work is done by the electron due to electrical attraction. Consequently, the energy of the electron decreases i.e. it becomes negative. It becomes more and more negative as the electron moves nearer and nearer to the nucleus.

Hydrogen atom contains only one electron, but its spectrum consists of a large number of lines. This is explained by the fact that a sample of hydrogen contains very large number of atoms. When energy is supplied to the sample of hydrogen, different atoms absorb different amount of energy. The single electron in different atoms will absorb different amount of energy and shift to different energy levels such as second, third, fourth or even higher energy levels. The electrons then tend to fall back to one or other of the lower energy levels. The various possibilities by which electrons fall back from the various excited states to lower energy levels are shown in (Fig. 3.11). During each transition, energy is released which appears in the form of radiations of specific frequency and specific wavelength.

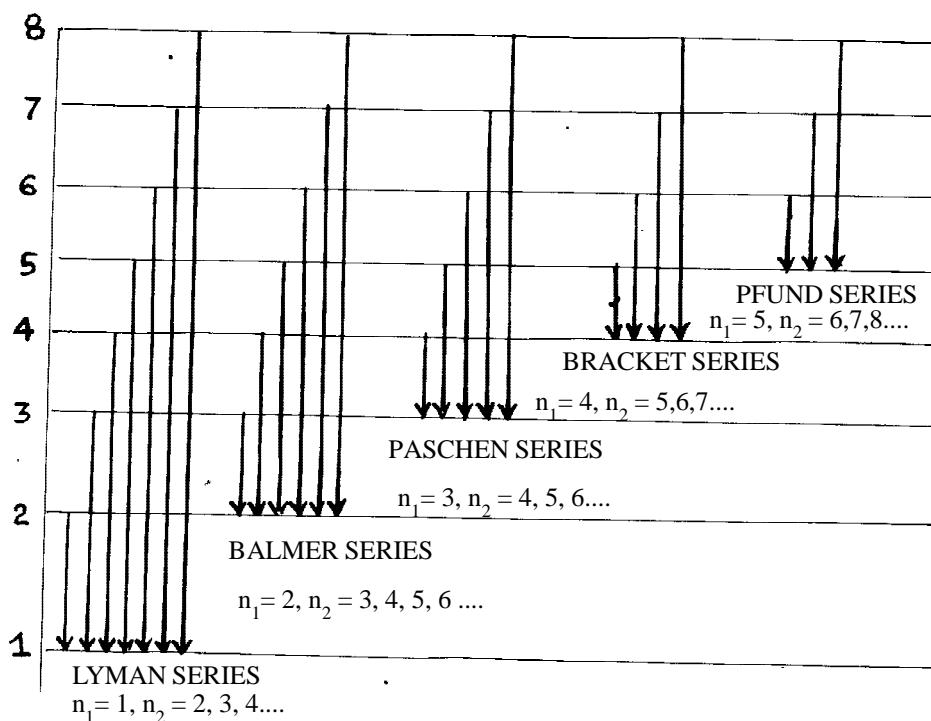


Fig.3.11 Origin of hydrogen spectrum.

Suppose the electron lies in the energy level n_2 where its energy is E_2 and electron jumps to lower energy level n_1 where its energy is E_1 . Then according to the equation of electron energy,

$$E_2 = \frac{-2\pi^2 me^4}{h^2 n_2^2} \text{ and, } E_1 = \frac{-2\pi^2 me^4}{h^2 n_1^2}$$

Difference in energy, $\Delta E = E_2 - E_1 = h\nu$

$$\text{or, } h\nu = \frac{-2\pi^2 me^4}{h^2 n_2^2} + \frac{2\pi^2 me^4}{h^2 n_1^2}$$

$$\text{or, } v = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Emission of various series of spectral lines observed in the emission spectra of hydrogen can be explained with the help of equation (2). **Lyman series** is produced when electron jumps from second, third, fourth or higher energy levels to the first energy level. Frequencies of various lines of this series are obtained by substituting $n_1 = 1$ and $n_2 = 2, 3, 4$ etc in equation (2). Similarly, frequencies for lines of **Balmer series** lines are obtained by putting $n_1 = 2$, $n_2 = 3, 4, 5, 6$ etc. In the same way for **Paschen series**, $n_1 = 3$, $n_2 = 4, 5, 6, 7$ etc. **Brackett series** $n_1 = 4$, $n_2 = 5, 6, 7, 8$ etc and **Pfund series** $n_1 = 5$, $n_2 = 6, 7, 8$ etc.

The frequencies of the spectral lines of different series calculated by equation (2) almost agree with the experimentally determined values. **This has offered a strong support in favour of the Bohr's theory of hydrogen atom.**

Ritz combination principle — Equation (2) given above is similar to **Ritz equation**

$\bar{v} = \frac{1}{\lambda} = \frac{v}{c} = R = \left(\frac{1}{x^2} - \frac{1}{y^2} \right)$. Here R is called the **Rydberg constant**, which is given by $R = \frac{2\pi^2 me^4}{h^3 c}$. The value of 'R' is found to be 109737 per cm which is comparable to the experimental value of 109678 per cm obtained by Ritz. Equation for the various series of spectral lines of hydrogen atom is similar to the Ritz equation. This gives further support to the Bohr's theory of atom.

Limitations of Bohr's model — Using spectrosopes of high resolving power the line spectra of hydrogen was found to consist of a group of very **fine lines**. To explain this **Sommerfeld** put forward the idea of **elliptical orbits**. Thus. the circular orbit of Bohr is a special case of elliptical orbits. Hence, Bohr's theory is referred as **Bohr - Sommerfeld theory** . Following are the limitations of the theory.

1. Spectra of many electron atoms can not be explained by Bohr's theory.
 2. Bohr's orbits are planar, but according to the modern concept electron moves in three dimensional orbits.
 3. It does not accept the dual (wave and particle) nature of electron.
 4. According to Bohr's theory the position and momentum of electron can be determined which is objected by Heisenberg's uncertainty principle.

3.9 DUAL NATURE OF ELECTRON

Einstein in 1905 suggested that light has a **dual character**, particle as well as wave. In 1923, French physicist Louis de Broglie suggested that matter has also a dual character, particle and wave. Therefore, according to him electron has also the dual character. He derived an expression for calculating the wavelength ' λ ' of a particle of mass 'm' moving with velocity 'u' according to which $\lambda = \frac{h}{mu}$.

The equation was derived in the following manner.

According to Einstein, $E = mc^2$,

$$\text{also } E = hv.$$

$$\text{Equating, } hv = mc^2.$$

Since $v = \frac{c}{\lambda}$, substituting the value of v ,

$$\text{we have } \frac{hc}{\lambda} = mc^2$$

$$\text{or, } \lambda = \frac{h}{mc}$$

Substituting 'c' with velocity of electron 'u', the equation becomes $\lambda = \frac{h}{mu}$.

or, $\boxed{\lambda = \frac{h}{p}}$ where p = momentum = mu . (**de Broglie equation**)

3.10 QUANTUM NUMBERS

Quantum numbers are identification marks for the electrons or in other words they give the addresses of the electrons. In an atom, there can be many electrons which are alike. So they can only be identified by the quantum numbers.

There are four quantum numbers. These are :

1. Principal quantum number 'n'.
2. Azimuthal quantum number 'l'
3. Magnetic quantum number 'm'.
4. Spin quantum number 's'.

All the quantum numbers are discussed below.

1. **Principal quantum number (n)** — It determines the shell or energy level or orbit of the electron. It has integral values 1, 2, 3, 4 etc which indicates the shells or energy levels K, L, M, N etc respectively. It also determines the total energy of the electron

in an energy level. $En = \frac{-2\pi^2 me^4}{\pi^2 h^2}$, where En = Energy of the electron in n^{th} orbit and

π , m, e and h have their usual meaning. From the wave mechanical concepts, principal quantum number gives the **size** of electron wave.

- 2. Azimuthal quantum number (l)** — It is also called secondary quantum number or angular momentum quantum number or orbital quantum number. It determines the sub-energy level of the electron. It also determines the energy contribution due to the angular momentum or orbital motion of the electron. From the wave mechanical concept it determines the shape of electron wave.

' l ' carries 'n' number of values. It has values from 0 to $n-1$. Depending upon the value of ' l ' the sub-shells of the electron are indicated.

Value of ' l '	Sub-Shell
0	s
1	p
2	d
3	f

When $n = 1$, the electron is in K-shell and ' l ' value is '0' indicating that the electron is present in s-subshell or orbital.

When $n = 2$ electron is in L - shell, ' l ' has values 0 and 1, which indicates that in M - Shell, s and p - sub shells are present. When $n = 3$, electron is in M-Shell, the ' l ' values are 0, 1, 2, which indicates that in M-Shell, s, p, and d - sub shell are present. Similarly, when $n = 4$ for N-shell, ' l ' values are 0, 1, 2, 3 which indicates that in N-shell, s, p, d and f- subshells are present.

3. Magnetic quantum number (m) : Motion of the electron in an orbit is comparable to flow of electric current in a loop. The flow of current generates a magnetic field which interacts with external electric or magnetic field and as a result the electrons in a given energy sub-level orient themselves in certain specific region of space around the nucleus. These regions of space are called orbitals.

Thus, magnetic quantum number determines the orientation of orbital in space or the number of orbitals of a particular type in a shell or energy level. 'm' can have values from +1 through '0' to -1. The number of values it carries is $(2l + 1)$.

For example when $l = 0$, m has only one value '0' which means in a shell there can be only **one** 's' orbital.

When $l = 1$, $m = -1, 0$ and $+1$, thus there can be three p-orbitals in a shell i.e. p-orbitals are three in number or it has **three** orientations.

When $l = 2$, $m = -2, -1, 0, +1, +2$, five values, thus d-orbitals will be five in number or it has **five** orientations.

Similarly, when $l = 3$, $m = -3, -2, -1, 0, +1, +2, +3$, seven values. Thus, f orbital is seven in number or it has **seven** orientations.

4. Spin quantum number (s) — Electron during its motion around the nucleus also rotates or **spins** about its own axis. A charged particle which spins about its own axis behaves as a small magnet. Spin of the electron adds to the angular momentum and contributes to the total energy. The electron can spin in clockwise or anticlockwise direction and accordingly spin quantum number 's' has two values i.e. $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively. Thus there can be maximum two electrons with opposite spins in an orbital.

3.11 PAULI'S EXCLUSION PRINCIPLE

Position of an electron in an atom can be ascertained by the four quantum numbers. These quantum numbers give idea about the position of electron in the main energy level (n), sub-energy level (l), orientation of sub-energy level (m) and the direction of spin (s). It is possible to identify the electron by means of the quantum numbers and these serve as address for the electron. But identification of electrons is possible only on the basis of restriction imposed by the Pauli's exclusion principle.

It states that **no two electrons in a given atom can have all the four quantum numbers same**. Maximum three quantum numbers can be same, but the fourth quantum number must be different, otherwise it will not be possible to identify the electron.

For example, suppose there are two electrons in the K-shell of an atom. Let us write down the quantum numbers for the two electrons.

	n	l	m	s
Ist electron	1	0	0	$+\frac{1}{2}$
2nd electron	1	0	0	$-\frac{1}{2}$

Thus, three quantum numbers are same, but the fourth one is different. In any orbital there can be maximum two electrons of opposite spin. since these two electrons are in K-shell, they are in the s-orbital of K-shell.

3.12 HEISENBERG'S UNCERTAINTY PRINCIPLE AND THE CONCEPT OF PROBABILITY

The principle states— "**It is not possible to determine exactly both position and momentum of a small particle like electron simultaneously.**"

According to Bohr's model, the electron in an orbit is at a fixed distance from the nucleus and its position and velocity can be determined. But according to uncertainty principle it is not possible to determine both position and momentum of the electron.

The physical significance of the principle can be known from the following. In order to observe something, light photons must strike the object. Electron is a small particle like photon. During the observation due to the impact of photon on the electron, the position and

velocity of the electron will suffer a change. Hence, the position and velocity can not be determined simultaneously.

Uncertainty principle is expressed mathematically as,

$$(\Delta_x)(\Delta_p) \approx \frac{h}{4\pi}$$

where ' Δ_x ' is the uncertainty in determining position and ' Δp ' is the uncertainty in determining momentum. If ' Δ_x ' becomes very large, Δ_p , becomes very small and momentum can be determined. When Δ_p is very large, Δ_x becomes very small and position can be determined.

Thus, Bohr's concept of definite orbit or definite position of the electron becomes vague. Only it is possible to predict the probability of locating an electron of definite energy in a given region in space.

CONCEPT OF ORBITAL

While Bohr's model restricts the electron to a definite orbit at a fixed distance from the nucleus, the wave mechanical model gives merely the probability of locating the electron at a given distance from the nucleus. Thus, **the orbital is the region in space around the nucleus where there is maximum probability of finding the electron.**

Difference between Orbit and Orbital —

Orbit	Orbital
<ol style="list-style-type: none"> It is the circular path around the nucleus in which electron moves It has a circular shape In it electron moves in one plane In the orbit position and momentum of the electron can be determined. In the orbit the maximum number of electrons is determined by $2n^2$ rule. 	<ol style="list-style-type: none"> It is the three dimensional space around the nucleus where there is maximum, probability of finding the electron. The shape of different orbitals are different In the orbital electron moves in three dimensional space. In the orbital position and momentum of the electron can not be determined simultaneously. In an orbital there can be maximum two electrons of opposite spin.

SHAPES OF ORBITALS

s-orbital - Since s-orbital has only one orientation, it is spherically symmetrical about the nucleus and is undirectional. As the size of the orbital depends on the value of the principal quantum number, 2s-orbital is larger than 1s orbital (Fig. 3.12). Each s-orbital is symmetrical along the three axes, x, y and z.

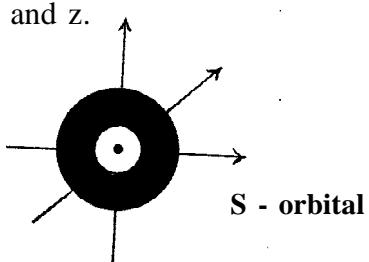


Fig. 3.12

p - orbitals : There are three p-orbitals (p_x , p_y and p_z). Since they are of equal energy, they are oriented along the three axes x, y and z which are mutually at right angles to each other. Each orbital looks like two pears attached at their narrow ends. It looks like a dumbbell or it has the shape of a flattened sphere. The lobes of p_x , p_y and p_z orbitals are directed along the three axes x, y and z respectively (Fig. 3.13 – a, b, c)

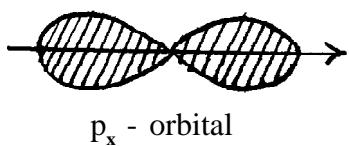


Fig. 3.13 (a)

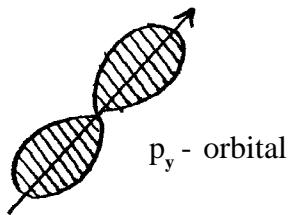


Fig. 3.13 (b)

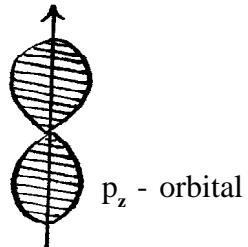


Fig. 3.13 (c)

d - orbitals : There are five d-orbitals. These are of equal energy, but differ only in their orientations in three dimensional space. Three of these orbitals (d_{xy} , d_{yz} , d_{zx}) project in between the coordinate axes x–y, y–z and z–x respectively. The other two orbitals ($d_{x^2-y^2}$, d_{z^2}) lie along the coordinate axes. (Fig. 6.14)

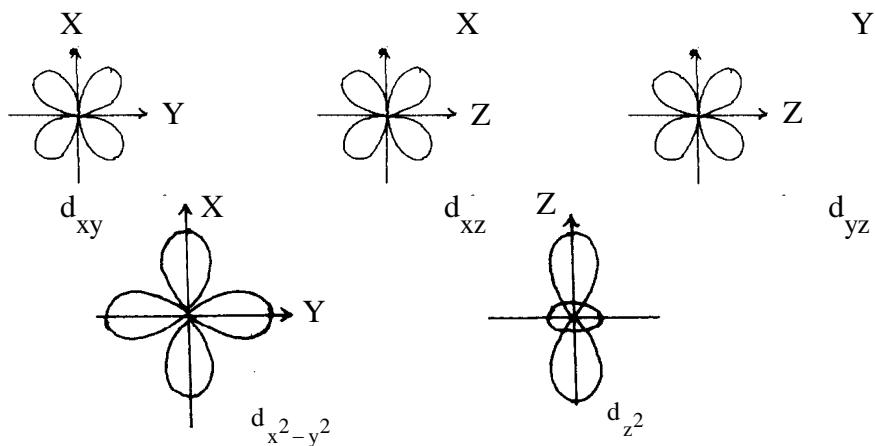


Fig. 3.14 Shapes of d - orbitals

3.13 AUFBAU PRINCIPLE

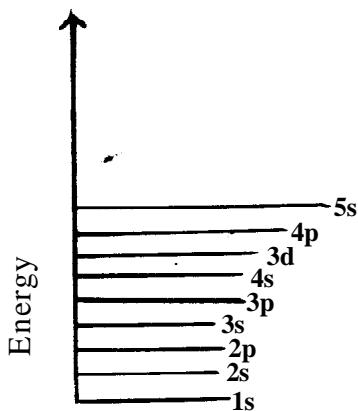
The meaning of "aufbau" is *building up*. It states that **electrons enter various orbitals in the increasing order of energies**. It means that the orbital of lowest energy is filled up first and then electrons go to the orbitals with increasing order of energies. The sequence of filling up of orbitals is shown below (Fig 3.15). The following rules are taken into account during filling up of the orbitals.

- (n+l) Rule - The orbital with lower (n+l) value possesses lower energy therefore is filled up first.

e.g. 4s orbital is filled up prior to 3d orbital, $n+l = 3 + 2 = 5$

(ii) If the $(n+l)$ value is same for both the orbitals, then the orbital having lower 'n' value is filled up first.

e.g. 3p orbitals are to be filledup prior to 4s orbital For 3p, $n+l = 3+1 = 4$ and for 4s, $n+l = 4+0 = 4$.



A new electron enters the orbital where $(n+l)$ value is minimum. In case the values of $(n+l)$ are same, the new electron enters the orbital where n value is minimum.

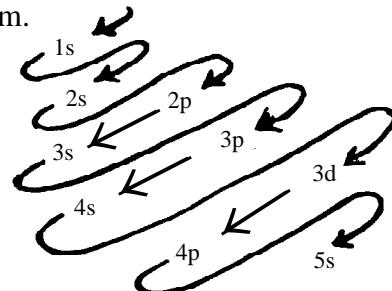


Fig. 3.15 - Sequence of filling of the orbitals.

3.14 HUND'S RULE

Hund's rule of maximum multiplicity states that "**electron pairing in p, d and f- orbitals take place only after all the orbitals of a given set have one electron each.**" On the basis of application of Hund's rule electronic configurations of some elements are shown below (Fig. 12.14)

	1s	2s	2p
Nitrogen (atomic number-7)	↑↓	↑↓	↑↑↑
Oxygen (atomic number-8)	↑↓	↑↓	↑↓↑↑
Fluorine (atomic number-9)	↑↓	↑↓	↑↓↑↓↑
Neon (atomic number-10)	↑↓	↑↓	↑↓↑↓↑↓

(Fig. 3.16)

3.15 ELECTRONIC CONFIGURATION OF ELEMENTS

Distribution of electrons in atoms of elements is guided by the following rules.

1. **$2n^2$ rule** – The maximum capacity of the different energy levels is given by this rule.

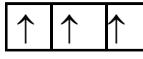
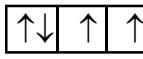
Energy level.	n	Maximum number of electrons.
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$

2. **Aufbau principle** - Electrons fill the orbitals in the increasing order of energies.
 3. **Pauli's exclusion principle** - An orbital can have maximum two electrons of opposite spin.
 4. **Hund's rule of maximum multiplicity** - Electron pairing in p,d,f orbitals does not take place till all the orbitals of the given set have one electron each.

Electronic configuration of atoms can be presented by box diagram method or according to the formula nl^x .

Box-diagram method : In this case each orbital is represented by a box and electrons are indicated by arrow in the box.

For example –

Carbon	(atomic number-6)			
Nitrogen	(atomic number-7)			
Oxygen	(atomic number-8)			

Electronic configuration by the formula nl^x .

$n = 1, 2, 3, 4$ etc, the main energy levels or shells

$l =$ orbital

$x =$ number of electrons in the orbital

For example –

Hydrogen (atomic number = 1) = $1s^1$

It has a single electron in the K-shell or first shell and s-orbital.

Helium (atomic number = 2) = $1s^2$

Lithium (atomic number = 3) = $1s^2 2s^1$

Electronic configuration of different atoms upto atomic number 30 is given below.

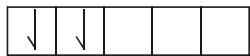
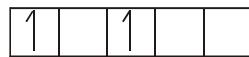
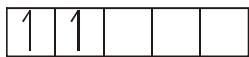
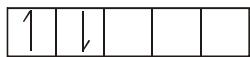
Element	Symbol	Atomic number	Electronic Configuration
Hydrogen	H	1	1s ¹
Helium	He	2	1s ²
Lithium	Li	3	1s ² 2s ¹
Beryllium	Be	4	1s ² 2s ²
Boron	B	5	1s ² , 2s ² 2p _x ¹
Carbon	C	6	1s ² , 2s ² , 2p _x ¹ , 2p _y ¹
Nitrogen	N	7	1s ² , 2s ² 2p _x ¹ 2p _y ¹ 2p _z ¹
Oxygen	O	8	1s ² , 2s ² 2p _x ² 2p _y ¹ 2p _z ¹
Florine	F	9	1s ² , 2s ² 2p _x ² 2p _y ² 2p _z ¹
Neon	Ne	10	1s ² , 2s ² 2p _x ² 2p _y ² 2p _z ²
Sodium	Na	11	1s ² , 2s ² 2p ⁶ 3s ¹
Magnesium	Mg	12	1s ² , 2s ² 2p ⁶ 3s ²
Aluminium	Al	13	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ¹
Silicon	Si	14	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ¹ 3p _y ¹
Phosphorus	P	15	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ¹ 3p _y ¹ 3p _z ¹
Sulphur	S	16	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ² 3p _y ¹ 3p _z ¹
Chlorine	Cl	17	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ² 3p _y ² 3p _z ¹
Argon	Ar	18	1s ² , 2s ² 2p ⁶ 3s ² 3p _x ² 3p _y ² 3p _z ²
*Potassium	K	19	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹
Calcium	Ca	20	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ²
Scandium	Sc	21	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹
Titanium	Ti	22	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ²
Vanadium	V	23	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ³
*Chromium	Cr	24	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ⁵
Manganese	Mn	25	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁵
Iron	Fe	26	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁶
Cobalt	Co	27	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁷
Nickel	Ni	28	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁸
*Copper	Cu	29	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ¹⁰
Zinc	Zn	30	1s ² , 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰

*Chromium should have the configuration $4s^2 3d^4$, but actually it has the configuration $4s^1 3d^5$ in the valence shell because $3d^5$ i.e half filled configuration is a **stable configuration**. Similarly, Copper should have the configuration $4s^2 3d^9$, but actually it has the configuration $4s^1 3d^{10}$, because $3d^{10}$ (completely filled) configuration is a **stable configuration**.

3.16 EXTRA STABILITY OF HALF FILLED AND COMPLETELY FILLED ORBITALS

There is a difference between electronic configuration and electronic arrangement. Electronic configuration tells us that how many electrons are present in a set of orbitals. But electronic arrangement tells us the manner in which the electrons are placed in a given set of orbitals.

Let us take the case of $3d^2$ configuration in Ti^{2+} ion. These two electrons can be placed in a set of five 3d orbitals in as many as 45 different ways. Some of the arrangements are shown below.



Thus a given electronic configuration may lead to a large number of electronic arrangements. When the two electrons are placed in same or different orbitals they are subjected to mutual repulsion. The more the repulsion the greater is the energy and less is the stability. A stable electronic configuration is always concerned with stable electronic arrangement of that configuration. Hund's rule of maximum multiplicity predicts the most stable electronic arrangement belonging to a given electronic configuration.

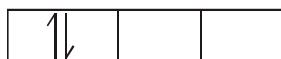
Hund's rule and its application

According to Pauli's exclusion principle "No two electrons in an atom can have an identical set of quantum numbers". Hence, if two electrons have the same spin i.e. the same spin quantum number they must have to occupy different orbitals since they can not have the same value of n, l and m. On the other hand, if the two electrons have opposite spin they can occupy the same orbital i.e. they have the same value of n, l and m.

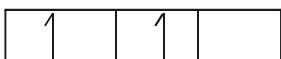
According to Hund's Rule

The most stable electronic arrangement is one in which there is maximum number of unpaired electrons.

The degenerate orbitals are orbitals of equal energy. This is due to the fact that the degenerate electronic arrangements have the same inter electronic repulsions and hence may have the same energy. Let us take 3 degenerate p-orbitals and find out the most stable electronic arrangement for a p^2 configuration. There are 15 ways of arranging these two electrons in a set of 3 p-orbitals.



(1)



(2)



(3)

In arrangement (1) the two electrons are placed in the same orbital. The electrostatic repulsion is more, so energy is more and this arrangement is least stable. The stability of arrangement of (2) or (3) is decided on the basis of concept of **exchange energy**.

Exchange energy

If the positions in space of the two electrons having parallel spins are exchanged, there is no change in electronic arrangement and this leads to decrease in energy. The pair of electrons is known as exchange pair and the decrease in energy per exchange pair of electrons is known as **exchange energy**. Exchange energy carries a -ve sign.

There is one exchange pair of electrons in arrangement (2) and none in arrangement (3). The arrangement (2) is thus associated with lower energy than arrangement (3). Thus arrangement (2) is more stable than arrangement (3).

Pairing Energy - The energy required for placing two electrons with antiparallel spins in the same orbital is known as **pairing energy**.

This **pairing energy** is having +ve sign. It tends to increase the energy of the system i.e. to destabilise it.

Consider the following arrangement for p³ configuration.



If E - Exchange energy (-ve sign)

stabilising

P - Pairing energy (+ve sign)

destabilising

Arrangement (1) → (-E + P), since one exchange pair of electrons (a, b) and one pair of electron (a).

Arrangement (2) → (-3E + 0), since three exchange pair of electrons (a,b) , (a,c) and (b,c) and no pair of electrons.

Arrangement (3) → (-E + 0), since one exchange pair of electrons (a,b) and no pair of electron.

Here, order of stability is 2 > 3 > 1

Thus, the electronic arrangement containing a set of exactly half filled degenerate orbitals is found to be most stable.

Stability of completely filled orbitals :

Consider the electronic arrangement of p⁴, p⁵, p⁶ configurations

p⁴

p⁵

p⁶



(1)



(2)



(3)

The relative stabilities of the three arrangements can not thus be predicted on the basis of aggregates of exchange energy and pairing energy. Experimentally it has been found that arrangement (3) is the most stable arrangement. Hence there must be some other stabilising factor in favour of arrangement (3).

The factor is symmetrical distribution of charge. Configurations having uniform or symmetrical distribution of charge in all directions are associated with lower energy and hence higher stability. Thus the configurations having exactly half filled orbitals or completely filled orbitals have symmetrical distribution of charge and hence are considered to be more stable.

Solved Problems

Example 1. Calculate the number of protons, neutrons and electrons in an isotope of the element having atomic number 9 and atomic weight 19.

Solution Atomic number = number of protons = number of extranuclear electrons = 9.

$$\text{Number of neutrons} = \text{Atomic mass} - \text{atomic number} = 19 - 9 = 10$$

Therefore, There are 9 protons, 9 electrons and 10 neutrons.

Example 2 An oxide of nitrogen has a molecular weight of 30 Find the total number of electrons in one molecule of the compound (Atomic numbers, N = 7, O = 8)

Solution Molecular formula weight of the compound = 30
 The oxide would have the formula = NO
 Atomic number of 'N' and 'O' are 7 and 8 respectively, So total number of electrons = $7 + 8 = 15$.

Example 3 A neutral atom of an element has 2K, 8L and 5M electrons. Find out the following : (a) Atomic number (b) Total number of s-electrons (c) Total number of p-electrons (d) Number of protons (e) valency of the element.

Solution Atomic number = no. of protons = no. of electrons = $2+8+5=15$
 Total no. of p-electrons = 2 in K-shell + 2 in L-shell + 2 in M-Shell = 6
 Total no. of p-electrons = 6 in L-shell + 3 in M - shell = 9
 No. of protons = 15
 Electronic configuraion = $1s^2, 2s^22p^6, 3s^2 3p^3$.
 Since there are 3-electrons in p-orbital, valency = 3.

Example 4 An atom with an atomic mass of 28 has a ground state electronic configuration $1s^2, 2s^2 2p^6, 3s^2, 3p^2$. Find the atomic number of element, number of electrons in valence shell, number of neutrons.

Solution Atomic number = 14, valency = 4
 Number of neutrons = $28 - 14 = 14$

Example 5 An electron has mass = 9.1×10^{-31} g. and is moving with a velocity of 10^5 cm/sec. Calculate its kinetic energy and wavelength where, h = Planck's constant = 6.625×10^{-34} erg. sec.

Solution $K.E = \frac{1}{2} mv^2 = \frac{1}{2} \times 9.1 \times 10^{-31} \times 10^5 \times 10^5 = 4.55 \times 10^{-18}$ ergs.
 $\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^5} = 7.28 \times 10^{-16}$ cm.

Example 6 Calculate the de Broglie wavelength associated with a particle having an energy of 7.7×10^{-13} J and a mass of 6.6×10^{-24} g. ($h = 6.6 \times 10^{-34}$ J.)

Solution Energy = $E = \frac{1}{2} mv^2 = 7.7 \times 10^{-13}$ J.
 $v = \sqrt{\frac{7.7 \times 10^{-13} \times 2}{6.6 \times 10^{-24}}} = 1.525 \times 10^5$ cm. sec $^{-1}$.
 $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{6.6 \times 10^{-24} \times 1.525 \times 10^5} = 6.56 \times 10^{-16}$ cm .

Example 7 Calculate the wavelength associated with an electron (mass = 9.1×10^{-31} g.) moving with a velocity of 10^3 m/sec. ($h = 6.6 \times 10^{-34}$ kg. m 2 sec $^{-1}$)

Solution $\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3}$

Example 8 The energy of the electron in the second and third orbit of hydrogen atom is -5.42×10^{-12} erg. and -2.41×10^{-12} erg. Calculate the wavelength emitted when the electron drops from the third to the second orbit. ($h = 6.626 \times 10^{-27}$ erg. sec.)

$$\begin{aligned}\text{Solution} \quad \Delta E &= E_2 - E_1 = -2.41 \times 10^{-12} - (-5.42 \times 10^{-12}) \text{ ergs} \\ &= 3.01 \times 10^{-12} \text{ erg.}\end{aligned}$$

$$\begin{aligned}\Delta E &= \frac{hc}{\lambda} \text{ or, } \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10} \text{ erg.sec}}{3.01 \times 10^{-12} \text{ erg.}} \\ &= 6.63 \times 10^{-5} \text{ cm or } 6630 \text{ A}^0\end{aligned}$$

Example 9 What is the mass of photon of sodium light?

$$\begin{aligned}\text{Solution} \quad \lambda &= 5894 \text{ A}^0 = 5.894 \times 10^{-7} \text{ metres, sec}^{-1} V = 3 \times 10^8 \text{ metres, } h = 6.6 \times 10^{-34} \text{ kg.m}^2 \text{ sec}^{-1} \\ \lambda &= \frac{h}{mv} \text{ or } m = \frac{h}{\lambda V} = \frac{6.6 \times 10^{-24} \times 10^3 \text{ g.m}^2 \text{ sec}^{-1}}{5.894 \times 10^{-7} \times 3 \times 10^8 \text{ m}^2 \text{ sec}^{-1}} = 3.73 \times 10^{-33} \text{ g.}\end{aligned}$$

Example 10 Wavelength of blue light is 4800 A^0 . Calculate the frequency and wave-number of light.

$$\text{Solution} \quad \lambda = 4800 \text{ A}^0 = 4800 \times 10^{-8} \text{ cm. } C = 3.0 \times 10^{10} \text{ cm.}$$

$$v = \frac{c}{\lambda} = \frac{3.0 \times 10^{10}}{4800 \times 10^{-8}} = 6.25 \times 10^{14} \text{ sec}^{-1}.$$

$$\text{Wave number} = \bar{v} = \frac{1}{\lambda} = \frac{1}{4800 \times 10^{-8}} = 2.08 \times 10^{-1} \text{ cm}^{-1}.$$

Example 11 Calculate the frequency of radiation of visible light having wavelength 750 cm .

$$\begin{aligned}\text{Solution} \quad C &= v \lambda \text{ or } v = \frac{c}{\lambda} \text{ Here } C = 3 \times 10^8 \text{ ms}^{-1}, \lambda = 750 \text{ nm.} \\ &\qquad\qquad\qquad = 750 \times 10^{-9} \text{ m.}\end{aligned}$$

$$v = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{7.5 \times 10^{-7} \text{ m}} = 4 \times 10^{14} \text{ s}^{-1} = 4 \times 10^{14} \text{ Hz.}$$

Example 12 Energy difference between two electronic states of hydrogen atom is $245.9 \text{ kJ mol}^{-1}$. Calculate the wavelength of light emitted when an electron drops from the higher to the lower state. ($h = 3.99 \times 10^{-13} \text{ kJ sec. mol}^{-1}$)

$$\begin{aligned}\text{Solution} \quad \Delta E &= hv = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{\Delta E} = \frac{3.99 \times 10^{-13} \text{ kJ Sec mol}^{-1} \times 3 \times 10^8 \text{ m sec}^{-1}}{245.9 \text{ kJ mol}^{-1}} \\ &= 4.867 \times 10^{-7} \text{ m} = 4.867 \times 10^2 \text{ nm.}\end{aligned}$$

Example 13 Calculate the wavelength of the third line in the Brackett series of hydrogen. ($R = 10.97 \times 10^6 \text{ m}^{-1}$)

Solution Rydberg equation, $\frac{1}{\lambda} = 10.97 \times 10^6 \text{ m}^{-1} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

For the Brackett series $n_1 = 4$ and $n_2 = 7$. substituting the values of n_1 and n_2 in the above equation.

$$\begin{aligned}\frac{1}{\lambda} &= 10.97 \times 10^6 \text{ m}^{-1} \left(\frac{1}{4^2} - \frac{1}{7^2} \right) = 10.97 \times 10^6 \text{ m}^{-1} (0.0420918) \\ &= 461747 \text{ m}^{-1} \\ \lambda &= 2.1 \times 10^{-6} \text{ m}.\end{aligned}$$

Example 14 Calculate the wavelength of spectral line when electron in a hydrogen atom undergoes a transition from an energy level with $n=4$ to $n=2$. What is the colour of radiation ?

$$\begin{aligned}\frac{1}{\lambda} &= 10.97 \times 10^6 \text{ m}^{-1} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 10.97 \times 10^6 \text{ m}^{-1} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= 10.97 \times 10^6 \text{ m}^{-1} (0.25 - 0.25) = 10.97 \times 10^6 \text{ m}^{-1} \times 0.1875 \\ \lambda &= 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm., colour of light = bluish green}\end{aligned}$$

Example 15 Calculate the momentum of a particle which has a de Broglie wavelength of 0.1 nm.

Solution $\lambda = 0.1 \text{ nm} = 0.1 \times 10^{-10} \text{ m} , = 10^{10} \text{ m. } \lambda = \frac{h}{p}, p = \text{momentum}$

$$p = \frac{h}{\lambda} = \frac{6.62 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{10^{-10} \text{ m}} = 6.62 \times 10^{-24} \text{ Kg. m. s}^{-1}.$$

Example 16 Write the values of 'l' and 'm' for an electron in 3d orbital

Solution For a d – orbital, $l = 2$

When $l = 2$, $m = \text{any one of } -2, -1, 0, +1, +2$.

Example 17 For an atom, the maximum value of 'm' obtained from experiment is +2. What are the possible values of n, l, and m)

Solution $l = 0 \text{ to } n-1 \text{ } m = -l \text{ through zero to } +l$.

When, $m = +2, l = 2, n = 3$ (since $l = n-1$)

and $m = -2, -1, 0, +1, +2$.

Example 18 An electron is present in 4s - sub shell. What are the possible values of n, l and m.

Solution $n = 4, l = 0, m = 0$

Example 19 An electron is present in 4f subshell. What are the possible values of quantum numbers.

Solution $n = 4, l = 3, m = \text{any one of } -3, -2, -1, 0, 1, 2, 3, s = + \frac{1}{2} \text{ and } - \frac{1}{2}$

Example 20 Quantum numbers of an electron are given below. In which orbital the electron will be present.

- Solution**
- (i) $n = 3, l = 1$, the orbital is $3p$
 - (ii) $n = 4, l = 0$, the orbital is $4s$

Example 21 Which of the following sets of quantum numbers are not permissible ?

- Solution**
- (i) $n = 2, l = 1, m = 0, s = -\frac{1}{2}$
 - (ii) $n = 2, l = 2, m = -1, s = -\frac{1}{2}$
 - (iii) $n = 3, l = 2, m = 0, s = -\frac{1}{2}$
 - (iv) $n = 3, l = 2, m = +1, s = 0$

- Solution**
- (ii) is not allowed as when $n = 2$, l can not be 2 (should be $n - 1$)
 - (iv) is not allowed. Here s can not be zero.

CHAPTER (3) AT A GLANCE

1. **Electron, proton and neutron** are the three fundamental particles of an atom.
2. **Charge of electron** is 1.602×10^{-19} coulombs and mass is 9.1×10^{-28} Kg.
3. **Electrons** are universal constituent of matter.
4. **Mass of proton** is 1.67×10^{-27} Kg where as that of neutron is 1.67×10^{-27} Kg.
5. **Atomic number** : The number of unit positive charge carried by the nucleus of an atom or the number of electrons present outside the nucleus of an atoms.
6. **Mass number** : The sum of the number of protons and neutrons present in the nuclus of an atom.
7. **Isotopes** : Atoms of same element having same atomic number but different mass number.
8. **Isobars** : Atoms of different elements having same mass number but different atomic numbers.
9. **Isotones** : Atoms of different elements which possess the same number of neutrons.
10. **Dual nature** of electron was suggested by de Broglie. According to him electron behaves both as a particle and also as a wave.
11. **Quantum numbers** are identification marks for the electrons in an atom. Position of an electron in an atom can be ascertained by these quantum nos. The four quantum numbers are Principal, azimuthal, magnetic and spin quantum number.

12. Pauli's Exclusion principle :

No two electrons in an atom can have the four quantum numbers same.

Heisenberg's uncertainty principle : It is not possible to determine exactly the position and momentum of an electron simultaneously.

14. Orbit is the circular path around the nucleus in which the electron moves where as **orbital** is the region of space around the nucleus where the probability of finding an electron is maximum.

15. There is only one 's' orbital, three p – orbitals (p_x , p_y & p_z), five d-orbitals (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{z^2}) and seven f-orbitals.

16. Hund's Rule of maximum multiplicity : States that electron pairing in p, d and f orbitals takes place only after all the orbitals of a given set has one electron each.

17. Aufbau Principle : Electrons enter the various orbitals in the increasing order of energy.

18. Some important relations :

$$\begin{aligned} \text{(a)} \quad \text{Planck's constant } h &= 6.62 \times 10^{-27} \text{ erg. sec.} \\ &= 6.62 \times 10^{-34} \text{ J. sec.} \\ &= 6.62 \times 10^{-34} \text{ Kg. m}^2 \cdot \text{sec}^{-1}. \end{aligned}$$

$$\text{(b)} \quad \text{Rydberg constant 'R'} = 109678 \text{ cm}^{-1}.$$

$$\text{(c)} \quad \text{Wave number 'y'} = \frac{1}{\lambda} R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{(d)} \quad \text{Energy 'E'} = hy = h \frac{c}{\lambda} = hc \nu$$

$$\text{(e)} \quad \text{de-Broglie wavelength } \lambda = \frac{h}{p} = \frac{h}{mv}.$$

$$\text{(f)} \quad \text{Heisenberg's Uncertainty Principl } \Delta x \times \Delta p \approx \frac{h}{4\pi}$$

QUESTIONS

(A) Very short answer type questions. (1 marks)

1. State Pauli's exclusion principle.
2. Write the electronic configuration of Cu^+ ion.
3. Give the no. of electrons present in P^{3-} ion.
4. Which quantum no. specifies the shape of an orbital in an atom ?
5. List the quantum numbers (n & l) of electrons for 3d orbitals.

(B) Short questions (2 marks)

1. State Aufbau Principle.
2. An atom has its K and L shells completely filled and five electrons in M - shell. Find out the total number of p electrons.
3. Which quantum number has different values for the two electrons of helium atom ?
4. Electronic configuration of an atom is $1s^2 2s^2 2p^2 3p^6 3s^2$. Determine its atomic number. How many neutrons are present in the nucleus if its atomic wt is 24 ?
5. State the number of neutrons and protons present in C^{12} and C^{14}
6. Give the quantum numbers of electron in hydrogen atom.
7. Calculate the energy of photon having frequency of $1.0 \times 10^{45} \text{ sec}^{-1}$ (planck's constant $h = 6.63 \times 10^{-34} \text{ J.S}$)
8. Name the different spectra of H-atom.
9. Write de Broglie equation.
10. Which is more stable configuration and why ? $4s^2 3d^9$ and $4s^1 3d^{10}$
11. What is the electronic configuration of an element of atomic number 25 ?
12. Give the value of n and l for each of the subshell 2p, 4s, 4d, 6f.
13. Write the quantum number for a 3d electron.
14. State Hund's rule.
15. What are the various quantum numbers of the valence electron of Na(11).
16. What was the objections to the Rutherford's model ? What it was overcome by Niels Bohr ?
17. Write down the value of the quantum numbers for the valency electron of sodium.
18. What is the maximum numbers that may be present in all the atomic orbitals with principal quantum numbers and azimuthal quantum number 2 ?
19. Write the n, l, m and s-values for an electron in 3d - orbital
20. How many protons & neutrons are present in $_{15}^{31}P$?

(C) Short questions (3 marks)

1. Write brief notes on : (each carry 3 marks)
 - (a) Heisenberg's uncertainty principle
 - (b) Aufbau principle
 - (c) Pauli's exclusion principle
 - (d) Hund's rule
2. State the postulates for Bohr's atomic model.
3. What are the limitations of Bohr's atomic model ?
4. Find out the number of electrons, protons and neutrons in K, Na^+ and O^{2-} .
5. A neutral element has mass number 39. It has got one neutron more than protons. Find out the number of electrons, protons and neutrons in this element.
6. The molecular mass of a saturated hydrocarbon is 58. Find out the total number of electrons in one molecule of the hydrocarbon.

7. Find out the total number of electrons in 1.6 gm of methane.
8. Explain why half-filled and completely filled orbital have extra stability.
9. Give the electron configuration in orbitals of the atoms of the elements Nitrogen, Chlorine and Sodium.
10. Write low the values of all the quantum numbers for the valency electrons of chlorine.
11. Represent mathematically :
 - (a) Energy of one quantum of light.
 - (b) Electron's angular momentum as postulated by Bohr.
 - (c) Relationship between energy and mass.

(D) Long questions

1. Give an account of Rutherford's nuclear atom. How did Bohr improve upon Rutherford's model of the atom ?
2. Derive de Broglie equation and state its significance.
3. What are quantum numbers ? Briefly describe the four quantum numbers.
4. Write a note on Pauli's exclusion principle.
5. What are the fundamental particles ? Write their properties.
6. Write a note on Aufbau Principle
7. Give an account of hydrogen spectrum.
8. Write notes on :
 - (a) shapes of s, p, d orbitals
 - (b) Hund's rule.
9. Write note on Aufbau Principle.
10. Discuss about the four quantum numbers and their significance.
11. Discuss Bohr's theory of atom. What are the defects of the theory ? How an orbital differs from that of an orbit ?
12. What are the various postulates of Bohr's model of atom ? Discuss its drawbacks.
13. What are quantum numbers ? Describe briefly the four quantum numbers.

ADDITIONAL QUESTIONS**Long answer questions :**

1. What are cathode rays ? Discuss its characteristics.
2. What observations of α -ray scattering led Rutherford to propose the model of atom ?
3. Give essential features of Bohr's model atom.
4. Discuss the nuclear model of atom.
5. What was the objection to Rutherford's model.
6. How do you explain the existence of various lines in the hydrogen spectrum ?
7. What are the defects of Bohr's model.

8. What is the significance of quantum numbers ? Describe the four quantum numbers.
9. **Write short notes on :-**
 - (a) Atomic number (b) Hund's rule (c) Pauli's exclusion principle. (d) Aufbau principle
 - (e) Dual nature of matter and de Broglie equation (f) Planck's quantum theory
 - (g) Concept of orbital.
10. How will you justify that electron is universal constituent of matter ?
11. Describe the shapes of s, p and d-orbital.
12. What are the differences between orbit and orbital.

SHORT ANSWER QUESTION

(A) Indicate true or false statements in the following :

- (i) Neutrons are produced when α -rays bombarded a metal sheet.
- (ii) X-rays are produced when cathode rays hit a metal anticathode.
- (iii) Energy of the electron in an orbit is negative as electron is negatively charged.
- (iv) Cathode rays can ionise gases.
- (v) Charge of the electron is same as that of proton with opposite sign.
- (vi) Bohr's theory can explain the spectra of all elements .
- (vii) Anode rays affect photographic plate.
- (viii) Isotopes of an element have same position in the periodic table.
- (ix) The energy of shell decreases with increase in the value of n .
- (x) The neutron was discovered by J.J. Thomson.
- (xi) The number of unpaired electrons in oxygen is 2.
- (xii) The shape of an orbital is given by azimuthal quantum number.
- (xiii) An electron radation energy spontaneously while in stationary orbit.
- (xiv) When azimuthal quantum number 'l' is one (1) it refers to 's' subshell.

(B) Give the correct answer :

- (i) What is the mass of an electron ?
- (ii) What is the charge of an electron ?
- (iii) What is the mass of a proton ?
- (iv) What is the electronic configuration of element of atomic number 24 ?
- (v) Which rule states that "no two electrons in atom will have all the four quantum numbers same"?
- (vi) What is the approximate size of nucleus ?
- (vii) Write the electronic configuration of the element of atomic number 29.
- (viii) What is the rule which gives the sequence in which electrons fill the orbital ?
- (ix) Name the rule of maximum multiplicity.
- (x) Draw the shape of d_{xy} orbital.

(C) Fill in the blanks (one mark) :

- (i) Principal quantum number gives the —— of electron wave.
- (ii) Azimuthal quantum number gives the —— of electron wave.
- (iii) Magnetic quantum number gives —— of orbitals in space.
- (iv) d - orbitals can accomodate maximum —— number of electrons.
- (v) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ is the electronic configuration of —— atom.
- (vi) An orbital represents —— motion of the electron around the nucleus.
- (vii) —— number of unpaired electrons are there in oxygen atom.
- (viii) Isotopes of the same element differ in their ——.
- (ix) Isotones are atoms of different elements having —— number of neutrons.
- (x) Atoms of different elements having same mass number but differing in atomic number are called ——.
- (xi) The maximum number of electrons on any arbit is ——.
- (xii) The atomic number of elements having maximum number of unpaired 3p electrons is ——.
- (xiii) If $n = 3$, then l can have values from —— to ——
- (xiv) The number of unpaired electrons in the ground state of carbon is —— .

(D) Multiple choice questions (one mark) :

- (1) Which of the following electronic configuration is permissible ?
 - (a) $1s^2 2s^2 2p_x^1 2p_y^1$
 - (b) $1s^2 2s^2 2p_x^2$
 - (c) $1s^2 2s^2 3s^2$
 - (d) $1s^2 2s^2 2p_y^2$
- (2) The number of neutrons in Zn^{+2} ion with mass number is :
 - (a) 34
 - (b) 36
 - (c) 38
 - (d) 40
- (3) The radius of atomic nucleus is of the order of
 - (a) 10^{-10} cm
 - (b) 10^{-13} cm
 - (c) 10^{-12} cm
 - (d) 10^{-15} cm
- (4) Electmagnetic radiation of maximum wavelength is :
 - (a) UV
 - (b) Radio Waves
 - (c) X-rays
 - (d) Infrared
- (5) Which of the following sets of quantum numbers is not permissible ?
 - (a) $2, 1, 0, +\frac{1}{2}$
 - (b) $2, 2, -1, +\frac{1}{2}$
 - (c) $2, 1, +1, -\frac{1}{2}$
 - (d) $3, 2, 0, -\frac{1}{2}$
- (6) The wavelength of spectral line for an electronic transition is inversely related to –
 - (a) number of electrons undergoing transition .
 - (b) nuclear charge of the atom.

- (c) Difference in energy of the energy levels involved in transition
 (d) velocity of the electron undergoing transition.
- (7) Energy of the electron in an orbit is determined by :
 (a) Principal quantum number
 (b) Azimuthal quantum number
 (c) Spin quantum number
 (d) Magnetic quantum number
- (8) Number of electrons present in an element having 2K, 8L and 5M electrons is :
 (a) 15 (b) 8 (c) 6 (d) 5
- (9) Bohr's model can explain
 (a) spectrum of hydrogen atom only
 (b) spectrum of an atom or ion having one electron only
 (c) spectrum of hydrogen molecule
 (d) solar spectrum
- (10) The triad of nuclei that is isotonic is :
 (a) ${}^6C^{14}$, ${}^7N^{15}$, ${}^9C^{17}$ (b) ${}^6C^{12}$, ${}^7N^{14}$, ${}^9C^{19}$
 (c) ${}^6C^{14}$, ${}^7N^{14}$, ${}^9C^{17}$ (d) ${}^6C^{14}$, ${}^7N^{14}$, ${}^9C^{19}$
- (11) Nitrogen is having three unpaired electrons according to
 (a) Hund's Rule
 (b) Aufbau Principle
 (c) Heisenberg's Principle
 (d) None of the above.
- (12) In an atom no two electrons can have the same value for all the quantum numbers. This was proposed by
 (a) Hund (b) Pauli
 (c) Dalton (d) Avogadro.
- (13) Correct set of four quantum numbers for valence electrons of rubidium ($Z = 37$) is
 (a) 5, 0, 0, $+\frac{1}{2}$ (b) 5, 1, 0, $+\frac{1}{2}$
 (c) 5, 1, 1, $+\frac{1}{2}$ (d) 6, 0, 0, $+\frac{1}{2}$
- (14) For azimuthal quantum number $l = 3$, the maximum number of electrons will be
 (a) 2 (b) 6
 (c) 0 (d) 14

ANSWERS

C. Fill in the Blanks

- | | | |
|-------------------|------------------------|---------------|
| (i) Size | (vi) Three dimensional | (xi) $2n^2$ |
| (ii) Shape | (vii) Two | (xii) 15 |
| (iii) Orientation | (viii) Mass number | (xiii) 0 to 2 |
| (iv) Ten | (ix) Same | (xiv) 2 |
| (v) K | (x) Isobars | |

B. Multiple Choice type

1. a **4.** b **7.** a **10.** a **13.** a **16.** d **19.** a **22.** a **25.** b **28.** a
2. d **5.** b **8.** a **11.** a **14.** d **17.** d **20.** c **23.** b **26.** c
3. b **6.** c **9.** b **12.** b **15.** d **18.** a **21.** d **24.** d **27.** a



UNIT – III

CHAPTER - 4

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

TOPICS DISCUSSED :

- Significance of classification
- Brief history of periodic table
- Modern periodic table
- Present form of periodic table
- Periodic trends in properties of elements
- Nomenclature of elements with atomic number greater than 100.

INTRODUCTION :

There are about 116 elements discovered till today. It is difficult to remember all the properties separately. For systematic study, it was necessary to classify them into different groups on the basis of their characteristics. Once the general behaviour is known, one can always go into details of specific behaviour of each element. The method of classifying the elements having somewhat similar physical and chemical properties is known as periodic classification of elements. The table which contains the elements so classified is called the Periodic table.

4.1 BRIEF HISTORY OF PERIODIC TABLE

In 1829, German chemist **Johann Dobereiner** suggested the relationship between atomic masses of elements with their properties. He noticed a similarity in properties of several groups consisting of three elements, called Triads. In each of the triads the average of the atomic masses of first and third element would be equal to the atomic mass of the second element. For example, in the Triad of Li (7), Na (23) and K (39), the average of the atomic masses of Li and K ($7+39$) would be equal to the atomic mass of the middle element Na (23). This relationship is called **Dobereiner's law of Triad**.

In 1864, **Newlands** observed that when the elements were arranged in the order of increasing atomic masses, elements with similar properties were repeated at intervals of seven i.e. every eighth element was similar in properties to the first one. He suggested this as **law of octaves**. e.g. lithium and sodium were considered to be one octave apart as in musical system.

Lother Meyer in 1869 plotted atomic volumes with atomic masses and found that similar elements occupied similar positions in the plot.

In 1869, a Russian scientist **Dmitri Mendeleev** made a significant contribution to develop the periodic table. Only 63 elements were known at the time and he studied the properties of these elements and gave a law of Periodic table which was stated as :

"The physical and chemical properties of the elements are periodic functions of their atomic masses". After the study of atomic structure, atomic number was considered as fundamental properties of an element. Mosley in 1913 proved that the properties of the elements depend on the atomic numbers rather than atomic masses. Mendeleev realised that the best way to arrange the elements should not be according to atomic masses, but according to atomic numbers.

Mendeleev's periodic table has the following advantages and drawbacks.

ADVANTAGES OF MENDELEEV'S PERIODIC TABLE

There were only 63 elements known when Mendeleev published his periodic table. Within one year of this, 23 new elements were discovered. Some of the advantages of Periodic table are :

- (1) **Prediction of new elements** : In Mendeleev's table there were some vacant places. Mendeleev predicted the properties of the elements that would occupy the vacant places. Actually after a few years of his prediction, these elements were discovered and fitted into the vacant places in the periodic table. These elements were scandium, germanium etc.
- (2) **Correction of atomic mass** : Mendeleev placed Be in Gr II along with Mg, Ca etc. These have valency two. The atomic mass of Be was found experimentally to be 13.5. Hence, it should be placed after 'C' whose atomic mass is 12. Mendeleev determined its equivalent mass and multiplying with 2, found its atomic mass to be 9.1.
- (3) **Atomic structure** : Mendeleev's periodic table helped in the study of electronic configuration of elements.

Drawbacks of Mendeleev's periodic table.

Mendeleev's periodic table had many limitations.

1. **Anomalous position of some elements** : The atomic masses of K, Ni and I are less than those of Ar, Co and Te respectively. In Mendeleev's table K follows Ar, Ni follows Co and I follows Te.
2. **Position of Triads** : In Mendeleev's table, the space for one element is occupied by three elements in the triads like Fe, Co and Ni. This is against the periodic law.
3. **Position of dissimilar elements** : Alkali metals and coinage metals differ in their physical and chemical properties. But these are placed in one group.
4. **Position of noble gases, lanthanides and actinides** : The noble gases, lanthanides and actinides were not known. Noble gases were placed in a separate group called zero group. Lanthanides and actinides have been given one position each which goes against periodic law.
5. **Position of hydrogen** : Hydrogen is similar to alkali metals and to halogens. The position of hydrogen is thus anomalous which can belong to Gr IA and Group VII A.
6. **Position of isotopes** : Mendeleev's periodic table does not speak about the positions of isotopes.

Modern Periodic Law :

The modern periodic law states that "the physical and chemical properties of elements are periodic functions of their atomic numbers".

The improvised and modified periodic table has seven horizontal rows called **periods**. The first period consists of two elements hydrogen and helium. The second period starts with lithium and is completed with neon. There are eight elements in this period. Similarly the third period starts with sodium and is completed with argon. This period also contains eight elements. The fourth period starts with potassium and ends with krypton. The fifth period is similar to fourth one. These are called long periods containing eighteen elements in each. However, the sixth period has 32 elements. The seventh period is incomplete.

Table 4.1 The old form of the Periodic Table.

GROUPS	I A	I B	I A	I B	I A	I B	I A	I B	I A	I B	I A	I B	ZERO
1st Period	1 H												2 He
2nd Period	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F						10 Ne
3rd Period	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl						18 Ar
4th Period	19 K 29 Cu	20 Ca 30 Zn	21 Sc 31 Ga	22 Ti 32 Ge	23 V 33 As	24 Cr 34 Se	25 Mn 35 Br	26 Fe 36 Fe	27 Co		28 Ni 36 Kr		
5th Period	37 Rb 47 Ag	38 Sr 48 Cd	39 Y 49 in	40 Zr 50 Sn	41 Nb 51 Sb	42 Mo 52 Te	43 Tc 53 I	44 R	45 U	46 R	47 H	48 Pb	54 Xe
6th Period	55 Cs 79 Au	56 Ba 80 Hg	57* La 81 Tl	72 Hf 82 Pb	73 Ta 83 Bi	74 W 84 Po	75 Re 85 At	76 Os 77 Ir 78 Pt					86 Rn
7th Period	87 Fr	88 Ra	89# Ac	104 Ku	105 Ha								

THE RARE EARTHS

*Lanthanide series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
#* Actinide series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The vertical columns are known as **groups**. There are nine groups starting from I to VIII and zero.

All the groups except zero and VIII are divided into two subgroups A and B. The elements placed to the left in the vertical column form subgroup A and those placed to the right form subgroup B. Zero group consists of noble gas elements. Group VIII consists of transition elements.

4.2 LONG FORM OF PERIODIC TABLE

In the long form of periodic table the elements are arranged in the order of increasing atomic number. This table has seven horizontal rows called **periods** and eighteen vertical columns known as **groups**.

Period : The seven periods are represented as period 1 to 7. First period contains two elements hydrogen ($1s^1$) and helium ($1s^2$). In these case s, the first shell (K) is completed. The second period starts with $n = 2$, the first member of which is lithium ($2s^1$) and the shell (L) is completed at neon ($2s^2 2p^6$).

PERIODIC CHART OF THE ELEMENTS

PERIODIC CHART OF THE ELEMENTS																		
NORMAL ELEMENTS (s-BLOCK)		NORMAL ELEMENTS (p-BLOCK)														ZERO GROUP (18)(0)		
PERIOD	Group		I-A		II-A		III-A		IV-A		V-A		VI-A		VII-A		He	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
1	H Hydrogen (1.007)	He Helium (4.003)	Li Lithium (6.941)	B Boron (10.812)	C Carbon (12.011)	N Nitrogen (14.007)	O Oxygen (15.999)	F Fluorine (18.998)	Ne Neon (20.179)	Ne Neon (20.988)	Ar Argon (39.968)	He Helium (4.003)	He Helium (4.003)	He Helium (4.003)	He Helium (4.003)	He Helium (4.003)	He Helium (4.003)	
2	Mg Magnesium (24.325)	Al Aluminum (26.9817)	Si Silicon (28.085)	P Phosphorus (30.9737)	S Sulfur (32.065)	Cl Chlorine (35.453)	Br Bromine (79.904)	Se Selenium (80.000)	Te Tellurium (127.50)	I Iodine (126.904)	Xe Xenon (131.28)	Kr Krypton (83.80)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	
3	Na Sodium (22.9897)	Mg Magnesium (24.325)	Al Aluminum (26.9817)	Si Silicon (28.085)	P Phosphorus (30.9737)	Cl Chlorine (35.453)	Br Bromine (79.904)	Se Selenium (80.000)	Te Tellurium (127.50)	I Iodine (126.904)	Xe Xenon (131.28)	Kr Krypton (83.80)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	Lu Lutetium (174.987)	
4	K Potassium (39.098)	Ca Calcium (40.08)	Sc Scandium (44.956)	Ti Titanium (47.98)	V Vanadium (50.9415)	Cr Chromium (51.996)	Mn Manganese (54.9380)	Fe Iron (55.847)	Co Cobalt (58.9020)	Ni Nickel (58.69)	Cu Copper (63.548)	Zn Zinc (65.38)	Ga Gallium (68.77)	As Arsenic (72.59)	Ge Germanium (74.9216)	Br Bromine (79.904)		
5	Rb Rubidium (61.4678)	Sr Strontium (67.62)	Y Yttrium (88.9056)	La Lanthanum (91.22)	Cr Chromium (92.9065)	Tb Terbium (98.4)	Pr Praseodymium (98.4)	Eu Europium (101.07)	Dy Dysprosium (102.9055)	Tb Thulium (105.42)	Ho Holmium (107.88)	Er Erbium (114.42)	Tm Thulium (118.60)	Yb Ytterbium (121.75)	Lu Lutetium (126.904)	Lu Lutetium (131.28)	Lu Lutetium (174.987)	
6	Cs Cesium (132.9054)	Ba Barium (137.39)	La Lanthanum (138.9175)	Hf Hafnium (178.44)	W Tungsten (183.85)	Ta Tantalum (180.9175)	Re Rhenium (186.207)	Os Osmium (189.2)	Ir Iridium (192.22)	Pt Platinum (195.08)	Au Gold (196.965)	Hg Mercury (200.59)	Tl Thallium (204.383)	Pb Lead (207.1)	Bi Bismuth (208.9894)	Po Polonium (209.91)	At Astatine (210.0)	Rn Radon (222)
7	Fr Francium (223)	Ra Radium (226)	Ac Actinium (227)	Rf Rutherfordium (227)	Ha Hassium (228)	Ere Ergodic (229)	Eos Einsteinium (230)	Eri Eriphium (231)	Ept Eptungium (232)	Ept Eptungium (233)	Ept Eptungium (234)	Ept Eptungium (235)	Ept Eptungium (236)	Ept Eptungium (237)	Ept Eptungium (238)	Ept Eptungium (239)	Ept Eptungium (240)	
INNER TRANSITION ELEMENTS (f-BLOCK ELEMENTS)																		
* LANTHANIDE SERIES		Ce Cerium (140.12)	Pr Praseodymium (140.907)	Nd Neodymium (141.24)	Sm Samarium (141.924)	Eu Europium (143.936)	Tb Thulium (151.96)	Dy Dysprosium (158.9294)	Tb Thulium (159.9294)	Ho Holmium (162.50)	Lu Lutetium (168.9394)	Lu Lutetium (169.942)	Lu Lutetium (170.945)	Lu Lutetium (171.947)	Lu Lutetium (172.948)	Lu Lutetium (173.949)	Lu Lutetium (174.950)	Lu Lutetium (175.951)
* ACTINIDE SERIES		Th Thorium (228)	Pa Protactinium (229)	U Uranium (231)	U Uranium (232)	U Uranium (233)	U Uranium (234)	U Uranium (235)	U Uranium (236)	U Uranium (237)	U Uranium (238)	U Uranium (239)	U Uranium (240)	U Uranium (241)	U Uranium (242)	U Uranium (243)	U Uranium (244)	

Table 4.2 Long form of Periodic Table

There are eight elements in this period. Similarly the third period ($n = 3$) starts with sodium ($3s^1$) and is completed at argon ($3s^23p^6$). This period also contains eight elements. The fourth period ($n = 4$) starts with the filling up of the $4s$ orbital and ends with the completed $4p$ orbital. This period which starts with potassium ($4s^1$) and ends with krypton ($4s^24p^6$) has ten more elements than the earlier one (eighteen elements in all). This is due to the elements in which the filling up of electrons in the $3d$ orbitals takes place after $4s$ orbital but before $4p$ orbitals. The fifth period ($n = 5$) is similar to the fourth one. However, the sixth period ($n = 6$) has 32 elements in which the filling up of electrons takes place in $6s$, $4f$, $5d$ and $6p$ orbitals in that order. The seventh period ($n = 7$) would have been similar to the sixth period, but it is incomplete.

Group : The eighteen groups are designated as Gr IA to VIIA, Gr IB to VIIIB, Group Zero and Gr VIII (three vertical columns). Group IA consists of elements hydrogen ($1s^1$), lithium ($2s^1$), sodium ($3s^1$) potassium ($4s^1$) etc. All these elements have the common outermost electronic configuration ns^1 . The elements of Group IIA have ns^2 configuration. Similarly elements from Group IIIA to group zero have common electronic configuration varying from ns^2np^1 to $ns^2 np^6$. In addition to the above group ten more columns are present between group IIA and IIIA. The elements present in them have common electronic configuration $(n - 1)d^{1-10}ns^{0-2}$. The first of these columns is called group III B which consists of elements scandium ($3d^14s^2$), yttrium ($4d^{10}5s^2$), lanthanum ($5d^1 6s^2$) and actinium ($6d^1 7s^2$) and the last one IIB having zinc ($3d^{10} 4s^2$); cadmium ($4d^{10}5s^2$) and mercury ($5d^{10}6s^2$). The elements present in columns 6, 7 and 8 are grouped as one group and called group VIII. In group III B there are additional 14 elements along with lanthanum and also with actinium. These elements have common electronic configuration $(n - 2)f^{1-14}(n - 1)d^{0-1}ns^2$ and have been shown separately in two rows below the periodic table usually called the lanthanide and actinide series. The other groups are known as IVB, VB, VIB, VIIIB, VIII and IB.

4.3 CAUSE OF PERIODICITY AND MAGIC NUMBERS

From the above discussion it is quite evident that when the elements are arranged in the increasing order of their atomic numbers similar elements are repeated at regular intervals. These intervals are 2, 8, 8, 18, 18, 32 and are known as **magic numbers**.

The elements belonging to a particular group have similar properties and they have similar electronic configuration. By adding the magic number to the atomic number of an element belonging to a particular group the atomic number of the subsequent elements may be found out.

For example, in Gr IA the elements are H (1), Li(3), Na(11), K(19), Rb(37), Cs(55) and Fr(87), the atomic numbers are 2, 8, 8, 18, 18, and 32 units apart. Since all these elements have same number of valence electrons we may regard "the repetition of similar electronic configuration after regular intervals" as the **cause of periodicity** of elements.

4.4 CLASSIFICATION WITH RESPECT TO s, p, d, f BLOCKS

The elements are classified into four blocks namely s, p, d and f depending on the type of orbital to which the last electron of the element enters.

- (i) **Elements of s - block :** These are the group IA (alkali metals like Li, Na and K) and group II A (alkaline earth metals like Be, Mg, Ca and Sr) elements with the outermost electronic configuration ns^1 and ns^2 respectively. This block is situated on the extreme left of the table.
- (ii) **Elements of p-block :** These are the elements in group IIIA to VIIA with the outermost electronic configuration varying between ns^2np^1 and ns^2np^5 . A typical series of these elements starts with $1s^22s^22p^1$ for B and $1s^22s^22p^5$ for F. Elements of zero group with ns^2np^6 configuration are also included in this block. Elements of s and p blocks are often called normal or representative elements. p-Block is situated on the extreme right of table.
- (iii) **Elements of d-block :** These are the **transition elements** (III B to II B in the centre of the periodic table) with common electronic configuration $(n - 1)d^{1-10} ns^{0-2}$. The 3d series of transition elements starts with scandium (21) and ends with Zn (30). The second series of transition elements starts with yttrium and ends with cadmium. Unlike representative elements, they usually form coloured ions and exhibit variable valency.
- (iv) **Elements of f block :** These are called **inner transition elements** arranged in two rows at the bottom of the periodic table such as rare earth or lanthanide (58 to 71) and actinide (90 to 103) containing incomplete 4f or 5f orbitals respectively. In addition to this, these elements also have incomplete $(n - 1)d$ orbitals. The outer electronic configuration of these elements remains essentially the same. Only the number of electrons in the inner orbitals (d or f) varies from element to element.

s-BLOCK		
1s	1	2
2s	Li	Be
3s	Na	Mg
4s	K	Ca
5s	Rb	Sr
6s	Cs	Ba
7s	Fr	Ra

d-BLOCK											
3	4	5	6	7	8	9	10	11	12		
3d	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
4d	Y	Zr	Nb	Mo	Tc	Ru	Rb	Pd	Ag	Cd	
5d	Ta	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
6d	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	

p-BLOCK							
13	14	15	16	17	18		
2p	B	C	N	O	F	Ne	
3p	Al	Si	P	S	Cl	Ar	
4p	Ga	Ge	As	Se	Br	Kr	
5p	In	Sn	Sb	Te	I	Xe	
6p	Tl	Pb	Bi	Po	At	Rn	
7p	—	Unq	—	Uuh	—	—	

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

Table 4.3 Classification of elements into s, p, d, f works

4.5 PERIODICITY IN PROPERTIES OF ELEMENTS :

ATOMIC AND IONIC RADII

The radius of an atom is the distance between the centre of the nucleus of an atom and its outermost electron shell. This determines the approximate size of the atom. In general atomic radius increases while going down the group of the periodic table. This is due to successive addition of new shells. Atomic size decreases across a period due to increase in nuclear charge. This increases nuclear attraction for the electrons. Therefore, atomic size decreases.

Table 4.4 Atomic radii in a group

Elements :	Li (3)	Na (11)	K(19)	Rb(37)	Cs(55)
Atomic radius (A°) :	1.23	1.57	2.03	2.16	2.35

Table 4.5 Atomic radii in a period

Elements :	Li (3)	Be(4)	B(5)	C(6)	N(7)	O(8)	F(9)
Atomic radius (A°) :	1.23	0.89	0.80	0.77	0.74	0.74	0.72

Several types of atomic radii such as covalent radii, vander Waal's radii and ionic radii are known.

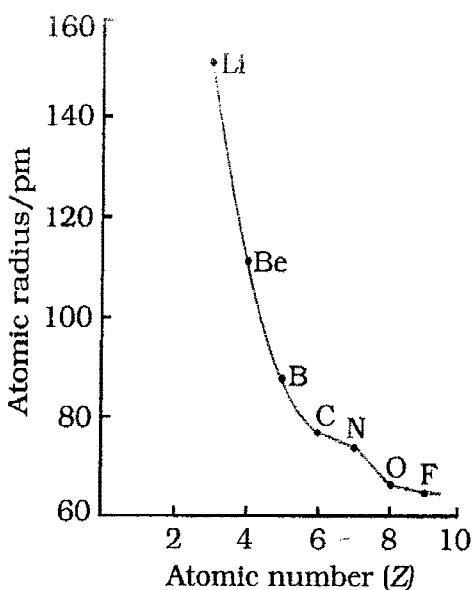


Fig 4.1(a) Variation of atomic radius with atomic number across the second period

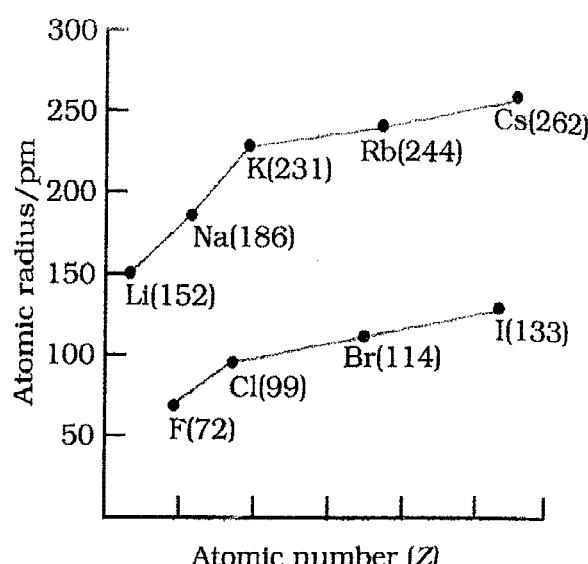


Fig 4.1(b) Variation of atomic radius with atomic number for alkali metals and halogens

- (a) Covalent radius :** It is defined as one half the distance between the nuclei of the two atoms forming a covalent bond. In a diatomic molecule, the internuclear distance is also called bond length.

Example 1 : Internuclear distance in a hydrogen molecule is 0.74A° ,

$$\text{Covalent radius of hydrogen} = 0.37\text{A}^{\circ} \quad \text{Diagram 12.1}$$

Example 2 : Internuclear distance in a chlorine molecule is 1.98A°

$$\text{Covalent radius of chlorine} = 0.99\text{A}^{\circ}.$$

- (b) van der Waal's radius :** It is defined as one half of the distance between the nucleus of two neighbouring nonbonded atoms.

Example 1: van der Waal's radius of hydrogen = 1.2A° .

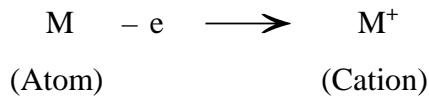
Example 2 : van der Waal's radius of chlorine = 1.8A° .

van der Waal's radius is greater than covalent radius.

- (c) Ionic radius :** It is the effective distance from the nucleus of an ion up to the point where its influence over the electron cloud ceases.

A positive ion (cation) is always smaller than the parent atom and a negative ion (anion) is always larger than its parent atom

When an atom loses one or more electrons positively charged ion or cation is formed.

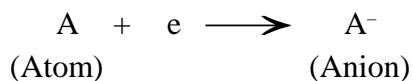


The number of electrons in a cation is always less than the number of protons. Effective nuclear charge increases. Sometimes, the formation of a cation involves removal of the outermost shell.

Table 4.6 Radii of atoms and cations

Atom	radius (A°)	Cation	radius(A°)
Li	1.23	Li^+	0.60
Na	1.57	Na^+	0.95
Mg	1.36	Mg^{2+}	0.60
Al	1.18	Al^{3+}	0.50

When an atom gains one or more electrons, negatively charged ion, an anion is formed.



The number of electrons in an anion is always greater than the number of protons. Effective nuclear charge decreases. The electron cloud expands.

Table : 4.7 Radii of atoms and anions

Atom	radius(A ⁰)	Anion	radius (A ⁰)
F.	0.72	F ⁻	1.36
Cl.	0.97	Cl ⁻	1.81
Br	1.13	Br ⁻	1.95
I	1.35	I ⁻	2.16

ATOMIC VOLUME

Atomic volume is defined as the volume in c.c. occupied by one gram atom of the element in the solid state and commonly called *gram atomic volume*. It is obtained by dividing the atomic mass of the element by its density.

$$\text{Atomic volume} = \frac{\text{Atomic mass}}{\text{Density}}$$

Thus, the atomic volume is the volume in c.c. occupied by 6.023×10^{23} atoms of an element and the volume of a single atom may be obtained by dividing gram atomic volume with Avogadro's number of atoms.

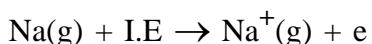
Atomic volume increases more or less regularly in going down a group due to the increase in the number of shells. The larger the number of shells, the bigger is the atomic volume. In going from left to right in a period, it decreases at first, becomes minimum in the middle and then increases. The variation is influenced by (i) nuclear charge (The increased nuclear charge attracts each electron more strongly towards the nucleus resulting in the decrease in the volume) and (ii) number of valence electrons (Towards the end of a period, the number of valence-electrons increases and therefore the volume of the atom increases so that it may accommodate all the electrons). These two factors combine to give the above observation.

Table 4.8. Atomic volumes of some elements

Group ↓ Period	→	IA	IIA	IIIA	IVA	VA	VIA	VIIA	Zero
1.	H							He	
	14.1							31.8	
2.	Li	Be	B	C	N	O	F	Ne	
	13.1	5.0	4.6	5.3	17.3	14.0	17.1	16.8	
3.	Na	Mg	Al	Si	P	S	Cl	Ar	
	23.7	14.0	10.0	12.1	17.0	15.5	18.7	24.4	
4.	K	Ca	Ga	Ge	As	Se	Br	Kr	
	45.3	29.9	11.8	13.6	13.1	16.5	23.5	32.2	

IONISATION ENTHALPY OR IONISATION ENERGY OR IONISATION POTENTIAL

Ionisation enthalpy or ionisation energy of an element is defined as the energy required to remove an electron from the isolated neutral gaseous atom. It is designated as Δ_iH .



This energy is measured in units of electron volt per atom or kJ mole⁻¹. One electron volt per atom is equivalent to 23 kilocalories or 96.3 kilojoules per mole. (Avogadro number of atoms)

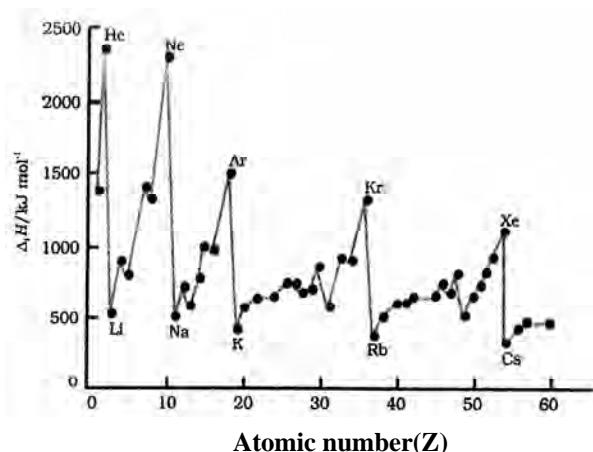


Fig 4.2 Variation of first ionization enthalpies (Δ_iH) with atomic number for elements with $Z = 1$ to 60

Factors affecting Ionisation Enthalpy.

- (i) **Size of atom :** The larger the size of the atom, the smaller is the ionisation energy. With the increase in atomic size the outer electrons lie further away from the nucleus and can be easily removed at the expense of lower amount of energy.
- (ii) **Effect of Nuclear charge :** With the increase in nuclear charge the electrostatic attraction between the nucleus and the outer electrons increases. Thus, the removal of outer electron becomes difficult leading to higher ionisation energy.
- (iii) **Number of electrons in the inner shell**
The inner electrons tend to shield the outer electrons from the pull of the nucleus as a result of which the outer electron can be easily knocked out. This effect is known as **screening effect**. This results in decrease of ionisation energy.
- (iv) **Half-filled or completely filled orbital** According to Hund's rule exactly half-filled or completely filled orbitals are more stable. So more energy is required to detach an electron from atoms having such orbitals and therefore more is the ionisation energy.
- (v) **Nature of electron to be removed :** The 's' electrons experience more attraction than the 'p' electrons since the 's' orbital is closer to the nucleus than the 'p' orbital of the same orbit. Thus removal of 's' electron involves more IE than that of 'p' electron. In general the IE follows the order s > p > d > f orbital of the same orbit.

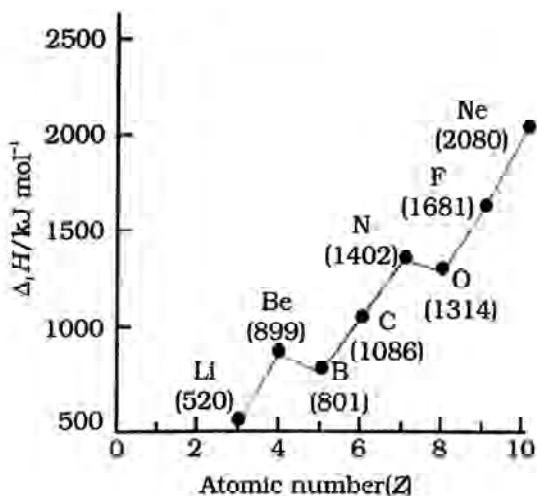
Ionization energy increases from Li to Ne with exception of B and O.

Table 4.9 (IE of elements in second period)

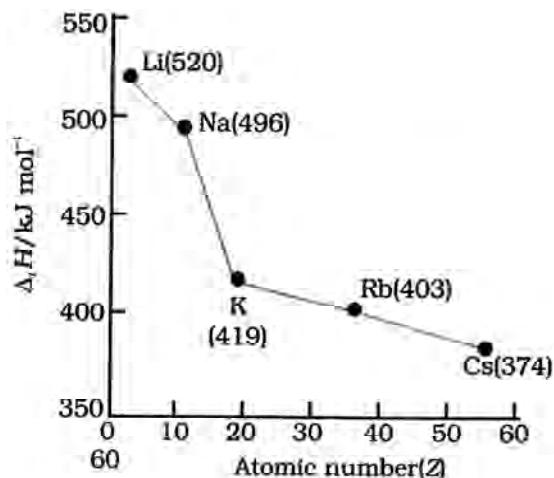
Element	Li(3)	Be(4)	B(5)	C(6)	N(7)	O(8)	F(9)
IE (kJ. mole ⁻¹)	520	900.	800	1086	1403	1314	1681

In general there is an increasing trend of IE across a period. This is due to increase in nuclear charge as we go across a period. The electrons are more strongly held by the attractive force between the nucleus and the electrons. In B(5) and O(8) removal of electron requires lower energy since the resultant ions have stable half-filled or full-filled orbitals.

On the other hand IE decreases as we go down the group. The outer electron is farther from the nucleus and the effect of nuclear charge is decreased by the presence of electronic shells.



4.3 (a)



4.3 (b)

Fig 4.3 (a) First ionization enthalpies (Δ_iH) of elements of the second period as a function of atomic number (Z) and **Fig. 4.3 (b)** Δ_iH of alkali metals as a function of Z.

Properties of elements and compounds as predicted by ionisation energy

- Lower value of ionisation energy indicates the greater reducing power of an element, hence greater reactivity.
- Basic character of an element can be roughly estimated.
- The value of ionisation energy provides us indication regarding the number of valence electrons. Abnormally high value of ionisation energy indicates the removal of electron other than valence electron.

Table : 4.10 (I.E of alkali metals)

Elements :	Li	Na	K	Rb	Cs
IE (kJ mole ⁻¹)	520	495	418	403	374

The ionisation energy to remove the second electron (IE_2) is higher than ionisation energy to remove the first electron (IE_1). The successive values of ionisation energy of an element show an increasing trend. The second electron has to be removed from a positive ion and this requires more energy.

ELECTRON GAIN ENTHALPY OR ELECTRON AFFINITY

The energy released when a neutral gaseous atom gains an electron is called electron affinity or electron gain enthalpy.



Electron affinity is a measure of tightness of binding of an extra electron to an atom. Electron affinity has also been renamed as **electron gain enthalpy** ($\Delta eg\ H^\circ$). The difference comes in the representation of values with sign only. Suppose the electron affinity of an element is 20 kJ mol^{-1} , its $\Delta eg\ H^\circ$ value will be -20 kJ mol^{-1} , because it is an exothermic process.

Factors affecting Electron affinity

- (i) **Atomic size** : Electron affinity decreases with increase in atomic size.
- (ii) **Nuclear charge** : More the nuclear charge stronger will be the attractive force for incoming electron. Thus more energy is released as a result of this attraction and more will be the electron affinity.
- (iii) **Electronic configuration** : An atom having stable electronic configuration has zero electron affinity. For example, the noble gases have ns^2np^6 configuration. These atoms have no tendency to gain electron, thus have zero value of EA. On the other hand the halogens have electronic configuration ns^2np^5 . In order to acquire stable configuration ns^2np^6 , halogens have maximum tendency to gain electron and therefore, are associated with high value of EA.

Elements of Group VIIA (halogens) have high electron affinity. This is because by gaining an electron these attain stable noble gas configuration. The electron affinity decreases as we go down the group because the attractive force of the nucleus decreases with increase in size. Fluorine has slightly lower electron affinity than chlorine probably due to compact $2p$ orbital in fluorine.

Table : 4.11 (Electron affinity of halogens)

Elements :	F(9)	Cl(17)	Br(35)	I(53)
Electron affinity (kJ mole^{-1})	322	348	324	295

Along a period, the nuclear hold on the outermost electron increases as we move from left to right and hence electron affinity increases.

Properties of elements and their compounds as predicted by Electron affinity

- (i) The oxidising power of an element can be predicted from the value of E.A. More the value of E.A more is the tendency to gain electron and greater is the oxidising power.

- (ii) The ionic character of the bond between two atoms can be predicted. By knowing the relative values of ionisation energy and electron affinity of the two elements the nature of bond between them can be predicted. Increase in difference of these two values decreases the ionic character.

ELECTRONEGATIVITY

When two dissimilar atoms i.e. H and Cl form a covalent bond, the electrons forming the bond are not equally shared. The electron pair is shifted to one of the atoms which becomes partially negatively charged. Thus, chlorine has greater electronegativity than hydrogen.

The electronegativities of various elements increase in a period of the periodic table. It is due to increase of nuclear charge which results in decrease in size. Electronegativity decreases in a group. Although atoms of chlorine and sulphur have the same size, chlorine has higher electronegativity than sulphur because of greater nuclear charge.

Both EA and EN measure the electron attracting power of an atom. But the former is concerned with an isolated gaseous atom whereas the latter, with an atom in a molecule.

Electronegativity may be expressed in the following three scales.

- (i) **Mulliken Scale :** According to Mulliken, electronegativity is taken as the average value of Ionisation energy and electron affinity of an atom.

$$EN = \frac{IE + EA}{2}$$

- (ii) **Alfred Rochow Scale :** Alfred and Rochow regarded electronegativity as the electrostatic force operating between the nucleus and the valence electrons. They expressed it as

$$EN = 0.359 \frac{Z}{r^2} + 0.744$$

where, Z is Effective nuclear charge

r is Covalent radius of atom (in A^0),

- (iii) **Pauling Scale :** The most widely used scale was that predicted by Pauling. It is based on excess bond energies. If X_A and X_B be the electronegativities of two atoms A and B

$$X_A - X_B = 0.208 \sqrt{\Delta}$$

where Δ = Actual bond energy - $\sqrt{(E_{A-A} \times E_{B-B})}$

The factor 0.208 arises due to conversion of kcal to electron volt (1ev = 23.01 kcal/mole).

Properties of elements as predicted by Electronegativity

- (i) Nature of bond between two atoms can be predicted. If the difference in value of EN between two atoms is more, more is the ionic character of the bond formed between them. If the difference is zero, this indicates the presence of a covalent band.

- (ii) Greater the value of electronegativity of an element more is its tendency to gain electron and therefore more is its oxidising power. This also indicates that the element is more nonmetallic in nature.

OXIDATION STATES

Mendeleev defined groups of elements on the basis of their valencies or oxidation states. The formulae of compounds formed by an element depends on the oxidation states. Valencies of the representative elements (s and p block elements) of Gr I A to VII A are generally given by the following simple formula.

If G = group number of the representative elements,
valency = G and (8 - G)

These are some exceptions to this rule. Transition elements show variable valency but all of them have a common valency of two.

It is of interest to know the connection between valency and electronic configuration. The outermost group of orbitals are known as valence orbitals. These are involved in chemical bonding. The electrons occupying the valence orbitals are referred to as valence electrons. The valency is determined by the valence electrons.

Table 4.12 Valency and Group

Group	1	2	3	4	5
Examples:	HCl	BeCl ₂	BCl ₃	CH ₄	NH ₃
	H ₂ O	CaCl ₂	Al ₂ O ₃	CO ₂	N ₂ O ₅
	LiCl	CaO	AlCl ₃	SiO ₂	PCl ₃
	Li ₂ O	SrO	TlCl ₃	SnO ₂	PCl ₅
	NaCl	BaO			

4.6 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBER MORE THAN 100 :

About the nomenclature of elements with atomic number greater than 100 new controversies came up in recent years. Usually the naming of the new elements had been traditionally done after the name of its discoverer or discoverers and the suggested name was ratified by the IUPAC. But sometimes it so happened that scientists before collecting the reliable data on the new element got tempted to claim for its discovery. For example, both American and Soviet Union scientists claimed credit for discovering elements 104. The Americans named it Rutherfordium while the Soviets named it Kurchatovium. To avoid such confusion, the IUPAC has made recommendation that until the discovery of a new element is proved and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for zero and numbers one to nine as

shown in Table 4.14. The roots are put together in order of digits which makeup the atomic number and "ium" is added at the end. The IUPAC names of elements with atomic number more than 100 are shown in 4.13.

Table 4.13 Nomenclature or elements with atomic number more than 100

Atomic Number	Name	Symbol	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	Seborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassmium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununnilium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	*	
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	+	
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	+	
118	Ununoctium	Uuo	+	

* Official IUPAC name yet to be announced

+ Elements yet to be discovered.

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 4.14 Notation for IUPAC Nomenclature of Elements with Atomic number more than 100.

CHAPTER (4) AT A GLANCE

1. **Atomic volume :** It is defined as the volume occupied by one gram atom of the element in the solid state at its melting point.
2. **Mendeleev's periodic law :** According to this law, the properties of elements are periodic function of their atomic masses.
3. **Modern periodic law :** The physical and chemical properties of elements are the periodic function of their atomic numbers.
4. **Covalent radius :** The covalent radius of an atom is one half the distance between the nuclei of the two atoms forming the covalent bond.
5. **van der Waal's radius :** It is defined as one half the distance between the two nearest nonbonded atoms.
6. **Ionic radius :** It is defined as the distance between the centre of the nucleus up to which the electron cloud is extended in an ion.
7. **Ionisation enthalpy or Ionisation energy :** It is defined as the amount of energy required to remove an electron from the isolated neutral gaseous atom.
8. **Electron gain enthalpy or Electron affinity :** It is defined as the amount of energy released when an electron is added to the neutral gaseous atom. If electron affinity is 20 kJ mol^{-1} , then electron gain enthalpy will be -20 kJ mol^{-1} .
9. **Electronegativity :** It is defined as the power of an atom in a molecule to draw the shared pair to electron towards itself.

Summary : The physical and chemical properties of the elements are periodic function of atomic numbers. Vertical columns are called **groups**. The horizontal rows are known as **periods**. Long form periodic table has sub groups with eighteen vertical columns. It has s,p,d and f blocks. A number of physical and chemical properties of elements vary periodically with atomic number. These properties include atomic and ionic radius, ionisation energy, electron affinity, electronegativity and oxidation states.

QUESTIONS**GROUP - A****I. Multiple choice question : (One mark)**

1. Long form of periodic table is based on
 - (a) Atomic mass
 - (b) Atomic number
 - (c) Atomic size
 - (d) Electron affinity
2. Which pair of elements is chemically most similar ?
 - (a) Na, Al
 - (b) Cu, S
 - (c) Ti, Zr
 - (d) Zr, Hf
3. Elements of 1 give colour in Bunsen burner due to
 - (a) Low IP
 - (b) Low MP
 - (c) Softness
 - (d) one electron in the outermost shell.
4. Elements of same vertical group of the periodic table have
 - (a) Same atomic size
 - (b) Same electronic configuration
 - (c) Same number of electrons in the outermost shell of their atoms.
 - (d) Same number of atoms.
5. The element with highest value of 1st ionisation potential is
 - (a) B
 - (b) C
 - (c) N
 - (d) O
6. The ion having highest radius is
 - (a) Al^{3+}
 - (b) N^{3-}
 - (c) Na^+
 - (d) F^-
7. Atomic radii of Fluorine and Neon in A° units are respectively given by
 - (a) 0.72, 1.60
 - (b) 1.60, 1.60
 - (c) 0.72, 0.72
 - (d) None of these
8. Which of the following electronic configuration represents an inert gas ?
 - (a) 2, 8, 1
 - (b) 2, 8, 8
 - (c) 2, 1, 7
 - (d) 2, 8, 2
9. The maximum tendency to form unipositive ion is for the element with the following electronic configuration.
 - (a) $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^1$
 - (b) $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^1$
 - (c) $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^2$
 - (d) $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^3$
10. Characteristic of transition element is
 - (a) Incomplete d-orbital
 - (b) Incomplete f - orbital
 - (c) Incomplete s- orbital
 - (d) Incomplete p- orbital.

22. Which of the following atoms possesses the smallest volume?
 (a) S (b) Si (c) P (d) He
23. Ionisation potential of an element does not depend upon
 (a) Electrical neutrality (b) Nuclear charge
 (c) Penetrating effect (d) Shielding effect
24. Zero group was introduced by
 (a) Mendeleev (b) Ramsay
 (c) Lothar Meyer (d) Johnson

GROUP - B

II. Very short answer type questions (one mark)

1. Which of the following has the smallest size ?
 Na^+ , Mg^{+2} , Al^{+3}
2. Which of the following has the smallest electron affinity ?
 Na , O, C, F
3. Which element has the electronic configuration ?
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
4. Name any two elements of Group 14 of the periodic table.
5. Name any two elements of Group 16 of the periodic table
6. Name the group of the periodic table in which the element having atomic number 6 is placed.
7. Between iodine and iodide ion which has the larger size ?
8. Which of the following has the largest size ?
 Na , Na^+ , N, F
9. Write the electronic configuration of the second element of Gruop 16 of the periodic table.
10. Between lithium and sodium which is more electropositive ?
11. Which of the following has the lowest electron affinity ? K, B, C, F
12. Name two elements of group 5 of the periodic table.
13. Which of the following elements shows variable valency ?
 Iron, sodium, calcium, strontium,
14. Name any two elements of group 2 of the periodic table.
15. Which one of the following elements has the lowest electronegativity ? P,N,O,F
16. Which of the following has the highest ionisation potential ? Na, He, Ca, Mg, P
17. Arrange the following in order of increasing size : Cl , Cl^+ , Cl^-
18. Name the elements in the group 1 of the periodic table.

19. Which two elements of the second period of the periodic table have both positive and negative oxidation number ?
20. Write the electronic configuration of an element present in 4th period and 16 group.
21. Why is ionisation energy of Mg greater than Al ?
22. Which of the following has smallest ionisation energy ?

F, Na, Cl, Mg, Cs

III. Short answer type questions : (Two marks)

1. State Mendeleev's periodic law.
2. The ionic radii of alkaline earth metals are smaller than those of the nearest alkali metals. Why ?
3. What is electron affinity ? How does it vary in a period.
4. Why are elements of group I and 2 of the periodic table called s- block elements.
5. The electronic configuration of the element is $1s^2 2s^2 2p^6 3s^2 3p^6$. In which group of the periodic table will it be placed and why ?
6. Justify the position of carbon and lead in the second group.
7. Explain with reasons :
 - (a) Alkali metals do not form dipositive ions.
 - (b) Electronegativity values of inert gases are zero.
8. How does the metallic character of elements generally vary in periods and groups of the periodic table ?
9. How does ionisation energy vary in a period and in a group ? Give reasons.
10. Mg^{2+} ion is smaller than O^{2-} ion although both have the same electronic structure. Explain.

IV. Short answer type questions : (Three marks)

1. Write two characteristics of d-block elements.
2. Name the group of elements classified as s, p and d blocks.
3. Why ionisation energy of Nitrogen is greater than that of oxygen?
4. Between Na and Mg which has higher second ionisation energy and why?
5. Third period has eight and not eighteen elements. Explain.
6. Alkali metals do not form dipositive ions, why ?
7. Why first ionisation energy of Mg is more than that of Al?
8. The ionic radii of alkaline earth metals are smaller than those of the nearest alkali metals? Why?
9. Give four characteristic properties of group 14 elements.
10. Justify the position of carbon and lead in the periodic table on the basis of electronic configuration.

V. Long answer type questions : (Seven marks)

1. Describe the long form of periodic table. What advantages it has over the Mendeleev's periodic table ?
2. What is periodic law ? Discuss how the properties of the elements vary in periodic table.
3. How the properties of the elements vary in each group and each period of the periodic table ?
4. What are electron affinity and ionisation energy ? Explain.
Arrange nitrogen, oxygen and fluorine in the increasing order of their ionisation energy giving reasons.
5. What is long form of periodic table ? How do the properties of elements vary in groups and periods of the periodic table ?
6. Describe long form of periodic Table. How and why ionisation energy vary in groups and periods ?
7. Write notes on – (5 marks)
Variation of size of atoms in Periods & Groups.
8. Write notes on s,p,d,f blocks of elements of the periodic table.

ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS

- | | | | | |
|---------------|----------------|----------------|----------------|----------------|
| 1. (b) | 6. (b) | 11. (d) | 16. (c) | 21. (a) |
| 2. (c) | 7. (a) | 12. (b) | 17. (d) | 22. (d) |
| 3. (a) | 8. (b) | 13. (c) | 18. (b) | 23. (a) |
| 4. (c) | 9. (a) | 14. (b) | 19. (d) | 24. (b) |
| 5. (d) | 10. (a) | 15. (d) | 20. (a) | |



UNIT – IV

CHAPTER - 5

CHEMICAL BONDING AND MOLECULAR STRUCTURE

INTRODUCTION :

Atom is the smallest particle of an element, which may or may not have free existence. But most of the substances exist in the form of clusters or aggregates of atoms. Any such cluster, in which atoms of same or different elements combine together is called molecule. The molecule is electrically neutral and have free or independent existence. For example, hydrogen, oxygen, nitrogen, chlorine etc. exist as diatomic molecules. Here, these diatomic molecules are more stable than their constituent atoms.

Hence, a chemical bond is defined as the force of attraction which holds the constituent atoms in a molecule. It is generally represented by a dash (–), which is used to link the constituent atoms.

But, the stability of monoatomic gaseous molecules of noble gases, like He, Ne, Ar etc. led the scientists to raise the following questions:

- (i) Why do certain elements combine to form molecule, while certain other elements like He, Ne, Ar etc. exist as monoatomic gases and do not form molecules ?
- (ii) What is the nature of force that binds the atoms together ?

5.1 WHY DO ATOMS COMBINE ?

The elements like, He, Ne, Ar, Kr, Xe and Rn are placed at the zero group in the periodic table. These are called inert gases. They do not combine with other elements and also they do not form even diatomic molecules. However, recent researches have shown that, they do enter into chemical combinations with some specific elements under certain specific conditions, forming chemical compounds. The word, inert, therefore, is no longer considered appropriate, so they are called **noble gases**. The word noble, signifying that they enter into very few chemical reactions.

The outer electronic configurations of noble gases are given below ;

Element	Atomic number	Outer electronic configuration (Valence shell electrons)
Helium	2	1s ²
Neon	10	2s ² p ⁶
Argon	18	3s ² p ⁶
Krypton	36	4s ² p ⁶
Xenon	54	5s ² p ⁶
Radon	86	6s ² p ⁶

Atoms of noble gases are considered to be most stable. Therefore, s²p⁶ configuration (8 electrons) in the outer energy level (valence shell) constitutes a structure of maximum stability, except He, where 2 electrons are present.

Following points are required to be understood for the causes of combination of atoms.

- Electronic structure :** Noble gas elements are stable. They contain 8 electrons (except He) in their valence shell. Hence, elements having less than 8 electrons in their valence shell enter into chemical combination. The valence electrons in two or more combining atoms rearrange to form molecules.
- Net attractive forces between atoms :** When two atoms approach each other, the following two types of forces operate between them.
 - Attractive forces between the electrons of one atom and nucleus of the other.
 - Repulsive forces between the electrons and nuclei of the two atoms.

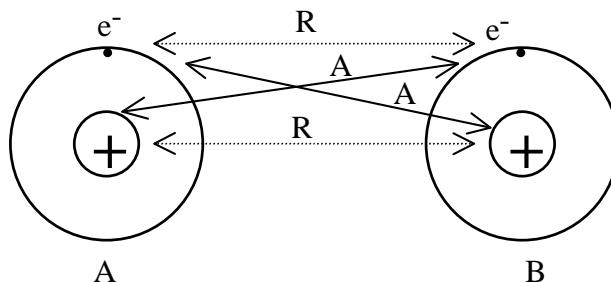


Fig: 5.1 Attractive (A) and Repulsive (R) forces between two atoms.

These two types of interactions counteract each other. When the resultant force is attractive, the two atoms combine. But when the resultant force is repulsive, the atoms do not combine.

- Lowering of energy :** For chemical combination, the resultant force is attractive, which results with decrease of energy. Because, during their approach, some work has been done by the system. Hence, it is clear that atoms combine with the net decrease in energy.

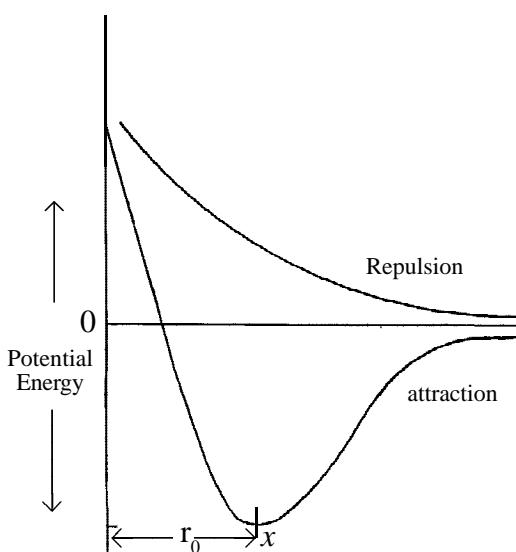


Fig : 5.2 Potential energy curve.

4. **Octet rule :** Kossel and Lewis (1916) observed that, atoms of noble gases have 8 electrons in the valence shell. These are stable and enter into few chemical reactions. Thus, atoms having less than 8 electrons in the valence shell are reactive and capable of chemical combination. In order to complete their octet, the atoms of such elements mutually share or transfer one or more valence electrons.

Thus, each combining atom has a tendency to attain the nearest noble gas configuration of maximum stability and minimum energy, in order to form a compound.

5.2 VALENCE ELECTRONS

Kossel and Lewis (1916) proposed ‘Electronic Theory of Valency’ and their generalisations are as follows;

- (i) The presence of 8 electrons in the valence shell of an atom, like that of noble gases (except He, where the no. of such electrons is 2) constitutes the stable electronic structure of an atom.
- (ii) The capacity of an atom to take part in chemical combination is determined by the number of valence electrons that is, electrons present in the outermost orbit of an atom.
- (iii) During chemical combination, the transfer of one or more valence electrons from one atom to another or mutual sharing of valence electrons amongst themselves takes place.
- (iv) By the process of transference or by the mutual sharing of valence electrons, each combining atom acquires the nearest stable noble gas configuration.
- (v) The number of electrons, which an atom loses or gains or mutually shares to attain noble gas configuration is called its valency.

When the two isolated atoms are at infinite distance apart from each other the potential energy of the system is taken to be zero. As the distance between the atoms decreases the potential energy decreases. At a certain point 'x' the potential energy becomes minimum. This point is attributed to the formation of molecule. The distance between the two nuclei is the bond length r_0 . With further decrease in internuclear distance, net repulsion takes place and the potential energy suddenly increases. Thus, right hand portion of curve is attributed to net attraction whereas the left hand portion to net repulsion.

5.3 TYPES OF CHEMICAL BOND

The following types of chemical bonds are possible, depending upon the process of valence electron rearrangement between the constituent atoms.

- (i) Ionic or electrovalent bond.
- (ii) Covalent bond.
- (iii) Co-ordinate covalent bond.
- and (iv) Hydrogen bond.

I. IONIC OR ELECTROVALENT BOND :

Definition : Ionic bond may be defined as the union of two or more atoms, through the redistribution of valence shell electrons by the process of transference of electrons from one atom to another, so that all the atoms acquire the stable noble gas configuration of minimum energy.

By the process of transference of one or more valence electrons, the atom which loses electrons, acquires positive charge and becomes positive ion or cation. Similarly, the atom which gains the electrons, acquires negative charge and becomes negative ion or anion. In this way, the two atoms become oppositely charged ions. The two oppositely charged ions acquire the electronic configuration of nearest noble gas. The electrostatic attraction between the oppositely charged ions is called the **ionic or electrovalent bond**. The electrostatic attraction always tends to decrease the potential energy. Hence, the potential energy of the system is much less now than it was before the formation of the ionic bond.

This type of bond is also known as **heteropolar bond**. The compounds which contain electrovalent bond are called electrovalent or ionic compounds.

Examples of ionic compounds :

(a) **Formation of sodium chloride :** Here, the constituent atoms sodium (At. No. 11) and chlorine (At. No. 17) have the following electronic configuration.



There is only one electron in the valence shell of sodium atom and seven valence shell electrons in case of chlorine atom.

Hence, sodium has a tendency to lose the outermost electron to chlorine atom, in order to acquire the stable configuration of Neon. Similarly, chlorine atom has a tendency to gain one electron in order to acquire the nearest noble gas configuration of argon.

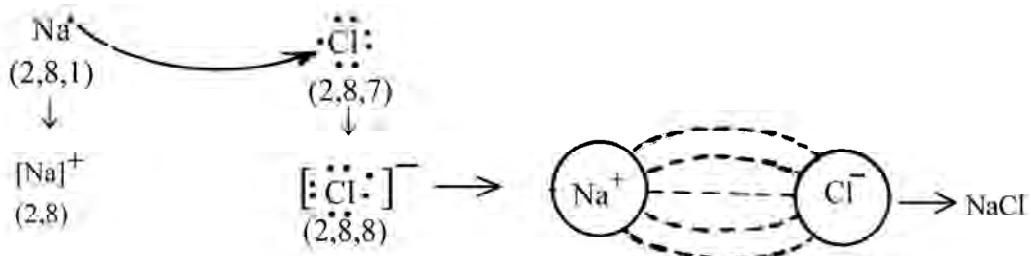
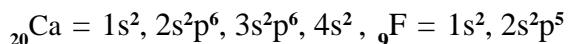


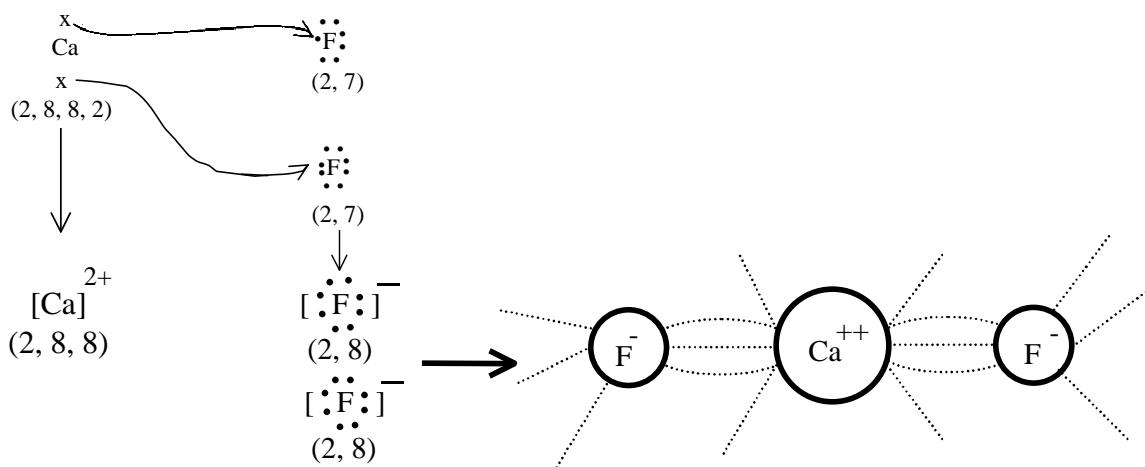
Fig : 5.3 Formation of sodium chloride.

Finally, the positive and negatively charged ions get attracted by the electrostatic forces of attraction. Ionic bond is strong as it is formed by a large decrease of energy. Here, each ion is a charged particle. It is surrounded by an electric field. This field is non-directional, that is, it is uniformly distributed about the ion. Ionic bond is, therefore, considered as non-directional.

- (b) Formation of Calcium Fluoride :** Here the constituent atoms calcium (At.No. 20) and fluorine (At.No. 9) have the following electronic configuration.



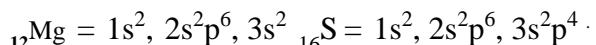
Calcium has two valence shell electrons. It can lose two electrons and attain the nearest noble gas configuration of argon. Similarly, two fluorine atoms can gain one electron each and attain the noble gas configuration of neon.



Finally, the oppositely charged ions get attracted by electrostatic forces of attraction.

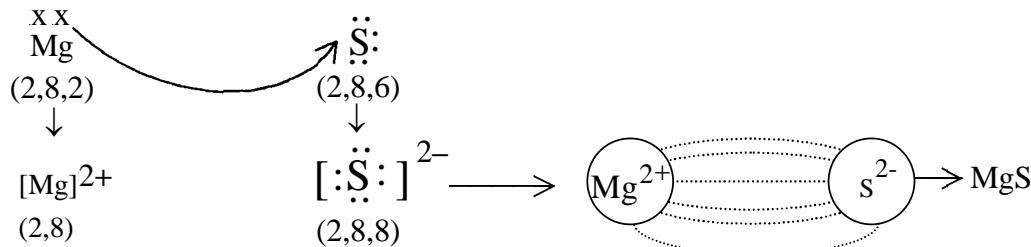


- (c) Formation of magnesium sulphide :** Here the electronic configuration of constituent atoms, magnesium (At. no.12) and sulphur (At. no.16) are given below.



Magnesium has two valence shell electrons. It can lose two electrons and attain the nearest noble gas configuration of neon. Similarly, sulphur atom has a tendency to gain two electrons and acquire the nearest noble gas configuration of argon.

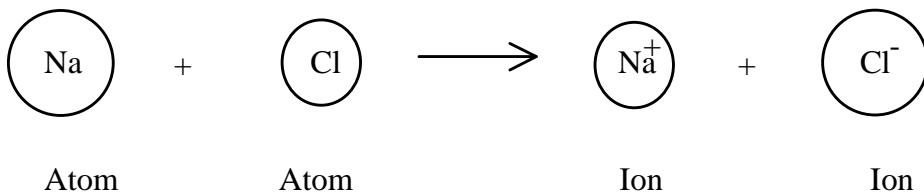
Finally, the two oppositely charged ions get attracted by electrostatic forces of attraction.



Difference between atoms and ions :

It must be remembered that ions differ from the corresponding atoms in several respects. These are given below.

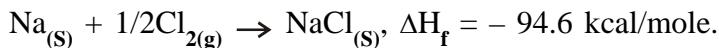
- i. The ions are charged particles, may be positive or negative, whereas atoms are perfectly neutral.
- ii. Ions have the stable $s^2 p^6$ configuration in the outer energy level. But all atoms have not the stable configuration. Therefore, ions are more stable than the corresponding atoms.
- iii. Generally, a positive ion is invariably smaller in size and a negative ion is invariably larger than the corresponding atom.



Born - Haber cycle :

Lattice energy of ionic solids can be calculated by applying Born-Haber cycle. **Lattice energy** is defined as the energy released during the formation of one mole of a crystal of the ionic solid from the constituent gaseous ions.

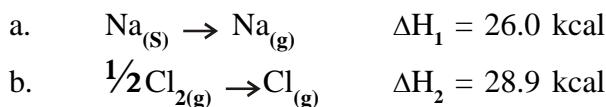
Let us consider the formation of one mole of crystalline sodium chloride (NaCl) from sodium solid and chlorine gas. The heat change involved in the reaction is $-94.6 \text{ kcal per mole}$. The reaction is represented as,



ΔH_f = heat of formation of one mole of sodium chloride.

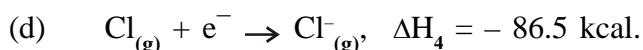
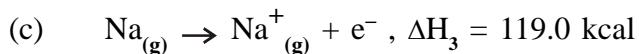
The above reaction may be considered to take place through the following three hypothetical steps.

- (i) The first step involves the sublimation of one mole of solid sodium into gaseous state and dissociation of half a mole of chlorine gas into gaseous chlorine atom.

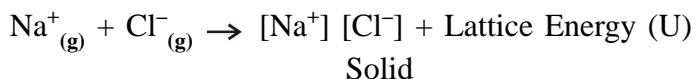


These processes are involved the absorption of energy equal to 26.0 and 28.9 kcal and are called heat of sublimation and heat of dissociation respectively.

- (ii) In the second step, the gaseous atoms of sodium and chlorine are converted to gaseous ions. The energy absorbed for the formation of gaseous sodium ion from gaseous sodium atom is called ionisation energy. Also the energy released for the formation of gaseous chlorine atom is called electron affinity.



- (iii) The final step involves combination of gaseous sodium ion and chloride ion to give one mole of sodium chloride crystal lattice. The energy released in this process is called lattice energy.



According to Hess's law, the heat of formation of one mole of sodium chloride will be the same irrespective of the fact whether it takes place directly or through the three hypothetical steps involved.

$$\text{Hence, } \Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

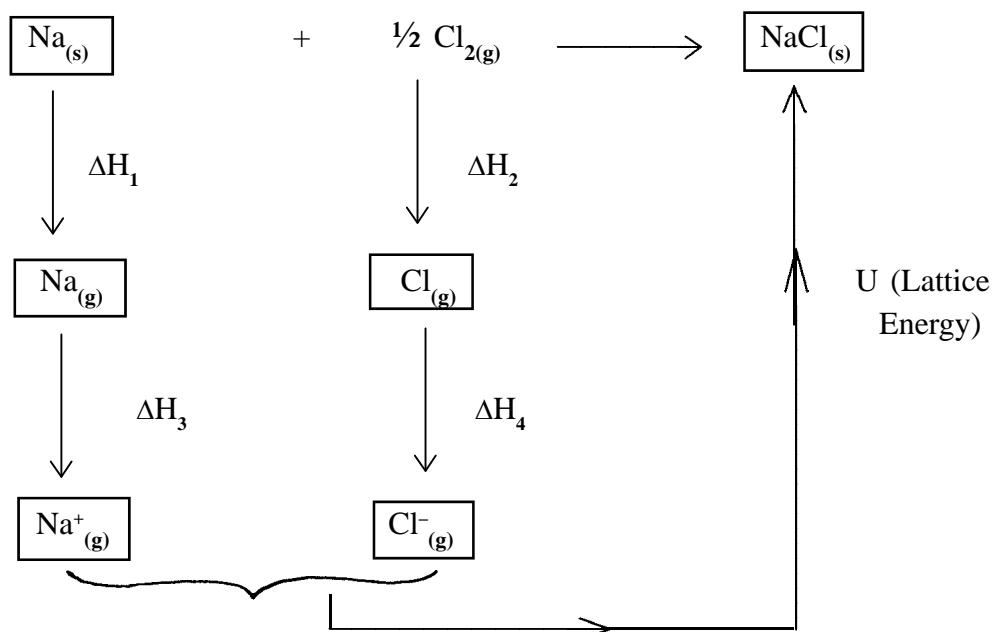
$$\text{Hence, } -94.6 = 26.0 + 28.9 + 119.0 - 86.5 + \text{Lattice Energy.}$$

$$\therefore \text{Lattice Energy} = -182.0 \text{ kcal/mole.}$$

The negative sign indicates that the energy is released or evolved.

Since, the formation of ionic bond is possible only if there is a net decrease in the potential energy of the system, the lattice energy is responsible for the formation of the ionic bond.

The Born - Haber Cycle explained above may be represented as below.

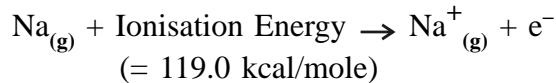


Factors influencing formation of ionic bond :

From the above discussion, we may conclude that the following three factors favours the formation of ionic bonds. between metals and non-metals.

- (i) The ionisation energy of the metal atoms should be low.
 - (ii) The electron affinity of the non-metal atoms should be high.
 - (iii) The lattice energy of the ionic compound formed should be high.
- (i) Low ionisation energy :** Ionisation energy is the amount of energy required to remove an electron from the neutral gaseous atom and form a cation.

For example,

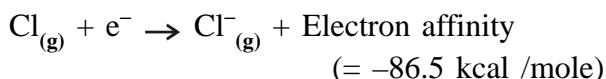


We know, for the formation of ionic bond, the overall energy of the system should be minimum.

Since, energy is absorbed during ionisation, therefore, lesser the ionisation energy, greater is the tendency of an atom to change itself into a cation. That is why, alkali metals form ionic bonds more readily than alkaline earth metals, which have high ionisation energy.

- (ii) High electron affinity :** The second atom gain electron and therefore, an anion is formed. This process is accompanied by the release of energy, known as electron affinity.

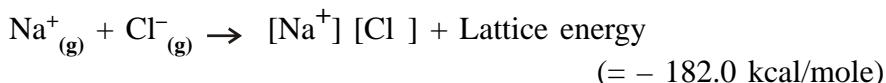
For example



Since, energy is released during the formation of an anion, therefore, greater the value of electron affinity, greater will be the ease of formation of anion.. That is why halogens (with high electron affinity) form ionic bonds more readily than chalcogens (O, S, etc).

- (iii) High lattice energy :** Lattice energy is the amount of energy released to form one mole of crystalline ionic solid.

For example,



Since, energy is released, therefore, greater the lattice energy, stronger will be the ionic bond.

We know that the electrostatic forces of attraction between the oppositely charged ions will be high, at high lattice energy.

But, according to Coulomb's law, the electrostatic forces of attraction, $F = \frac{q_1 \cdot q_2}{d^2}$

where, q_1 and q_2 are the respective charges of ions and d is the distance between the ions. So, if the size of the ions are small, the inter-ionic attraction will be increased. Hence, greater will be the strength of the ionic bond.

Characteristics of Ionic compounds :

The important characteristics of ionic compounds are as follows :

- (i) Physical state :** Due to the strong electrostatic forces of attraction between the oppositely charged ions in ionic solids, ionic compounds are hard and rigid.

- (ii) **High density :** The strong electrostatic forces of attraction between the oppositely charged ions in ionic compounds bring them very close to one another. Consequently, the volume decreases and its density becomes high.
- (iii) **High melting and boiling points :** Ionic compounds have high melting and boiling points due to the strong inter-ionic forces of attraction. A considerable amount of heat energy is required to overcome this force and cause fusion or vapourisation of ionic compounds.
- (iv) **Electrical conductivity :** Ionic compounds do not conduct electricity in solid state. But they conduct electricity in the molten state. The anions and cations in ionic compounds remain intact occupying fixed positions in the crystal lattice, due to electrostatic forces of attraction. Therefore, the ions are unable to move when an electric field is applied. Hence, no current flows.

But in the molten state, since the cations and anions are mobile, they conduct electric current.

- (v) **Solubility in water :** Ionic compounds are highly soluble in polar solvents like water and insoluble in non-polar solvent like benzene, chloroform etc. This arises due to the high dielectric constant of polar solvents. These compounds follow the principle of like dissolves like, that is, polar compounds are soluble in polar solvents.

Electrovalency :

The number of electrons gained or lost by an atom to form an ionic bond is called its electrovalency. Hence, electrovalency of sodium is 1 and that of calcium is 2.

But, iron, cobalt and nickel show variable electrovalency. They form divalent as well as trivalent ions.

Metal	Configuration of atoms	Ion	Configuration of ions
Fe	2, 8, 3s ² p ⁶ d ⁶ , 4s ²	Fe ⁺⁺	2,8, 3s ² p ⁶ d ⁶
Co	2, 8, 3s ² p ⁶ d ⁷ , 4s ²	Co ⁺⁺	2,8, 3s ² p ⁶ d ⁷
Ni	2, 8, 3s ² p ⁶ d ⁸ , 4s ²	Ni ⁺⁺	2,8, 3s ² p ⁶ d ⁸

The outer electronic configuration of above divalent ions are not as stable as the s²p⁶ configuration. Hence, these ions can easily lose one of the d-electron producing trivalent ions, like, Fe³⁺, Co³⁺ and Ni³⁺ ions. These ions are relatively more stable, since the effective positive charge on the nucleus is now higher and it prevents the elimination of any more electron.

Hence, electrovalency of iron, cobalt and nickel may be 2 or 3. Similarly, copper shows variable electrovalency as 1 or 2.

II COVALENT BOND :

Introduction : G.N. Lewis in 1916, first suggested that atoms may combine with one another by mutual sharing of electrons in their valence shells. The shared electrons are counted towards the stability of both the atoms and hence these atoms attain the nearest noble gas configurations. This type of bond is called **covalent bond**. The compounds formed by this process are called covalent compounds.

Hence, covalent bond is formed by the process of equal sharing and equal distribution of valence shell electrons between the atoms.

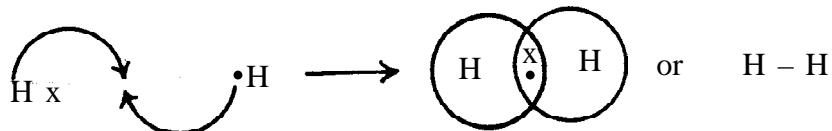
Definition : Covalent bond is defined as the union of two or more atoms through the redistribution of valence shell electrons by the process of mutual sharing amongst themselves, so that all the atoms acquire the stable noble gas configuration of minimum energy.

Examples :

A. Formation of single bond :

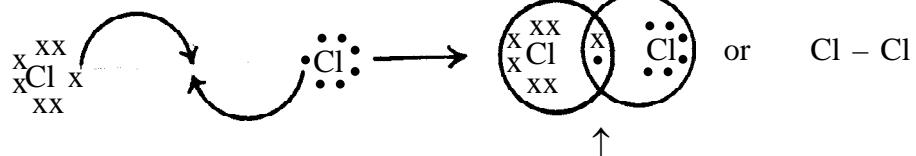
1. **Formation of hydrogen molecule :** Hydrogen (At.No.1) has electronic configuration, $1s^1$. When two hydrogen atoms approach each other, each contributes one electron to the common pair which is then shared equally by both the atoms and thereby acquiring the stable configuration helium atom.

Thus,



2. **Formation of chlorine molecule :** In a chlorine molecule two chlorine atoms are combined together by means of a covalent bond. Chlorine (At.No.17) has electronic configuration $1s^2, 2s^2 p^5$. So chlorine has seven electrons in its valence shell. Here each chlorine atom contributes one electron to form a common pair and the common pair of electron is then shared equally by the two chlorine atoms. Thus, both the chlorine atoms attain stable electronic configuration of argon.

Thus,



(2, 8, 7)

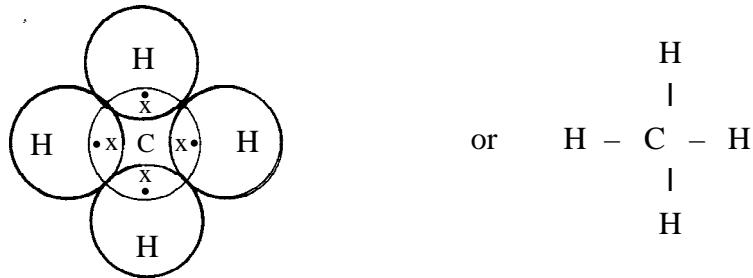
(2, 8, 7)

(2, 8, 8) (2, 8, 8)

- 3. Formation of methane :** In methane the central atom carbon is linked with four hydrogen atoms by means of four single covalent bonds as shown below.

Carbon (At No. 6) has the electronic configuration : $1s^2, 2s^2 p^2$.

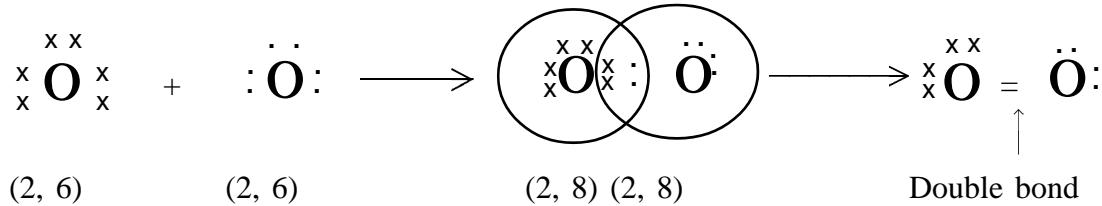
Hydrogen (At. No.1) has the electronic configuration : $1s^1$.



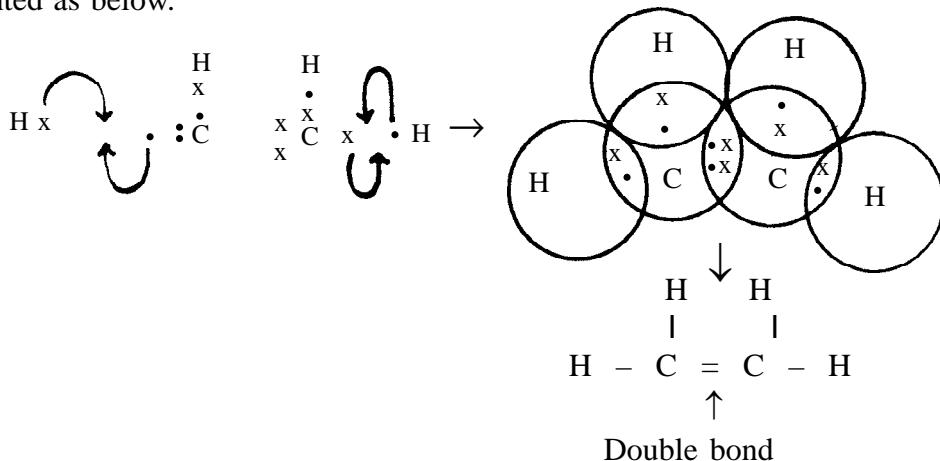
B. Formation of double bonds :

When two electron pairs are shared between the two atoms, double bond results. It is denoted by two dashes (=).

- 1. Formation of oxygen molecule :** The atomic number of oxygen is 8. Its electronic configuration is $1s^2 2s^2 p^4$. Hence each oxygen atom has six valence electrons. So it is deficient of two electrons. For the formation of an oxygen molecule, each oxygen atom contributes two electrons. Thus, two electron pairs so formed are distributed equally between them and attain the stable noble gas configuration of neon.



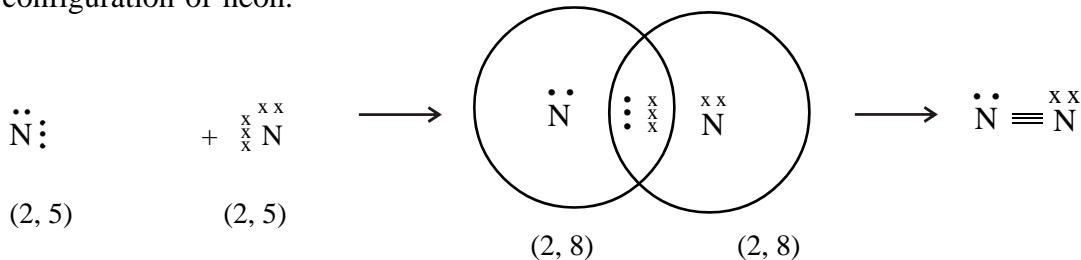
- 2. Formation of ethylene molecule (C_2H_4) :** The formation of ethylene molecule is represented as below.



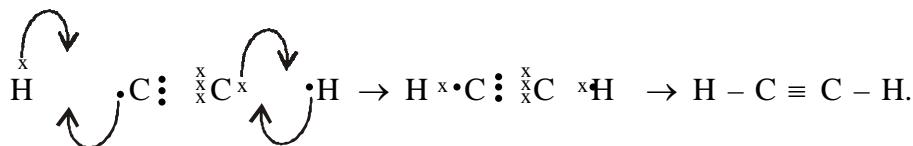
C. Formation of triple bonds :

When three electron pairs are shared between two atoms a triple bond results. It is denoted by three dashes (=).

- Formation of nitrogen molecule :** The nitrogen (At.No.7) has the electronic configuration $1s^2 2s^2 2p^3$. Hence each nitrogen atom has five valence electrons. In order to form a nitrogen molecule, each nitrogen atom contributes three electrons. Thus, three electron pairs formed are then shared equally between the atoms in order to attain the noble gas configuration of neon.



- Formation of acetylene (C_2H_2) :** The formation of acetylene molecule can be represented as given below.



Factors influencing the formation of covalent bond :

The following factors influence the formation of covalent bond.

- High ionisation energy :** Atoms having high ionisation energy are incapable of forming cations. Therefore, they favour covalent bond formation.
- Equal electron affinities :** Atoms having equal electron affinities favour covalent bond formation, since covalent bond is formed due to equal sharing of electrons.
- Electronegativity :** Atoms having either little difference or no difference in their electronegativities favour covalent bond formation. This is because, in such cases, the transfer of electron from one atom to the another is hindered.

Covalency and variable covalency :

The number of electrons contributed by an atom for sharing, to establish a covalent bond is called its covalency. The covalency of hydrogen is one, while oxygen, nitrogen, and carbon have covalencies 2, 3, 4 respectively.

But the covalency of phosphorus in PCl_3 is three and five in PCl_5 .

Characteristics of covalent compounds :

- The characteristics of covalent compounds are described below.
- (i) **Physical state :** Most of the covalent compounds exist either in gaseous or liquid state. This is due to the weak force of attraction between the atoms constituting the covalent bond.
 - (ii) **Low melting and boiling points :** The force of attraction between the constituent atoms in covalent compound is weak in comparison to ionic compound. Hence, the melting and boiling points of covalent compounds are low.
 - (iii) **Bad conductors :** Covalent compounds are bad conductors of electricity and carry no current, because they do not ionise by passing electric current through them.
 - (iv) **Solubility :** Covalent compounds are usually insoluble in polar solvents like water. However, they dissolve in non-polar or organic solvents, like, benzene, carbon tetrachloride etc.
 - (v) **Slow rates of reaction :** Since covalent compounds show molecular reactions, their rates of reaction are slow.
 - (vi) **Isomerism :** Covalent bonds are rigid and directional. So they can give rise to different arrangements of atoms in space. Therefore, covalent compounds can appear in different structures in space with different properties. This property is called **isomerism**, which is exhibited by covalent compounds.

5.4 BOND PARAMETERS :

1. Bond Length : The equilibrium distance between the nuclei of two bonded atoms in a molecule is known as bond length (also called bond distance or inter-nuclear distance). Bond length of a molecule can be determined by various methods like electro-negativity method, electron diffraction method, neutron diffraction method and molecular spectra method.

As it is possible to measure the radius of an isolated atom or ion, the following concepts are used to define atomic and ionic radius. These are covalent radius, vanderWaals radius and ionic radius. The covalent radius is defined as half of the distance between the nuclei of two similar atoms, covalently bonded to form molecule.

$$r_A = \frac{d_{A-A}}{2}$$

vander Waals radius of an element can be defined as half of the inter nuclear distance between the nuclei of the adjacent atoms, belonging to two neighbouring molecules of that element, in the solid state. Ionic radius is the distance between the nucleus of the ion and the point upto which the nucleus exerts its attractive force on the electron cloud of the ion.

2. Bond Order : Bond order (also called as bond multiplicity) is defined as the number of covalent bonds formed between two atoms in a given molecule. For example, bond order in H₂ is 1, in O₂ is 2 and in N₂ is 3, which also indicates the number of shared pairs of electrons between the atoms. It is observed that with the decrease of bond order between the two atoms, the bond length between the atoms increases. Thus, the relation between bond order and bond length is expressed as,

$$\text{Bond Order} \propto \frac{1}{\text{Bond Length}}$$

It is also a fact that with increase in bond order, bond energy increases; i.e. Bond order \propto Bond energy.

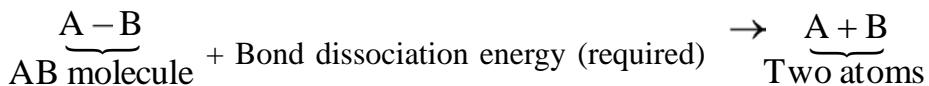
3. Bond Angle : The angle between the bonding electron pairs in a given molecule or an ion is called bond angle. For example, HCH bond angle in CH₄ molecule is equal to 109.5°. It is very helpful in understanding the distribution of orbitals around the central atom in a molecule or an ion and also the shape of the molecule or ion. The magnitude of bond angles is affected by the following factors.

- (i) Number of lone pairs of electrons on the central atom of a given molecule or an ion.
- (ii) Electronegativity and size of central atom and other atoms in a molecule.
- (iii) Presence of multiple bonds in a molecule.

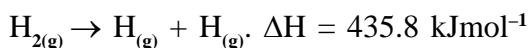
4. Bond Energy : In the formation of a bond some amount of energy is released. This energy is called ‘bond formation energy’ or simply ‘bond energy’ or ‘bond enthalpy’.



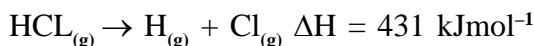
Likewise, in the dissociation of a bond, some amount of energy is required, which is called as ‘bond dissociation energy’.



Bond energy is defined as the amount of energy required to break one mole (one Avogadro's number) of bonds, formed between the constituent atoms (in gaseous state). For example,



Similarly, bond energy of HCl molecule is 431 kJmol⁻¹



The most important application of bond energy is that this can be used to evaluate the heat of reaction of a given process.

5.5 LEWIS STRUCTURE :

The concept of electron dot structure was given by Lewis. The electron dot structure will enable us to understand the formation of a bond between the constituent atoms.

The essential points for representation of an atom are as follows :

- The symbol for an element represents the nucleus and the electrons in the inner energy levels, which are not involved in bond formation.
- The dots on the symbol represent the number of valence electrons, that is electrons present in the outermost energy level.
- When combination takes place between two similar atoms, valence electrons on two atoms are represented differently. Dots are put on one atom and crosses on the other.

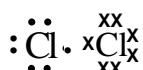
Example :1.(a) The atomic number of chlorine is 17.

Its electronic configuration is $1s^2, 2s^2p^6, 3s^2p^5$

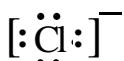
The outer electronic configuration is $3s^23p^5$

It is written as, $\text{:}\ddot{\text{Cl}}\text{:}$.

- Cl represents the nucleus of chlorine and 10 (2, 8) inner electrons.
 - Seven dots on it represent valence electrons.
- (b) The formation of chlorine molecule is represented as,

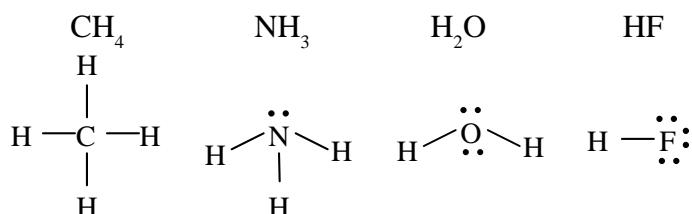


- (c) The formation of chloride ion is represented as,



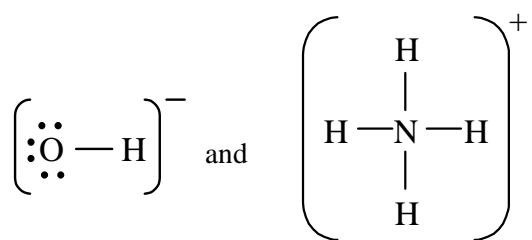
Here, one electron is added to the chlorine atom. Hence, chloride ion attains the electronic configuration of argon, with the electronic configuration 2, 8, 8.

- In the Lewis structure of a molecule, a covalent bond between atoms is ordinarily shown as straight line between atoms, Unshared electron pairs, belonging entirely to one atom are shown as dots. The Lewis structures for the molecules formed by hydrogen with C, N, O and F are



In each case the central atom (C, N, O, F) is surrounded by eight valence electrons and a single electron pair is shared between two bonded atoms. These bonds are called **single bonds**. Depending upon the number of shared pairs of electrons, **double bonds and triple bonds** occur. (see later).

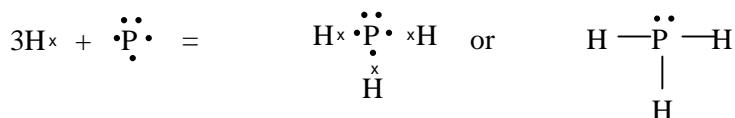
Many polyatomic ions can be assigned simple Lewis structures. For example, the OH^- and NH_4^+ ions can be shown as :



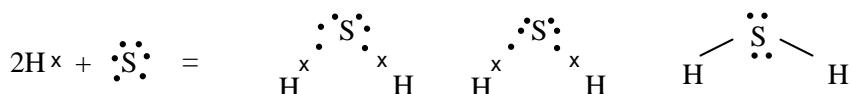
With OH^- ion, this is one more than the number contributed by the neutral atoms ($6 + 1 = 7$). The extra electron is accounted for by the -1 charge of the ion. With the NH_4^+ ions, 4 hydrogen atoms and a nitrogen atom supply 9 ($4 + 5 = 9$) valence electrons. One of these is missing in the NH_4^+ ion, accounting for its $+1$ charge.

Electron Dot (Lewis) structure of a few simple molecules and ions.

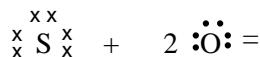
(a) Phosphine



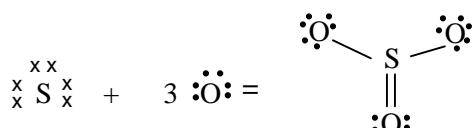
(b) Hydrogen sulphide



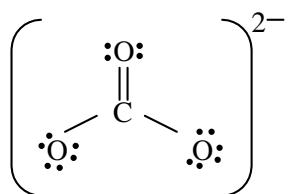
(c) Sulphur dioxide



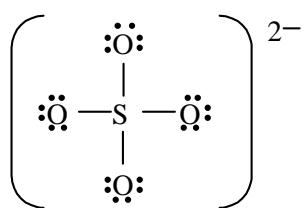
(d) Sulphur trioxide



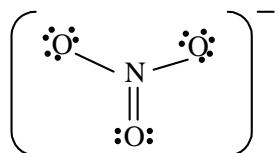
(e) Carbonate ion CO_3^{2-}



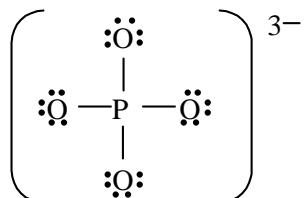
(f) Sulphate ion SO_4^{2-}



(g) Nitrate ion NO_3^-



(h) Phosphate ion PO_4^{3-}



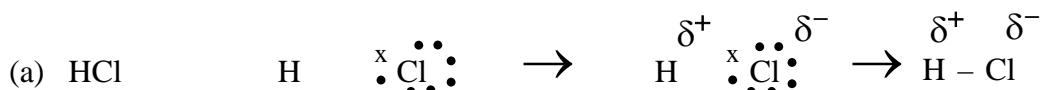
5.6 POLAR CHARACTER OF COVALENT BONDS :

A covalent bond is formed by equal contribution and equal sharing of valence shell electrons between the constituent atoms in a molecule. But, we know, electronegativity of an atom in a molecule is its relative power or tendency to attract the shared pair of electrons towards itself. The electronegativity values of some of the elements are given in the following Table-5.1.

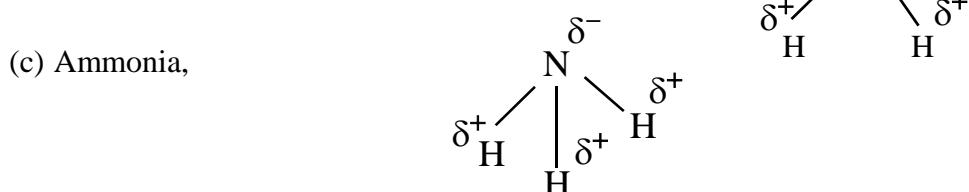
Table: 5.1 Electronegativity of some common elements.

Name of the element	Electronegativity value
Hydrogen	2.1
Boron	2.0
Carbon	2.5
Nitrogen	3.0
Oxygen	3.5
Fluorine	4.0
Chlorine	3.0
Bromine	2.8
Iodine	2.5

Polar covalent bonds : From the above discussion, we may conclude that, if in a molecule the values of electronegativity of constituent atoms differ much, then the shared pair of electron is shifted slightly towards more electronegative atom. As a result of which, there occurs charge separation. Thus, the more electronegative atom acquires a partial negative charge and less electronegative atom gets a positive charge. These are written as δ^+ and δ^- .



(b) Water,



Greater the difference in the electronegativities of the atoms, greater is the charge separation. Since, here dipole results, these bonds are called **polar covalent bonds**.

Non-polar covalent bonds : When a molecule is formed by two similar atoms or by the atoms which differ very slightly in their electronegativities, then such a molecule is said to be **non-polar**. In such molecules, the shared electron pair remains exactly midway between the two nuclei and no charge separation takes place.

Examples : H₂, Cl₂, F₂, O₂, N₂, CH₄ etc.

Ionic character of bonds and polar molecules (Dipole moments) :

Heteronuclear molecules are made up of different kinds of atoms. More electronegative atom withdraws the shared pair of electrons more towards itself and acquires partial negative charge. The other atoms acquires the same amount of positive charge. Such molecules having positive and negative charges, separated by some distance form dipoles and thus possess dipole moments.

Dipole moment :

The degree of polarity of a bond or a molecule is usually expressed in terms of dipole moment. The **dipole moment** is defined as the product of the magnitude of the charges and the distance between them.

Mathematically,

$$\text{Dipole moment } (\mu) = e \times d$$

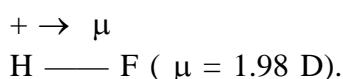
Here, e = magnitude of charges or net +ve or -ve charge and is of the order of 10^{-10} e.s.u.

d = distance between the charges, that is, bond length and is of the order of 10^{-8} cm.

Thus, the values for dipole moments of molecules are of the order of 10^{-18} e.s.u – cm. This quantity is called a Debye and is represented as D. For example, dipole moment of HCl is 1.03×10^{-18} e.s.u – cm and is expressed as 1.03 D.

Representation :

The dipole moment is a vector quantity having magnitude as well as direction. The direction of dipole moment is indicated with the help of an arrow head (+ →) pointing towards the more electronegative element. For example, the dipole moment of HF is shown as,



Dipole moment in diatomic molecules :

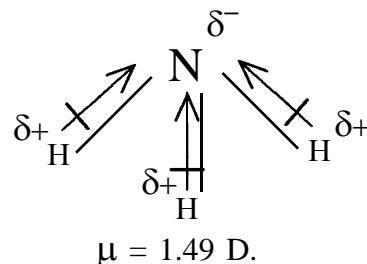
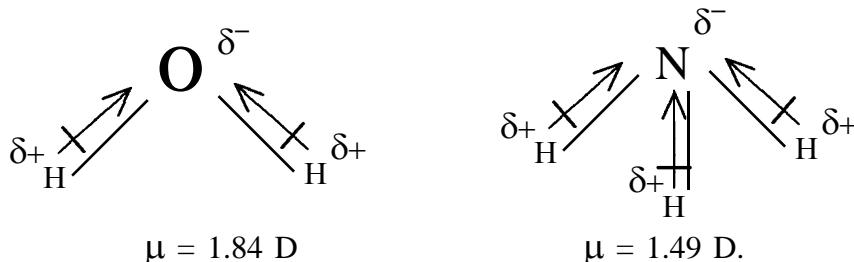
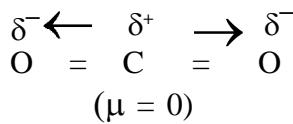
A diatomic molecule has two atoms bonded to each other by a covalent bond. The dipole moment of a diatomic molecule with one polar bond is equal to the dipole moment of its individual bond. For example, HF has one polar bond. Its dipole moment is 1.98 D, which is the same as that of single H – F bond.

Dipole moment in molecules having more than one polar bond

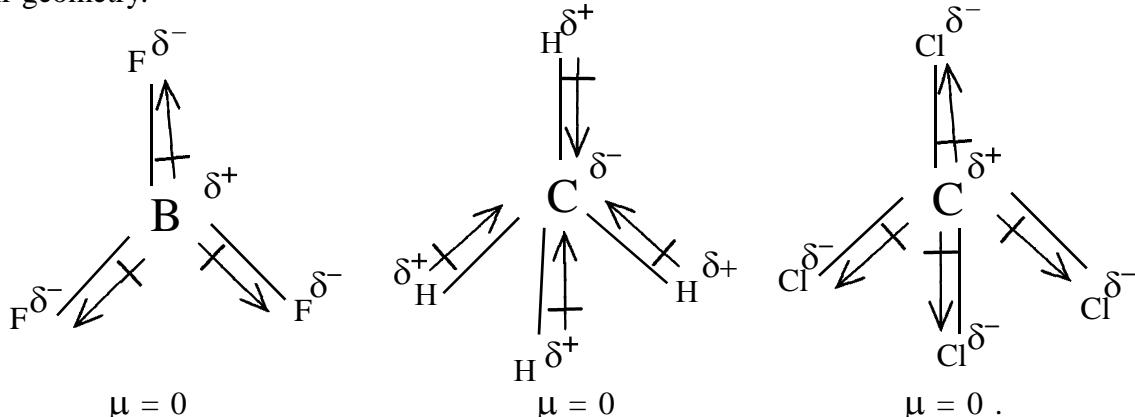
The dipole moment of a molecule with more than one polar bond is equal to the resultant of dipole moments of all the individual bonds. It also depends upon the orientations of the bonds in a molecule in space.

For example, carbon dioxide and water are both triatomic molecules having two polar bonds. But dipole moment of carbon dioxide is zero, whereas that of water is 1.84 D. This difference in dipole moments is due to the difference in their structures.

Carbon dioxide is a linear molecule. The dipole moment of each C = O bond is 2.3 D. But, the resultant dipole moment is zero due to its linear structure. Hence, CO₂ is a non-polar molecule. But, water is a polar molecule having dipole moment 1.84 D. It is due to the bent structure of water. Due to the bent structure of water, the dipole moment of each O – H bond can not cancel out and shows a resultant dipole moment. Similarly, the dipole moment of ammonia molecule is 1.49D, which is the resultant of three polar N – H bonds oriented in space at an angle of 107° with respect to each other.



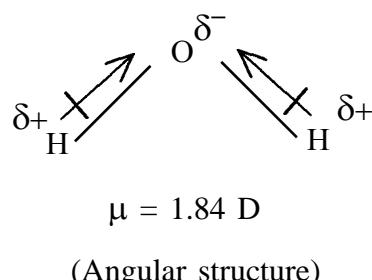
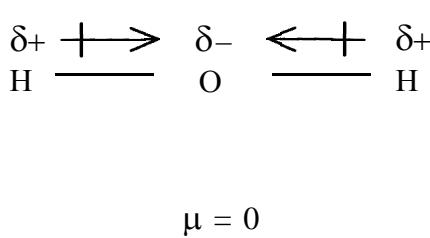
Similarly, BF₃, CH₄ and CCl₄ have no resultant dipole moment, because of their geometry.



Applications of dipole moment :

Some of the applications of dipole moment are described below :

- (i) **Shape of molecules :** Dipole moment values can help in predicting the shape of molecules. For example, water can have a linear or an angular structure.



If water will have linear structure, its dipole moment should be zero. But experimental data shows that water has a dipole moment of 1.84 D, which is possible with angular structure. Thus, water molecule can not be linear, but must have an angular shape. Similarly, since the net dipole moment value of carbon dioxide is zero, it must have a linear structure.

(ii) Distinction between polar and non-polar molecules :

The dipole moment values can also be used to predict the polar and non-polar nature of molecules. If a molecule has some specific dipole moment, it is a polar molecule. For example, water ($\mu = 1.84$ D), and NH_3 ($\mu = 1.49$ D) are polar molecules. But, if a molecule has zero dipole moment, it is a non-polar molecule. For example, H_2 , N_2 , Cl_2 , BF_3 , CH_4 and CCl_4 (where, $\mu = 0$) are non-polar molecules.

We have observed that covalent compounds containing non-polar bonds are non-polar in nature. But a covalent compound containing polar bonds may be polar or non-polar in nature. This can be seen from the Table 5.2.

Table 5.2 : Dipole moment of some common molecules.

Molecule	Nature of bond	Dipole moment	Nature of molecule
H_2 , O_2 , Cl_2	Non-polar	0	Non-polar
CO_2 , BF_3			
CH_4 , CCl_4	Polar	0	Non-polar
HF	Polar	1.98 D	Polar
H_2O	Polar	1.84 D	Polar
NH_3	Polar	1.49 D	Polar
SO_2	Polar	1.60 D	Polar
HCl	Polar	1.03 D	Polar
CHCl_3	Polar	1.02 D	Polar

(iii) Degree of polarity : The degree of polarity in molecules can be predicted by the dipole moment values. For example, HF ($\mu = 1.98$ D) has greater dipole moment than HCl ($\mu = 1.03$ D). Hence, HF is more polar than HCl .

CALCULATION OF PERCENTAGE OF IONIC CHARACTER FROM DIPOLE MOMENT

Dipole moment (μ) is defined as the product of charge (e) and the internuclear distance i.e the distance of separation between two nuclei. $\mu = e \times d$, Charge is expressed in esu and distance 'd' in cm, so μ is expressed in esu. cm or in terms of debye (D). $1\text{D} = 1 \times 10^{-18}\text{ esu. cm}$. Consider the case of HX where 'X' is a halogen atom.

- (i) **If the bond is ionic** i.e $\text{H}^+ \text{X}^-$, there is complete transfer of electrons from H to X, the bond has an appreciable value of dipole moment. Dipole moment is determined by the product of electronic charge and the internuclear distance between H and X :
- (ii) **If the bond is covalent**, the value of dipole moment would be negligibly small.
- (iii) **If the bond is polar covalent**, the value of dipole moment lies inbetween the value for a pure covalent bond and a pure ionic bond.

The value of dipole moment in this case is given by the product of charge separated due to polarisation and the internuclear distance.

Thus the value of μ depends upon the magnitude of ionic character developed in the bond.

$$\text{Percentage of ionic character} = \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of pure ionic bond}} \times 100$$

For example :

(a) In case of HF molecule

Internuclear distance ‘d’ = 0.92A°

If the molecule is ionic H^+F^-

$$\mu = e \times d$$

$$= 4.8 \times 10^{-10} \text{ esu} \times 0.92 \times 10^{-8} \text{ cm}$$

$$= 4.42\text{D}.$$

The actual dipole moment of HF = 1.98D

$$\text{So, percent ionic character} = \frac{\text{Actual DM} \times 100}{\text{DM of pure ionic bond}} = \frac{1.98 \text{ D} \times 100}{4.42 \text{ D}}$$

$$= 44.8 \sim 45$$

(b) In case of HCl

Internuclear distance = $127 \text{ pm} = 127 \times 10^{-12} \text{ m}$

Actual Dipole moment = $3.44 \times 10^{-30} \text{ coulombs metre.}$

Dipole moment of HCl considering it to be purely ionic compound

$$= e \times d = 1.6 \times 10^{-9} \text{ coulombs} \times 127 \times 10^{-12} \text{ m}$$

$$= 2.03 \times 10^{-29} \text{ cm}$$

$$\text{Percent ionic character} = \frac{3.44 \times 10^{-30} \text{ cm} \times 100}{2.03 \times 10^{-29} \text{ cm}} = 16.9 \sim 17$$

5.7 COVALENT CHARACTER OF IONIC BOND :

Ionic bonds possess some covalent character due to polarisation of ions.

During the formation of an ionic bond by two oppositely charged ions coming very close to each other, the cation attracts the electron charge cloud of the outer-most shell of the anion towards itself and hence the symmetrical shape of the anion. The ability of a cation to polarise an anion is called its ‘polarising power’ and the tendency of an anion to get polarised by a cation is called its ‘polarisability’. The cation, due to its smaller size and its electron cloud being strongly held to the nucleus, gets very less polarised by the anion. Greater is the polarising power of a cation, greater will be the amount of covalent character produced in the ionic molecule. **Fajans’ rule** explains the partial covalent character of ionic bonds with following conditions.

1. Higher is the positive charge on the cation, higher will be its polarising power and hence greater will be the magnitude of covalent character of an ionic bond.
2. Smaller is the size of the cation, greater is its polarising power and hence higher is the degree of covalent character in the ionic bond.
3. A cation with $ns^2p^6d^{10}$ configuration possesses higher polarising power than the cation having ns^2p^6 configuration and hence imparts more covalent character to the ionic bond.
4. Greater is the negative charge on the anion, more it gets polarised by the cation and hence more is the covalent character of ionic bond.
5. Larger is the size of the anion, more strongly it is polarised by the cation and consequently the covalent character increases.

5.8 VALENCE BOND THEORY :

Theis theory was proposed by **Heitler** and **London** (1927) and later extended by **Pauling** and **Slater** (1931). The main features of the theory are :

- (i) Valency shell atomic orbitals of th two atoms overlap to form a covalent bond.
- (ii) Only half filled atomic orbitals, i.e. orbitals with single electron can overlap and the resulting bond, thus, aquires a pair of electrons with opposite spins.
- (iii) Maximum electron density is found somewhere in the overlapped region. The force that binds the atoms in a covalent bond is due to the electrostatic attraction between the nuclei and the accumulated electron cloud between them.
- (iv) More the extent of overlapping, greater is the strength of the covalent bond. The amount of energy released per mole of bonds formed is called bond energy.
- (v) Covalent bonds show directional properties i.e. the direction of covalent bond is considered to be in the region of maximum electron destity in overlapping region.
- (vi) It so happens sometimes that paired electrons of the valency shell get unpaired and promoted to vacant orbitals of the same valency shell with slightly higher energy,

which can only explain boron's trivalence, carbon's tetravalency, phosphorus pentavalency etc.

Application of VB Theory :

Valency Bond Theory can be explained in simple way by considering the formation of hydrogen molecule. Consider two hydrogen atoms A and B approaching each other with nuclei N_A and N_B , while their electrons are denoted by e_A and e_B . When these atoms A and B are brought closer to each other, force of attraction as well as repulsion sets in between the atoms.

While attraction between nucleus of one atom and its electron, $N_A - e_A$ and $N_B - e_B$, along with nucleus of one atom and electron of other atom, $N_A - e_B$ and $N_B - e_A$, accounts for the attractive force, repulsive force is caused by the repulsion between electrons of two atoms, $e_A - e_B$, and nuclei of two atoms, $N_A - N_B$. It is the attractive force which brings the two atoms close to each other whereas the repulsive force tends to push them away.

When atoms A and B approach each other, a stage is reached where the attractive force balances the repulsive force and the two hydrogen atoms get bonded to form a hydrogen molecule. During the formation of the bond, energy is released, which is called 'Bond Energy' or 'Bond Enthalpy'. It is the same amount of energy which is needed to dissociate one mole of hydrogen molecule.



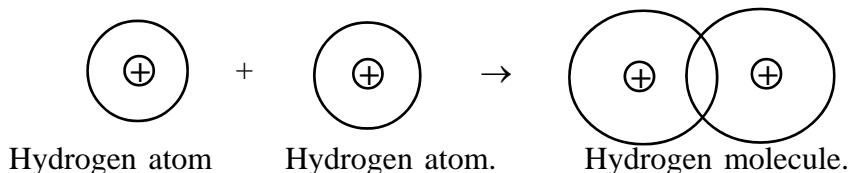
ORBITAL CONCEPT OF COVALENCY

We know, an orbital can accommodate maximum two electrons having opposite spins. But such atomic orbitals are unable to go for chemical combination. However, an atomic orbital containing a single electron in the valence shell have a tendency to combine with another atom having a single electron with opposite spin. This results in the formation of covalent bond between the atoms.

Thus, according to orbital theory a covalent bond is formed between two atoms by simply coupling of electrons with opposite spins present in the atomic orbitals of valence shells of the two atoms. Here the atomic orbitals overlap with each other, so that the electron pair belongs to each orbital. By doing so, the potential energy of the system decreases.

Example :

Formation of hydrogen molecule : The formation of a hydrogen molecule as a result of the overlapping of atomic orbitals of two hydrogen atoms is explained below. The point at which the potential energy is minimum the s-orbitals of two atoms overlap and form a covalent bond.



Types of covalent bonds :

The covalent bonds are of two types, depending on the nature of overlapping of various half-filled atomic orbitals.

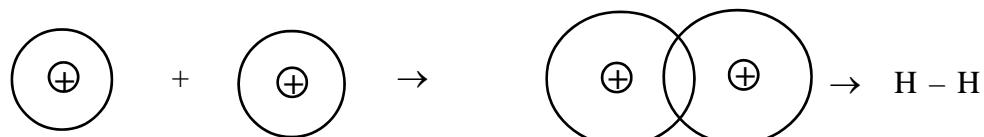
They are 1. sigma bond (σ - bond)

 2. Pi bond (π - bond).

- Sigma bond :** A sigma bond is formed by the overlapping of half-filled atomic orbitals of two atoms along their internuclear axis. This type of overlapping is also called **head on** overlapping or **end-to-end** overlapping. The sigma bond is fairly strong, as the extent of overlapping in it is maximum. Hence, s - s, s - p and p - p sigma bond formation is possible.

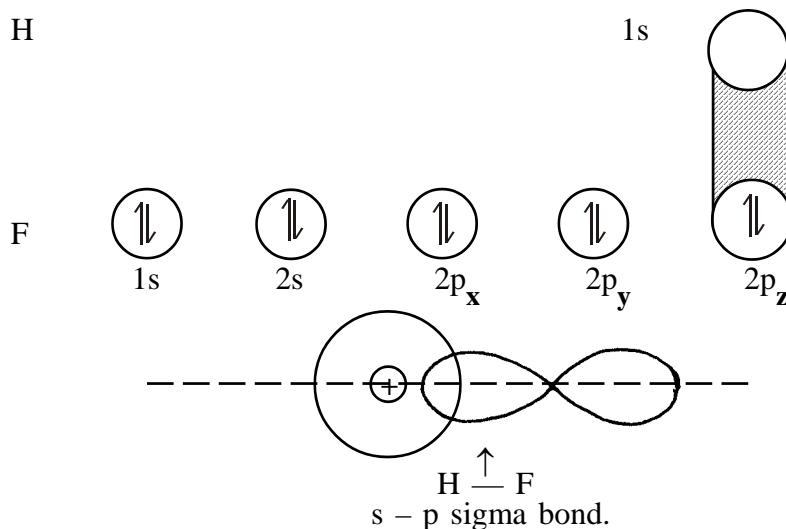
Examples :

- Formation of hydrogen molecule :** The sigma bond formed due to the s - s overlapping of atomic orbital is found in the hydrogen molecule. In this molecule, the half filled 1s orbital of one atom overlaps with the other atom along their axes and form a sigma molecular orbital.

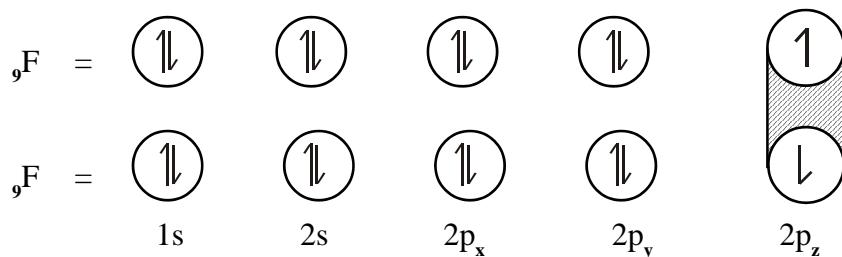


Hydrogen atom($1s^1$) Hydrogen atom ($1s^1$) s - s sigma bond.

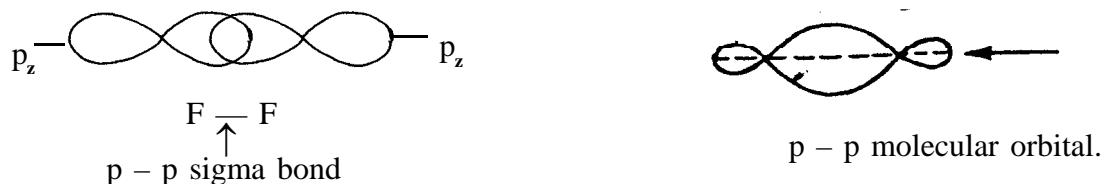
- Formation of Hydrogen fluoride molecule :** The electronic configuration of fluorine (Atomic No.9) is $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. It has one half filled $2p_z$ atomic orbital. Hydrogen atom has one half-filled $1s^1$ atomic orbital. When $1s$ atomic orbital of hydrogen and $2p_z$ orbital of fluorine overlap along their axes, a sigma bond is formed. Here, the nature of the sigma bond is s - p type.



(c) Formation of fluorine molecule :



Here, half - filled $2p_z$ atomic orbital of one fluorine atom overlap with $2p_z$ orbital of another fluorine atom along their axes to form p - p type sigma bond.

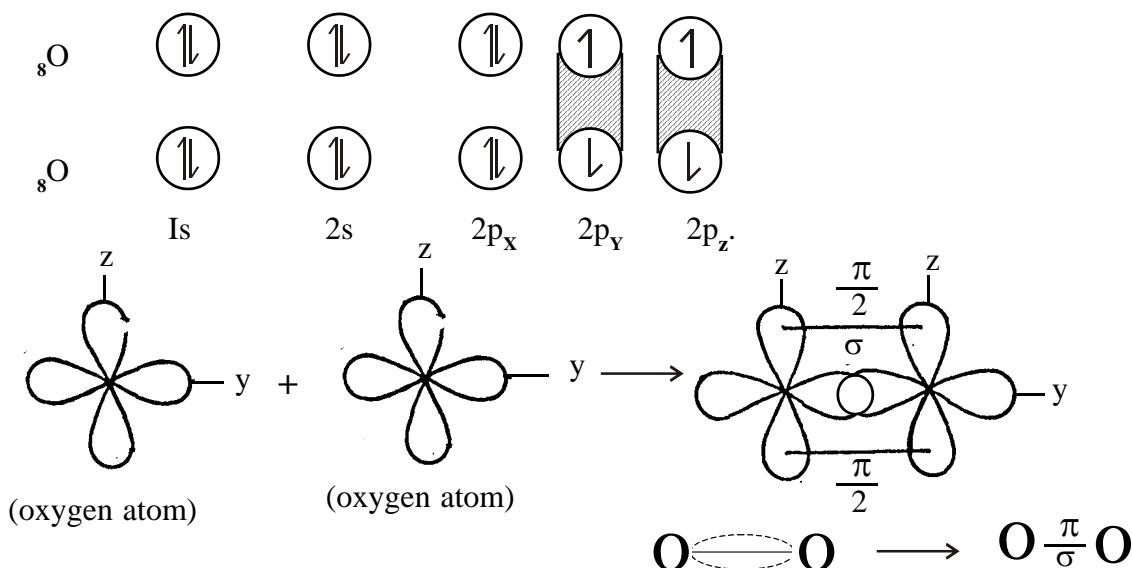


2. **Pi (π) bond :** A pi (π) bond is formed by the lateral or sidewise overlapping of half-filled atomic orbitals present in the valence shells of two atoms.

Here, the overlapping occurs above and below the internuclear axis. The Pi (π) bond is a weak bond, as the extent of overlapping is very small. The formation of π -bond restricts free rotation between the two atoms.

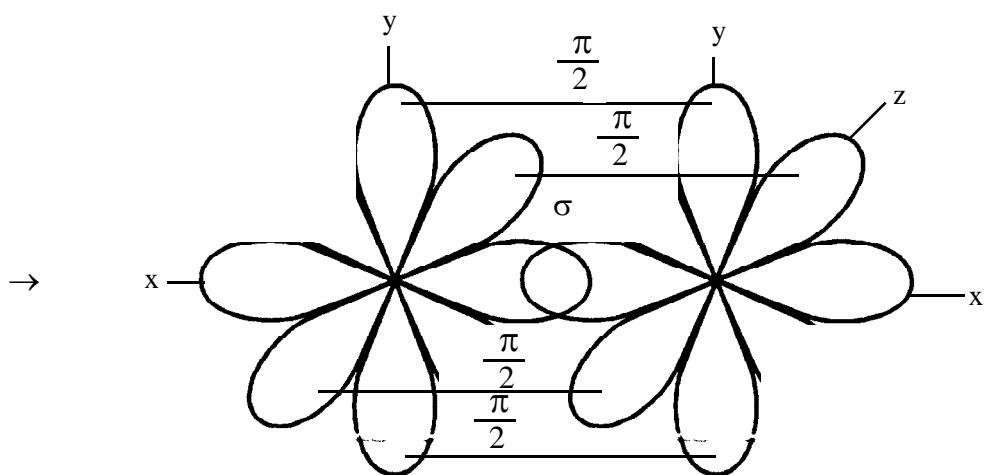
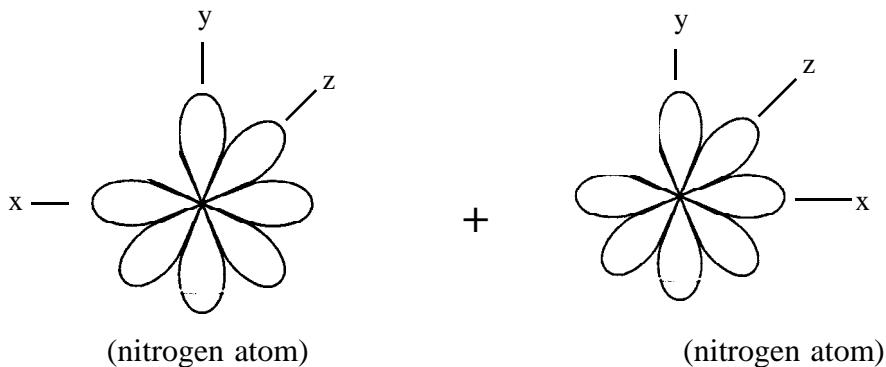
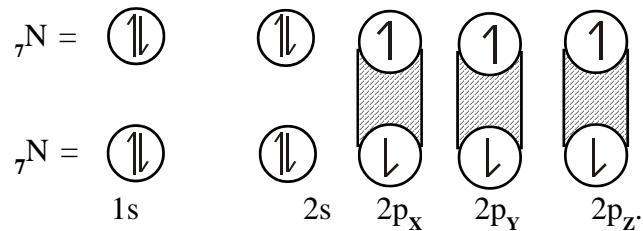
Examples :

- (a) **Formation of oxygen molecule :** The electronic configuration of oxygen (At.No. 8) is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$. Since, two p - orbitals are half filled, two oxygen atoms get attached by a double bond to form oxygen molecule.



Here, $2p_y$ atomic orbital of each oxygen atom overlap along their internuclear axes, to form a sigma bond. But, $2p_z$ orbital is at right angle to $2p_y$ orbital. Thus, $2p_z$ orbital of each oxygen atom overlap sidewise to form a π -bond.

- (b) Formation of nitrogen Molecule :** The electronic configuration of nitrogen (at. no. 7) is $1s^2 2s^2 2p_X^1 2p_Y^1 2p_Z^1$. Since, here, three p - orbitals are half-filled, two nitrogen atoms get attached by a triple bond to form nitrogen molecule.



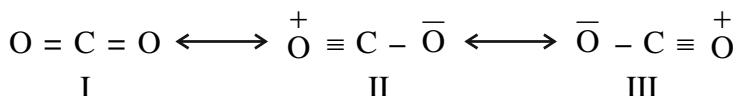
So, one nitrogen molecule consists of a σ – bond and two π -bonds between the atoms.

Comparison between sigma (σ) and pi (π) bonds

Sigma bond	Pi bond
<ul style="list-style-type: none"> i. A sigma bond is formed by the overlapping of half-filled atomic orbitals along their internuclear axes. ii. A sigma bond is strong, since the extent of overlapping in it is greater. iii. A sigma molecular orbital consists of a single electron cloud, which is symmetrical along the internuclear axis. iv. About the sigma bond, free rotation of atoms are possible. 	<ul style="list-style-type: none"> i. A Pi bond is formed by the sidewise overlapping of half-filled p-atomic orbitals. ii. A pi-bond is weak, since here the atomic orbitals overlap to a small extent. iii. Here, the overlapping of orbitals occur above and below the internuclear axis. Thus, π -molecular orbitals consists of two electron cloud. iv. The π - bond restricts the free rotation of atoms.

5.9 RESONANCE :

It is observed that certain molecules and ions can be represented by more than one valence bond structures but none of these structures can correctly account for the properties like bond length, bond energy etc. of the molecules or ions. According to this concept, if two or more alternate valence bond structures can be written for a molecule, the actual structure is said to be a resonance or mesomeric hybrid of all these alternate structures. For example, CO_2 molecule can be represented by the following three structures :



While the calculated values of $\text{C} = \text{O}$ and $\text{C} \equiv \text{O}$ bond lengths are 1.22\AA° and 1.10\AA° respectively, the experimental value of bond length between carbon and oxygen in CO_2 is 1.15\AA° , which suggests that none of the above structures is the correct structure of CO_2 . Thus, the correct structure of CO_2 molecule is a resonance hybrid of the above three structures. The resonating structures are also called resonance forms or canonical forms or mesomeric forms.

“When a molecule or ion can be represented by more than one Lewis structures, none of these structures is able to explain the properties of the molecule or ion and the true structure of the molecule/ion is a resonance hybrid of these various structures, the phenomenon is called resonance.”

Rules for writing resonating structures :

1. The relative position of all the atoms in each of the resonating structures should be the same and it is the position of electrons which differ.
2. There should not be much difference in energy between the canonical forms.

3. Each of the canonical forms must have same number of unpaired and paired electrons.
 4. It is mostly preferred that in the resonating structures, negative charge resides on more electronegative atom.

Characteristics of resonating structures:

1. None of the canonical forms can fully describe all the properties of the molecule or ion.
 2. All the structures contribute to the actual structure of the molecule or ion.
 3. In canonical forms, similar charges should not reside on adjacent atoms while dissimilar charges should reside on the adjacent atoms.
 4. Greater is the number of covalent bonds in a resonating structure, greater is the stability of that structure.
 5. More is the number of canonical forms, greater is the stability of the molecule.

Resonance energy :

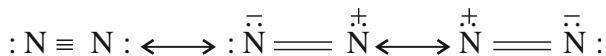
Resonance energy of a molecule is defined as the difference between the energy of its most stable mesomeric form (i.e. form with the lowest energy) and the energy of the structure determined experimentally.

For example, resonance energy of CO_2 is 126 kJ/mol, which implies that the energy of CO_2 molecule is less than that of the most stable resonating structure of this molecule by an amount equal to 126 kJ.

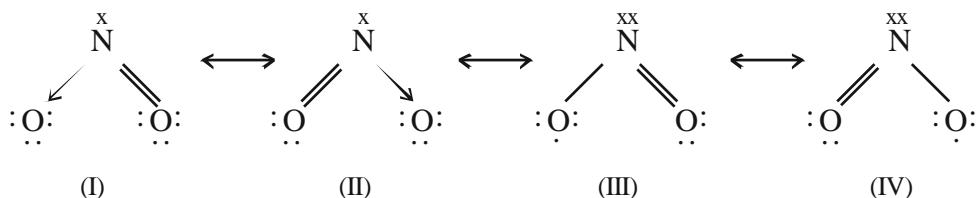
Resonance energy is considered as a measure of the stability associated with any molecule.

Resonance structures of some molecules and ions

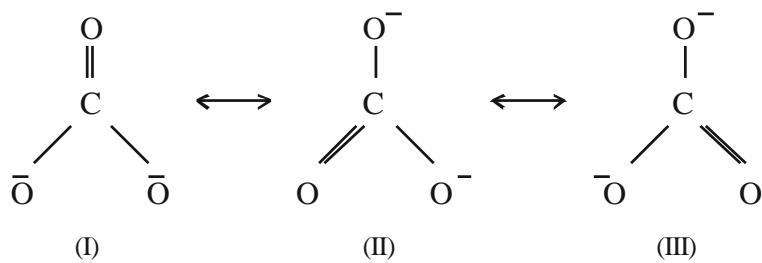
- (i) **Nitrogen molecule** : Its actual structure is supposed to be a resonance hybrid of the following resonating structures.



- (ii) **Nitrogen dioxide molecule :** It is a resonance hybrid of the following structures :



- (iii) **Carbonate ion** : Following resonance structures are written for the ion.



5.10 VSEPR THEORY - GEOMETRY OF COVALENT MOLECULES :

This theory is based on the repulsive interactions of pairs of valence electrons. The geometry of covalent molecules are determined basing on this theory. The main postulates of valence shell electron pair repulsion theory are as follows.

- (i) The orbitals are oriented in space, so that the distance between them is maximum and repulsion is minimum.
- (ii) The lone pair-lone pair repulsion is greater than the lone pair - bond pair repulsion, which, in turn is greater than the bond pair - bond pair repulsion.

That is, Lone pair - Lone pair repulsion > Lone pair - bond pair repulsion > Bond pair - bond pair repulsion.

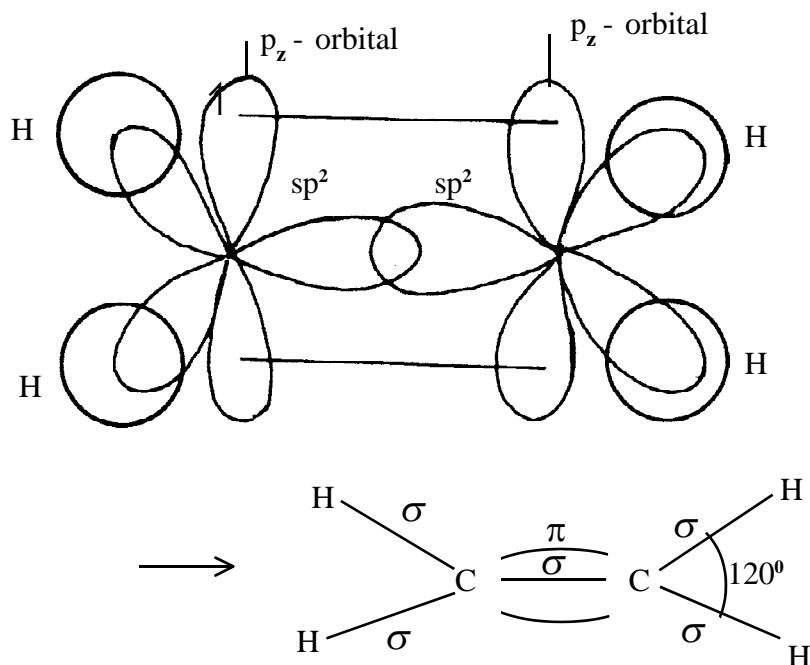
Shapes of other molecules :

1. **Shape of ethylene (C_2H_4) molecule :** In one ethylene molecule, two carbon atoms combine with four hydrogen atoms.

We know, the electronic configuration of carbon atom in the excited state is , $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

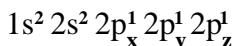
Here, $2s$, $2p_x$ and $2p_y$ orbitals of carbon atom after excitation hybridised to form three sp^2 -hybridised orbitals. Each sp^2 -hybrid orbital contain one half-filled electron.

First of all one sp^2 -hybrid orbital of each carbon atom overlap along the internuclear axis to form a sigma bond. Remaining two sp^2 -hybrid orbitals of each carbon atom overlap with s-orbital of hydrogen atom to form sigma bonds. The unhybridised $2p_z$ orbital of each carbon atom then overlaps laterally to form π -bond. Thus in between two carbon atoms, one sigma and one Pi-bond is formed. The shape of ethylene molecule is trigonal or planar and the bond angle is 120° .

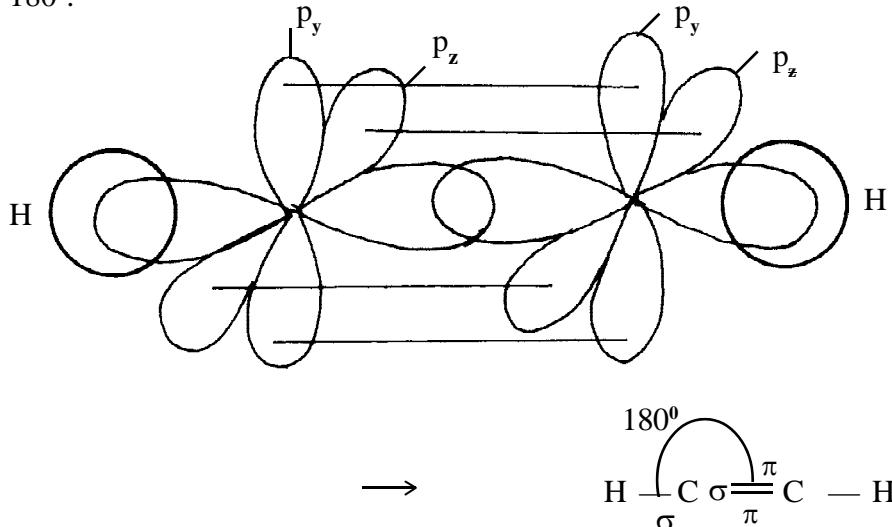


(Trigonal or Planar structure of ethylene)

- 2. Shape of acetylene (C_2H_2) molecule :** In one acetylene molecule, two carbon atoms combine with two hydrogen atoms. We know, the electronic configuration of carbon in excited state is,



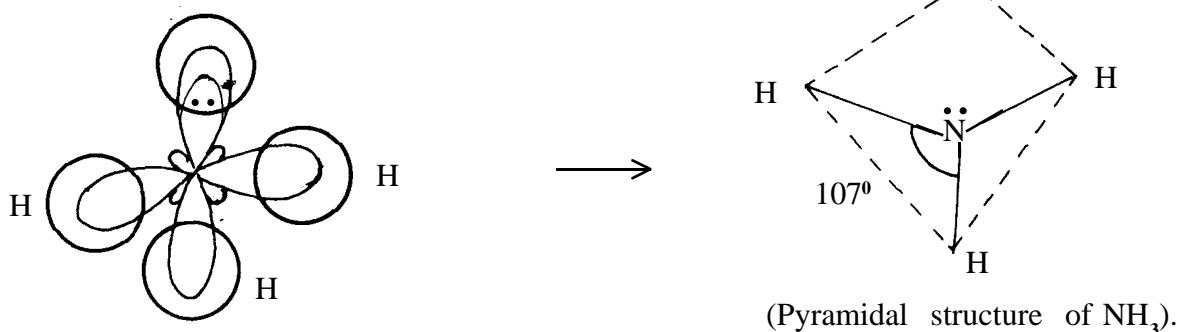
Here, $2s$ and $2p_x$ orbitals of carbon atom after excitation hybridised to form two sp-hybrid orbitals. One sp-orbital of each carbon atom overlap along their internuclear axes to form a sigma bond. The other sp-orbital of each carbon atom overlaps with $1s$ -orbital of hydrogen atom. Then the unhybridised $2p_y$ and $2p_z$ orbitals on each carbon atom overlap laterally to form two π -bonds. Hence, the shape of acetylene molecule is linear and the bond angle is 180° .



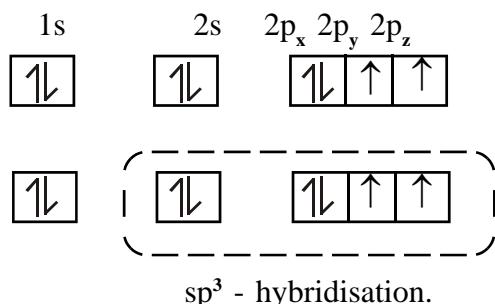
(Linear structure of acetylene)

- 3. Shape of Ammonia molecule :** The electronic configuration of nitrogen $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. Here, the central atom, nitrogen shows sp^3 -hybridisation and forms four sp^3 -hybrid orbitals. Each of the three half-filled sp^3 -hybrid orbitals overlaps with $1s$ -orbital of hydrogen atom to form sigma bonds. One lone pair of electron is present in the fourth sp^3 -orbital.

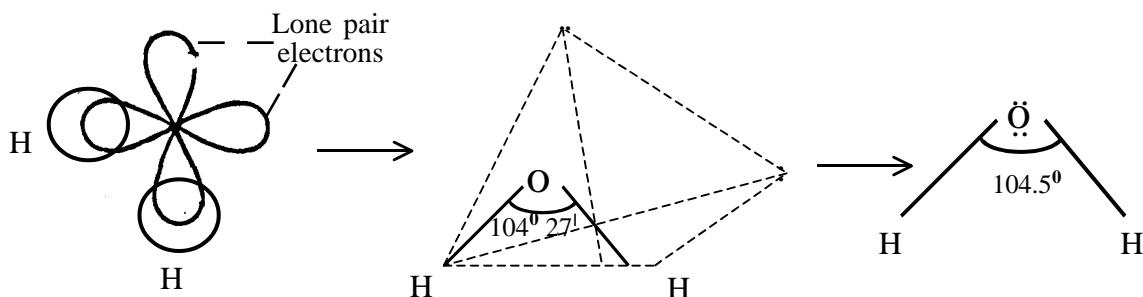
Here, due to lone pair-bond pair repulsion, according to VSEPR theory, the regular tetrahedral geometry is distorted. The shape of NH_3 molecule becomes pyramidal and the bond angle is reduced to 107°



- 4. Shape of water molecule :** In water, the central atom oxygen, has the following electronic configuration in the ground state.



Oxygen contains two unpaired electrons in its valence shell even in the ground state. So this can form two covalent bonds with hydrogen atoms, without involving hybridisation. But, in that case, the water molecule, involving only two orbitals should have been linear and non-polar, like BeCl_2 . But, this actually is not true. The water molecule is known to have a bent structure and it is highly polar. The reason for the bent structure is the central atom oxygen in water undergoes sp^3 -hybridisation. Out of the four sp^3 -orbital two contain lone pair electrons. Other two hybrid orbital containing half filled electron overlap with hydrogen atom forming two sigma bonds. Although the central atom shows sp-hybridisation, the shape of water is not tetrahedral. This is because of the greater lone pair - lone pair repulsion. Hence, the tetrahedral geometry of water distorted to 'V' shaped or bent. Thus, the geometry of water is 'V'-shaped and the bond angle is $104^\circ 27'$ or 104.5° .



5.11 HYBRIDISATION :

Introduction : The overlapping concept of half - filled atomic orbitals explains the formation of covalent bonds. According to this concept, the number of half-filled orbitals in an atom represents the number of covalency of that element..

For example :

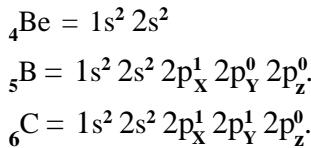
$$_1\text{H} = 1\text{s}^1$$

$$_7\text{N} = 1\text{s}^2 2\text{s}^2 2\text{p}_x^1 2\text{p}_y^1 2\text{p}_z^1$$

$$_8\text{O} = 1\text{s}^2 2\text{s}^2 2\text{p}_x^2 2\text{p}_y^1 2\text{p}_z^1$$

From the electronic configuration of above elements we know, the covalency of hydrogen is one. But the covalency of oxygen is two and that of nitrogen is three. Hence, hydrogen is monovalent, oxygen is divalent and nitrogen is trivalent.

But beryllium, boron and carbon furnish interesting cases of compound formations. The electronic configuration of these elements are,



According to orbital theory, beryllium should behave as a noble gas, since it has no half-filled orbital. Since boron and carbon has one and two half-filled orbitals, boron should be monovalent and carbon should be divalent. But this is not actually the case.

Beryllium forms a number compounds like BeH_2 , BeF_2 etc. in which it is divalent. Boron forms a number of compounds like BH_3 , BCl_3 etc. in which it is trivalent. Carbon forms large number of compounds in which it is tetravalent. The simple examples are CH_4 , CCl_4 etc.

In order to explain these anomalies, we make use of a new concept, called **hybridisation**. The phenomenon of hybridisation involves the following steps.

- (i) **Excitation** : If an atom in its valence shell has vacant orbitals, there is possibility of electron promotion or excitation from the paired orbitals to these vacant orbitals.

The promotion of electrons to the vacant orbitals of the same energy level is possible, because the energy difference between various orbitals of the same level is not much.

- (ii) **Re - orientation** : The atomic orbitals on the same atom containing half-filled electron now have identical energy. These atomic orbitals have an unusual ability to merge with one another in an additive way, forming the same number of new orbitals, called hybrid orbitals. The phenomenon is called hybridisation.

Definition : The phenomenon of redistribution of energy in different orbitals belonging to the valence shell of an atom to give new orbitals of equivalent energy is called **hybridisation**.

Conditions of hybridisation :

The conditions for hybridisation are as follows :

- (i) The orbitals of one and the same atom participate in hybridisation. Only the orbitals and not electrons get hybridised.
- (ii) The energy difference between the hybridising orbitals should be small.

Characteristics of hybridisation :

The characteristics of hybridisation are as follows :

- (i) The number of hybrid orbitals is equal to the number of hybridising orbitals.
- (ii) Like the atomic orbitals, a hybrid orbital can not have more than two electrons. These two electrons must also have opposite spins.

- (iii) The number of electrons in hybridising orbitals remain the same after hybridisation.
- (iv) A hybrid orbital which has an unpaired (single) electron can only take part in overlapping, that is bond formation.
- (v) The shape of the hybrid orbital is influenced by the most dominating orbital taking part in the process of hybridisation.
- (vi) The hybrid orbitals of a particular type are all similar in shape and energy, but they differ from one another largely in orientation in space.
- (vii) Due to the electronic repulsions in hybrid orbitals they try to remain away from one another as far as possible.

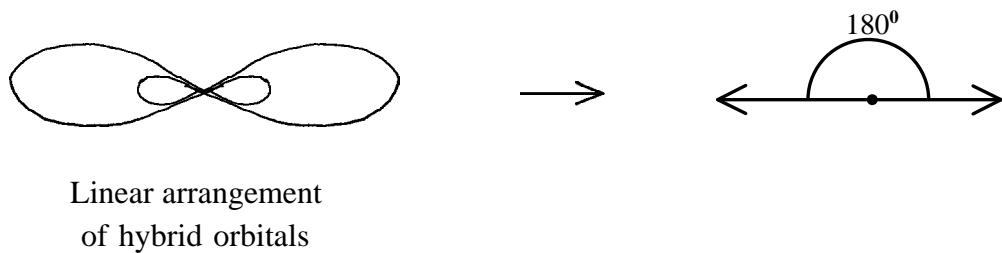
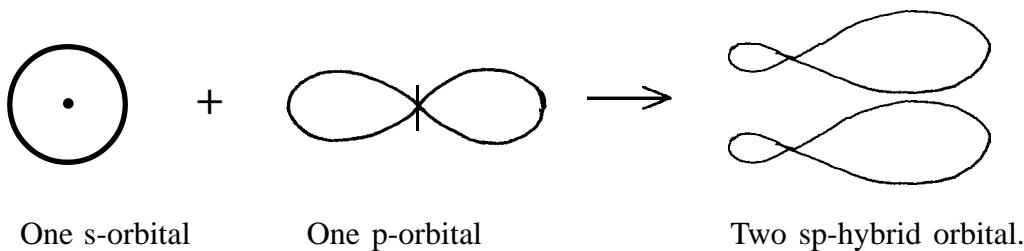
Types of hybridisation :

Hybridisation is classified as different types, depending upon the number and the nature of orbitals taking part in the process. The process of hybridisation involving the merger of s and p-orbitals are of following types.

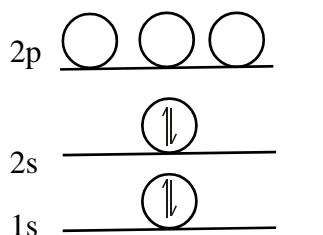
- (i) sp - hybridisation.
- (ii) sp^2 - hybridisation.
- (iii) sp^3 - hybridisation.

(i) sp - hybridisation : The process of hybridisation involving the merger of one s and one p-orbital is termed as sp-hybridisation. In this process, p orbital being the dominant one, the shape of the hybrid orbital is influenced by it. The number of hybrid orbitals become equal to two and these orbitals arrange themselves in a linear fashion at an angle of 180° between the axes of the two orbitals. In sp - hybrid orbitals the percentage of s and p - character is 50% each.

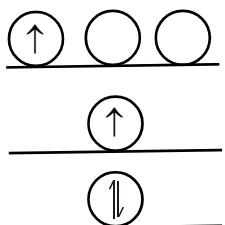
Illustration :



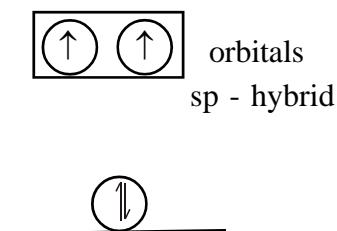
Examples : Formation of BeCl_2 molecule :



Be (in ground state)

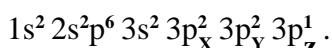


Be (in excited state)



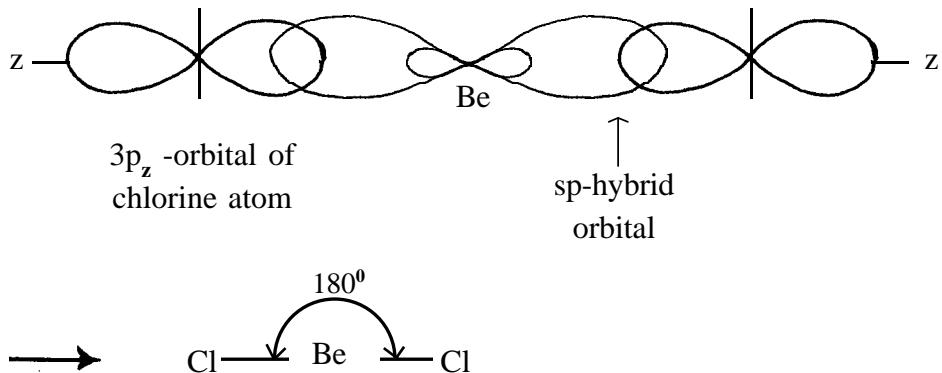
Be (in hybridised state)

The electronic configuration of chlorine is,

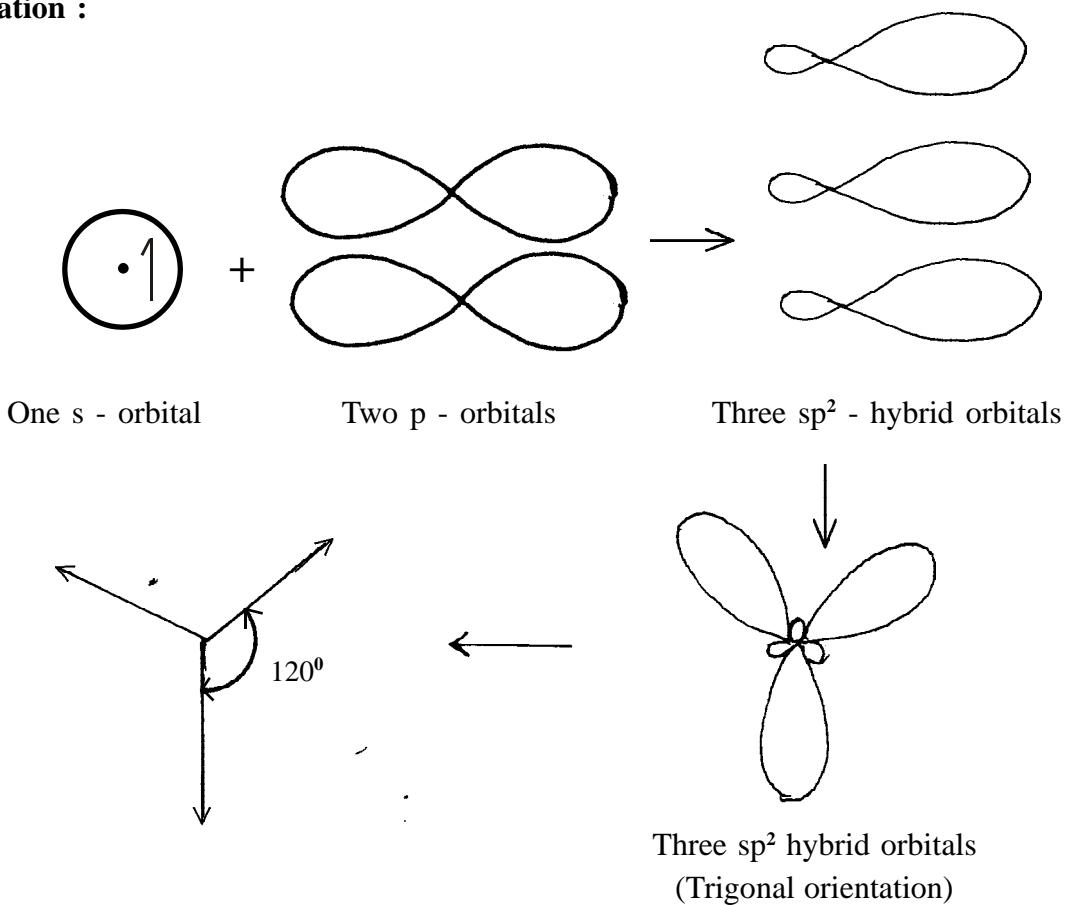


First of all with the approach of chlorine atoms, the beryllium atom gets excited by promoting one electron from $2s$ -orbital to $2p_x$ orbital. Then one $2s$ and one $2p_x$ orbital intermixed to produce two sp-hybrid orbitals. Each sp-hybrid orbital overlaps with the $3p_z$ orbital of chlorine atoms and forms BeCl_2 .

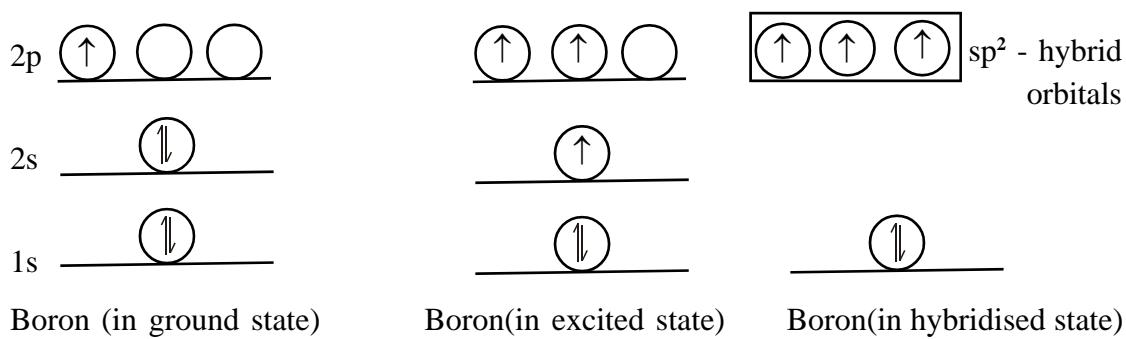
Two sp-hybrid orbitals overlap with two $3p_z$ orbitals of chlorine atoms in the head on fashion and form two sigma bonds. Since the shape of sp-hybrid orbital is linear, the shape of BeCl_2 is linear and the angle between them is 180° .



- (ii) **sp^2 - hybridisation :** The process of hybridisation involving the merger of one s and two p-orbitals is termed as sp^2 - hybridisation. Each sp^2 - orbital has 33% s - character and 66% p- character. The number of sp^2 - hybrid orbitals produced is equal to three. These hybrid orbitals arrange themselves in space making an angle of 120° with each other and the orientation is trigonal.

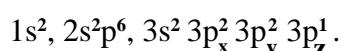
Illustration :**Example :** Formation of BCl_3 molecule :

Boron, the central atom in BCl_3 molecule shows following electronic configuration in ground state and also in excited state.

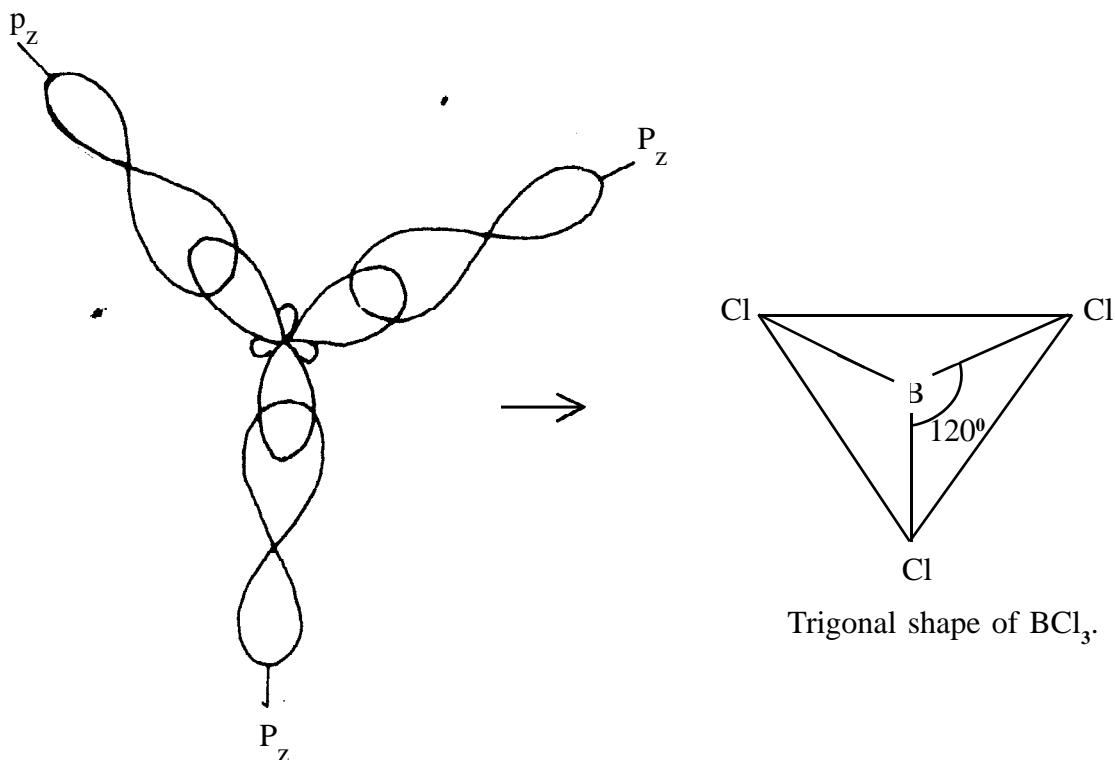


In boron trichloride, one boron atom combines with three chlorine atoms.

The electronic configurations of chlorine is

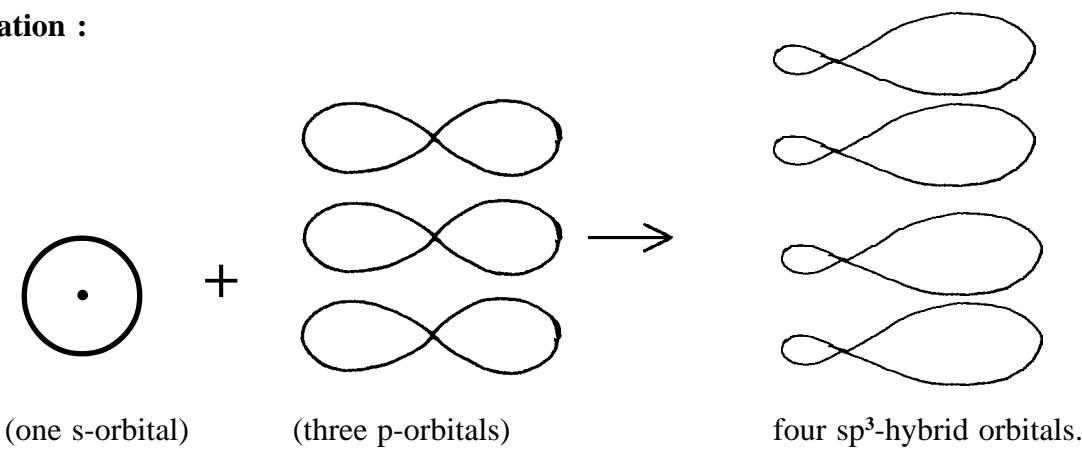


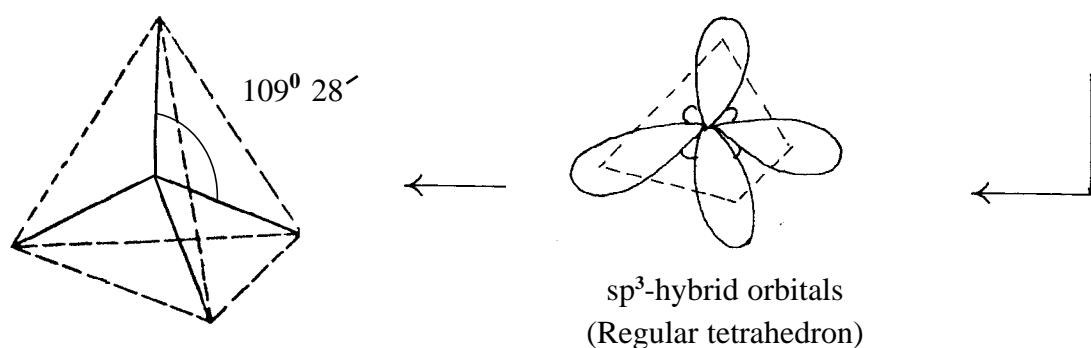
The sp^2 - hybrid orbitals of boron atom are directed in space making an angle of 120° with each other. Each hybrid orbital contain one half - filled electron. Now three $3p_z$ orbitals of chlorine with one electron in each overlap with three sp^2 -hybrid orbitals of boron, separately. As a result, three sigma bonds are formed. Therefore, the shape of BCl_3 is trigonal and the bond angle is 120° .



- (iii) **sp^3 -hybridisation :** The hybridisation arising out of the merger of one s and three p-orbitals is known as sp^3 -hybridisation. The total number of hybrid orbitals obtained in this case is four. These four sp^3 -hybrid orbitals arrange themselves in space with their lobes directed towards the corners of a regular tetrahedron making an angle of $109^\circ 28'$.

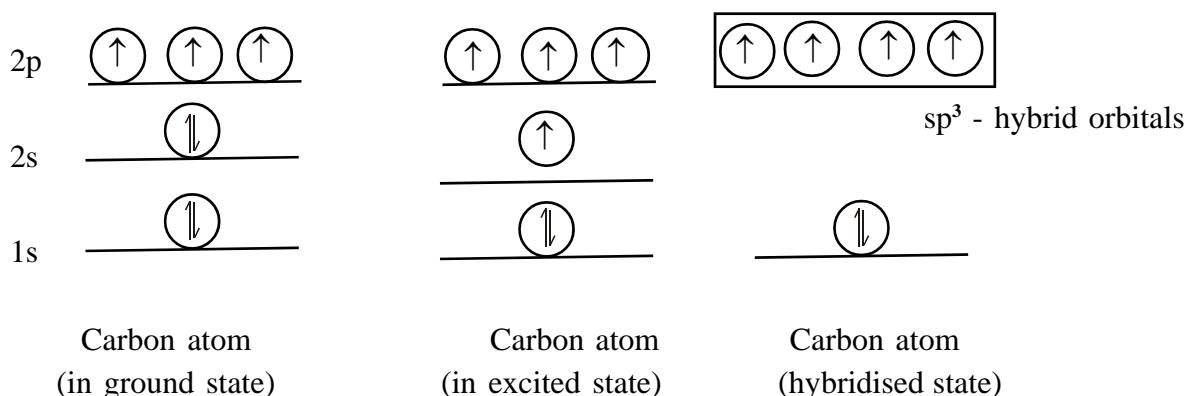
Illustration :





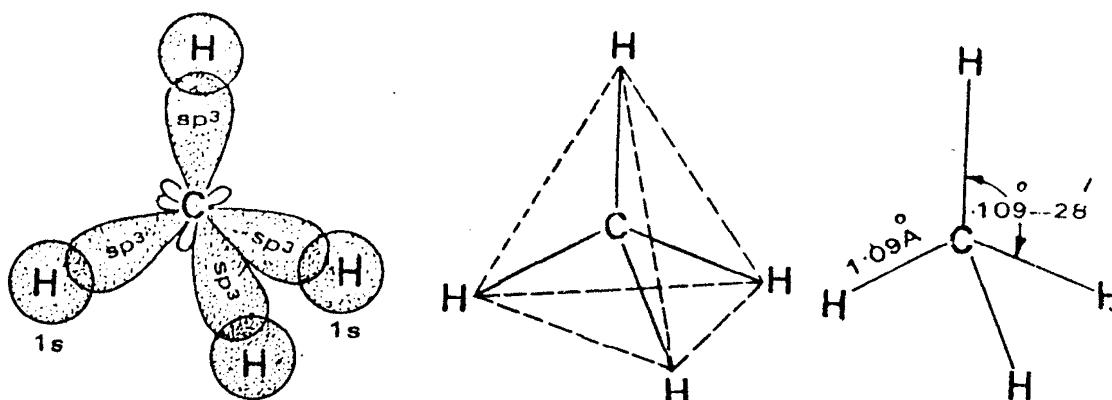
Example : Formation of methane (CH_4) molecule.

Carbon, the central atom in CH_4 molecule, shows following electronic configuration in ground state and also in the excited state.



In methane one carbon atom combines with four hydrogen atoms.

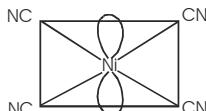
In CH_4 , the central atom carbon, shows sp^3 -hybridisation and produces four sp^3 hybrid orbitals. These sp^3 -hybrid orbitals are arranged in a regular tetrahedral fashion. Since each sp^3 -hybrid orbital contain half-filled electron, four hydrogen atoms (each containing half-filled electron) overlap with it. As a result of which four sigma bonds result. Therefore, the shape of CH_4 molecule is tetrahedral and the bond angle is $109^\circ 28'$.



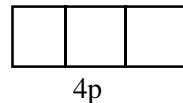
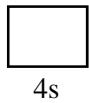
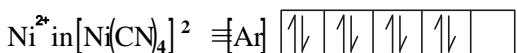
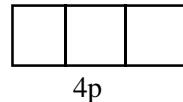
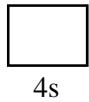
(Regular tetrahedral structure of CH_4 molecule).

(iv) COMMON TYPE OF HYBRIDISATION AND GEOMETRY OF COMPLEXES.

Co-ordination Number (CN)	Hybridisation	Geometry	Example
4	dsp^2	Square planar	$[\text{Pt}(\text{NH}_3)_4]^{2-}$, $[\text{Pt Cl}_4]^2$
5	dsp^3	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$
6	d^2sp^3	Octahedral	$[\text{Fe}(\text{CN})_6]^4$ (Inner d-complex)

Geometry of $[\text{Ni}(\text{CN})_4]^{2-}$ **Square planar structure of $[\text{Ni}(\text{CN})_4]^{2-}$**

CN⁻ is a strong ligand. The unpaired electrons in Ni²⁺ are paired making one inner d-orbital vacant for the ligand.



electron pair of ligand

dsp^2

Nature of hybridisation - dsp^2

Nature of complex - Inner d-orbital complex

Magnetic character - Diamagnetic

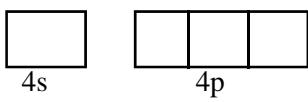
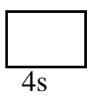
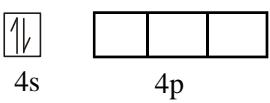
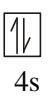
Geometry / Shape - Square planar

Bond Angle = 90°

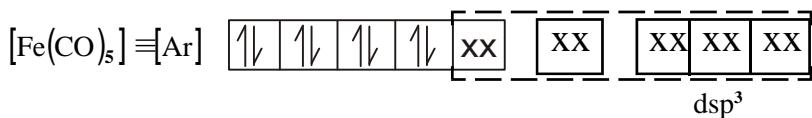
Geometry of $[\text{Fe}(\text{CO})_5]$

Oxidation number of Fe = 0

C.N. of Fe = 5



Unpaired electrons are paired and outer 4s electrons are accommodated in 3d



CO i.e carbonyl is a strong ligand, hence electronic configuration is affected. The unpaired electrons are paired.

Nature of hybridisation – dsp^3

Nature of complex – inner d-complex

Magnetic character - Diamagnetic

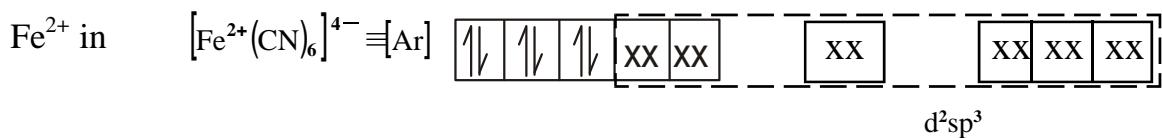
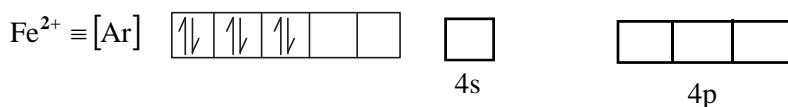
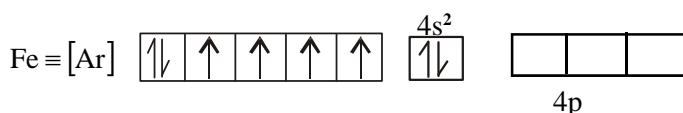
Geometry / Shape - Trigonal bipyramidal

Band angle - 120° and 90°

Geometry of $[\text{Fe}(\text{CN})_6]^{4-}$

Oxidation number of Fe = +2

C.N. of Fe = 6



CN^- is a strong ligand. It makes all the unpaired electrons paired. The six empty hybrid orbitals are required by six CN^- ligands.

Nature of hybridsation - d^2sp^3

Nature of complex - Inner d-complex

Magnetic character - Diamagnetic

Geometrical shape - Octahedral

Bond angle - 90°

Magnetic moment = 0 (zero spin complex or spin paired complex)

5.12 MOLECULAR ORBITAL THEORY (MOT) :

This theory was proposed by Hund and Mulliken. So this theory is known as **Hund-Mulliken theory**.

According to this theory,

- The atomic orbitals combine and form an orbital which is known as the molecular orbital.
- Orbitals of same energy level of each bonded atom involved in molecule formation lose their identity and merge together to give rise to an equivalent number of new molecular orbitals.
- All the electrons pertaining to both the bonded atoms are considered to be moving along the entire molecule under the influence of all the nuclei.
- Electrons while filling the molecular orbitals follow Pauli's exclusion principle as well as Aufbau's principle.
- The nomenclature, s, p and d used for atomic orbitals is replaced by σ , π and δ for molecular orbitals.
- The number of molecular orbitals formed is equal to the number of the atomic orbitals involved in their formation. Thus two atomic orbitals after interaction will produce two molecular orbitals. Of these two molecular orbitals, one is of lower energy than either of the two atomic orbitals and the other is of higher energy. The orbital having lower energy is known as **bonding molecular orbital** and orbital having higher energy is known as **antibonding molecular orbital**. The electrons present in these orbitals are called **bonding and antibonding electrons** respectively.
- Electrons which are present inside the shell of atoms and do not take part in bond formation are called **non-bonding** electrons.
- The antibonding molecular orbital is represented by a superscript asterisk (*).
- The bonding molecular orbitals are stable and the antibonding molecular orbitals are unstable.

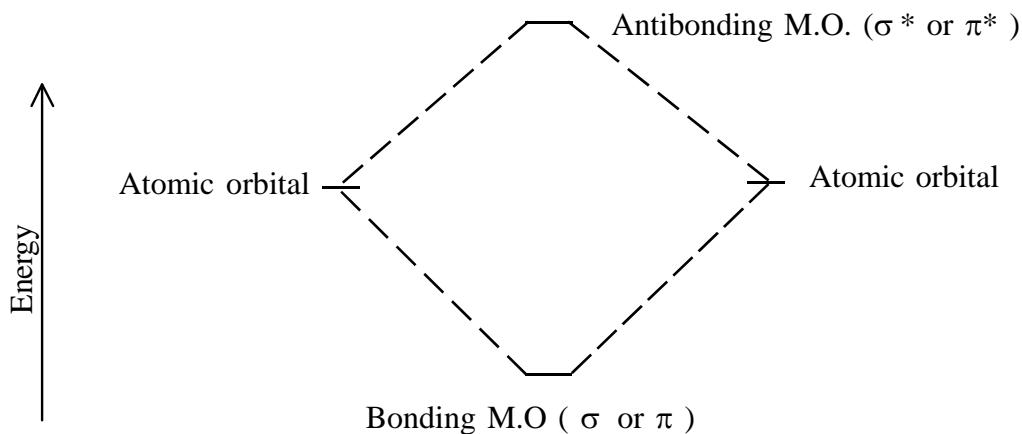


Fig 5.4. Formation of molecular orbitals by the combination of two atomic orbitals.

Table 5.3 Comparison between bonding and antibonding molecular orbitals.

Bonding molecular orbitals σ or π	Anti-bonding molecular orbitals σ^* or π^*
<p>1. These are formed by linear combination of two atomic orbitals when their wave functions are added. That is, $\psi_b = \psi_1 + \psi_2$</p> <p>2. It is formed when atomic orbitals with same signs of their lobes combine.</p> <p>3. Their energy is less than the combining atomic orbitals.</p> <p>4. They increase the electron density between the nuclei and therefore stabilise the molecule.</p>	<p>1. These are formed by linear combination of two atomic orbitals when their wave functions are subtracted. that is, $\psi_a = \psi_1 - \psi_2$</p> <p>2. It is formed when two atomic orbitals with opposite signs of their lobes combine.</p> <p>3. Their energy is more than the combining atomic orbitals.</p> <p>4. They decrease the electron density between nuclei and therefore destabilise the molecule.</p>

Rules of filling-up electrons in molecular orbitals :

Following rules are followed during the filling-up of the molecular orbitals with the available electrons.

- (i) The molecular orbitals are filled-up in the order of increasing energy. The molecular orbital with lowest energy is filled first (**Aufbau's principle**)
- (ii) Maximum capacity of electrons in a molecular orbital is **two**.
- (iii) If there are two or more molecular orbitals of same energy, these are first singly filled and then pairing starts. (**Hund's rule**)
- (iv) Whenever bonding of atoms is to take place, there should be an excess of bonding electrons over antibonding electrons. Thus, no bonding occurs, if the number of antibonding electrons is equal to or more than the number of the bonding electrons.

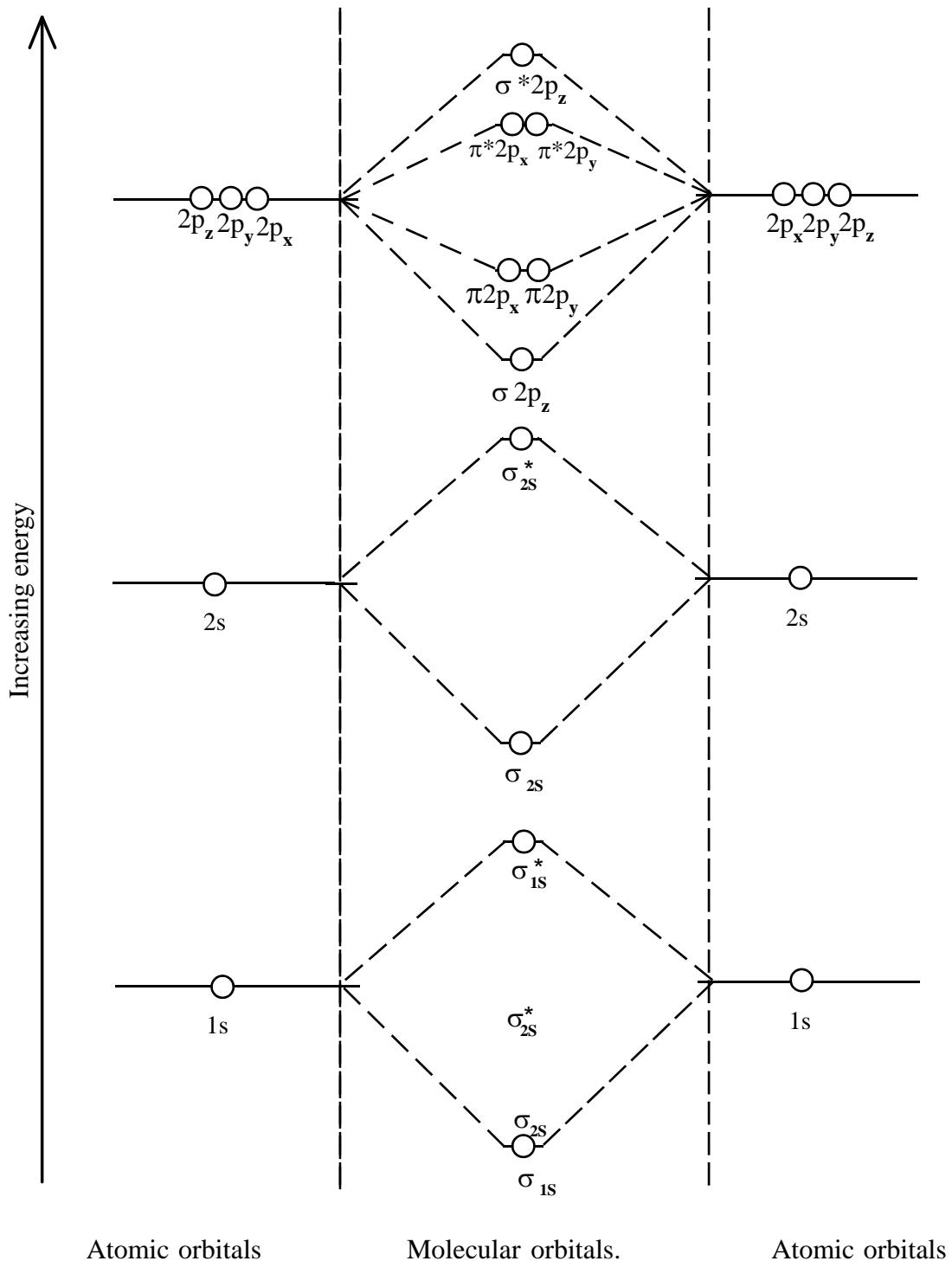


Fig : 5.5 Energy levels of different molecular orbitals.

Order of energy of molecular orbitals:

The molecular orbitals in order of their increasing energies, upto nitrogen molecule are,

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = < \pi^* 2p_y < \sigma^* 2p_z$$

But beyond nitrogen, the order is as follows ;

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

Electronic configuration and molecular behaviour :

The behaviour and nature of a molecule depends upon its electronic configuration. The electronic configuration can be used to predict the bond order, stability and magnetic behaviour of the molecule. These are described below.

- (i) **Bond order** : It is defined as the number of covalent bonds in a molecule.

$\text{Bond order} = \frac{1}{2}(N_b - N_a)$, where N_b is the number of bonding electrons and N_a is the number of antibonding electrons.

- (ii) **Stability of the molecule** : We know that the electrons in bonding molecular orbitals contribute towards the lowering of energy (stability), whereas the electrons in antibonding molecular orbital contribute towards increase of energy (instability).

Thus, If $N_b > N_a$; the molecule is stable : If $N_b < N_a$; the molecule is unstable :

If $N_b = N_a$; the molecule is unstable.

The stability of a molecule can also be expressed in terms of bond order

(a) If bond order is positive, then molecule is stable.

(b) If bond order is negative or zero, the molecule is unstable.

Higher the bond order, more is the stability of the molecule. Bond order and bond length are also related to each other as follows : Bond order $\propto \frac{1}{\text{Bond length}}$.

Bond order of nitrogen is three ($\text{N} \equiv \text{N}$) and that of oxygen is two ($\text{O} = \text{O}$).

Hence, N_2 is more stable than oxygen.

Stability of a molecule is directly proportional to the bond strength and inversely proportional to the bond length.

- (iii) **Magnetic character** : The molecule in which there are no unpaired electrons are diamagnetic. But the presence of one or more unpaired electrons is the cause of paramagnetism of the molecule. Greater the number of unpaired electrons, more is the paramagnetic behaviour.

Molecular orbitals in some simple molecules :

- (i) **Hydrogen molecule (H_2)** : Each hydrogen atom has one electron in its $1s$ -orbital. Therefore, diatomic hydrogen molecule has two electrons and two nuclei. Two $1s$ atomic orbitals thus, combine to form two molecular orbitals, like, σ_{1s} and σ^*_{1s} .

According to Pauli's exclusion principle, both the electrons are accommodated in bonding molecular orbital, which has lower energy.

Therefore, electronic configuration of H_2 molecule is, $\text{H}_2 = (\sigma 1s)^2$.

Hence, $N_b = 2$ and $N_a = \text{zero}$. $\therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = 1$.

Thus, two atoms are bonded together through one covalent bond. It is diamagnetic as there is no unpaired electron. The energy diagram is given below.

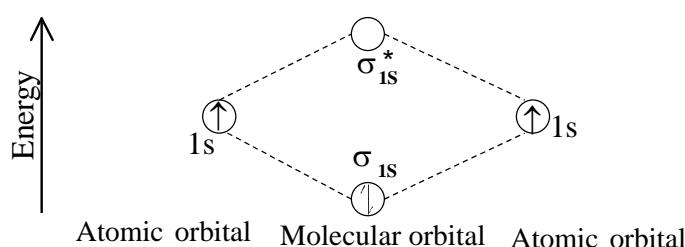


Fig. 5.6 Molecular orbital energy diagram for H_2 molecule.

- (ii) **Nitrogen molecule (N_2)** : Each nitrogen atom has seven electrons. Therefore, there are fourteen electrons in nitrogen molecule. These are filled in the increasing order of their energies.

Therefore, electronic configuration of nitrogen molecule is

$$N_2 = (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^2 .$$

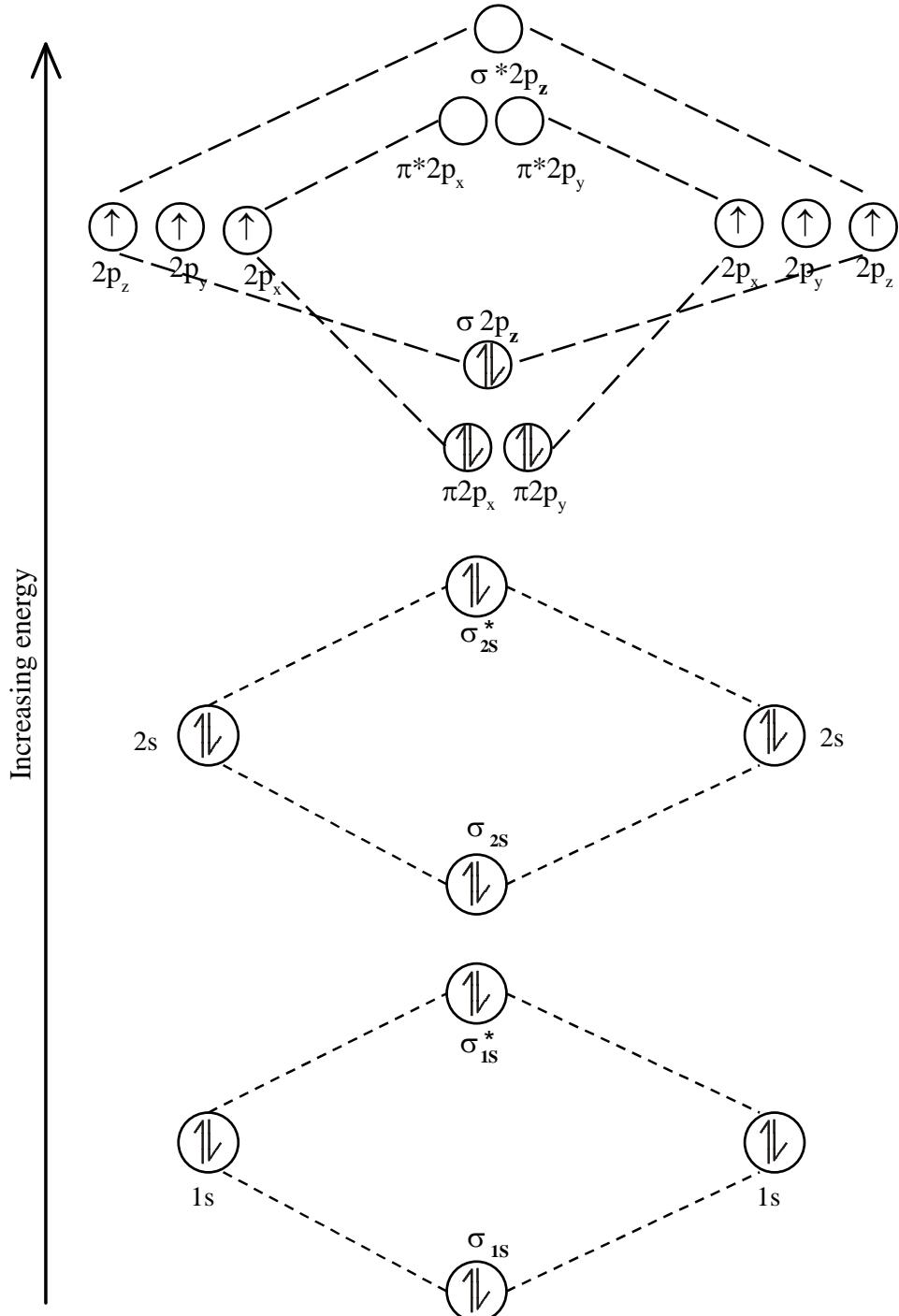


Fig.5.7 Molecular orbital energy diagram for N_2 molecule.

$$\text{Here, } N_b = 10 \quad N_a = 4 \quad \therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 4) = 3.$$

Hence, nitrogen consists of a triple bond between the two atoms. It is diamagnetic since no unpaired electron is present.

- (iii) **Oxygen molecule (O_2) :** Each oxygen atom has eight electrons. therefore, there are sixteen electrons in oxygen molecule. These are filled in the increasing order of their energies.

Therefore, electronic configuration of oxygen molecule is

$$O_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 = (\pi_{2p_y})^2, (\pi^*_{2p_x})^1 (\pi^*_{2p_y})^1.$$

$$\text{Here, } N_b = 10, N_a = 6 \quad \therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(10 - 6) = 2$$

Hence, there is a double bond in oxygen molecule. Due to the presence of two unpaired electron, it is paramagnetic. The energy diagram is given below :

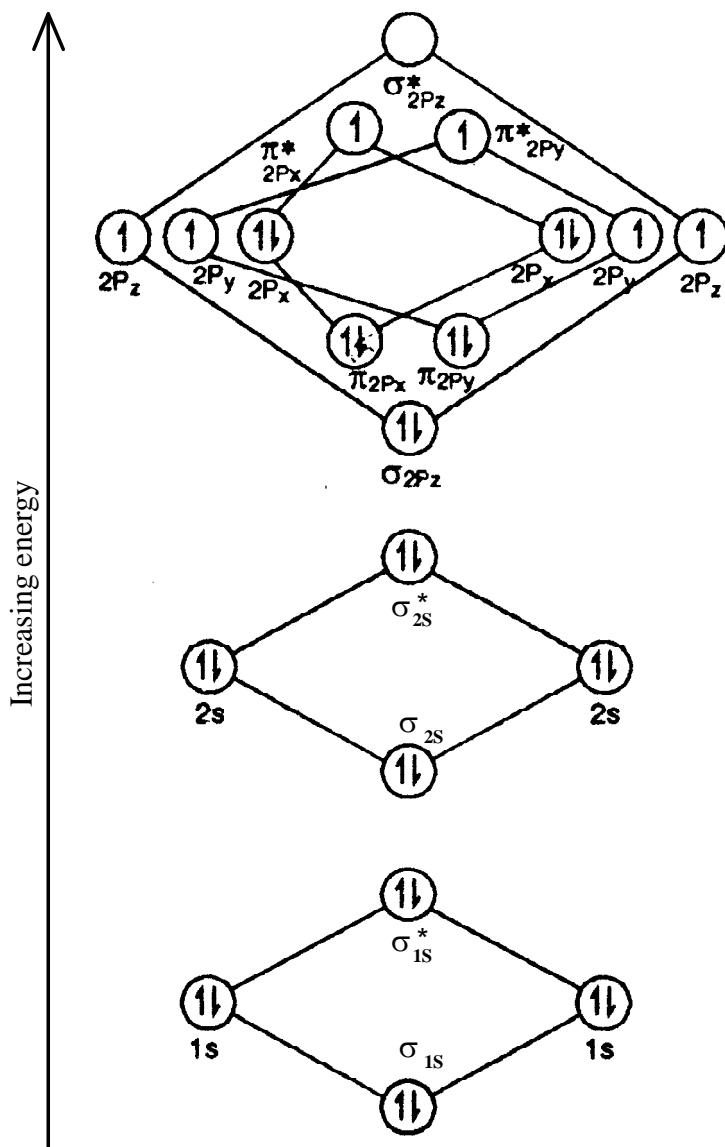
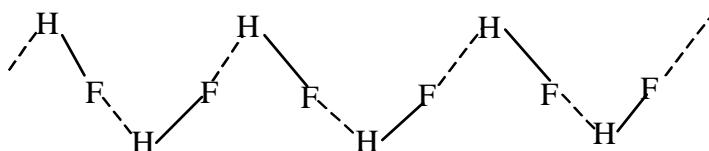


Fig. 5.8 M.O diagram for oxygen molecule.

5.13 HYDROGEN BOND :

We know HF is a polar compound. Due to the higher electronegativity of fluorine the electron pair shared between them lies far away from the hydrogen atom. Thus, hydrogen atoms are highly electropositive with respect to fluorine atom. The phenomenon of charge separation between hydrogen and fluorine atom in HF molecule is represented as, $H^{d+} — F^d$. Thus, due to the charge separation, the molecule behaves as a dipole. The electrostatic forces of attraction between such molecules are very strong. Thus, two or more molecules of HF may associate together to form large cluster of molecules as shown below.



Hydrogen bond is defined as the force of attraction which binds hydrogen atom of one molecule with highly electronegative atom of another molecule of the same substance.

The hydrogen bond is generally represented by dotted lines, as shown above.

It may be noted that, hydrogen atom is bonded to fluorine atom by a covalent bond in one molecule and by hydrogen bond to the fluorine atom in the adjacent molecule. Thus, hydrogen atom is seen to act as a bridge between the two fluorine atoms.

Conditions for formation of hydrogen bond :

- (i) The molecule should be polar covalent.
- (ii) One of the atoms in the molecule should be highly electronegative.
- (iii) The highly electronegative atom must be small in size.

So, fluorine, oxygen and nitrogen atoms satisfy the above conditions. Hence, all compounds containing hydrogen and one of these electronegative atoms show the property of hydrogen bonding. A hydrogen bond is very much weaker than a covalent bond.

Types of hydrogen bonding :

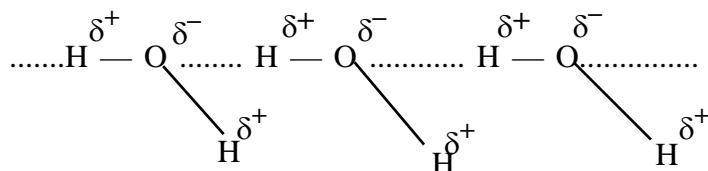
Hydrogen bonding are of two types.

- (i) Intermolecular hydrogen bonding
- (ii) Intramolecular hydrogen bonding.

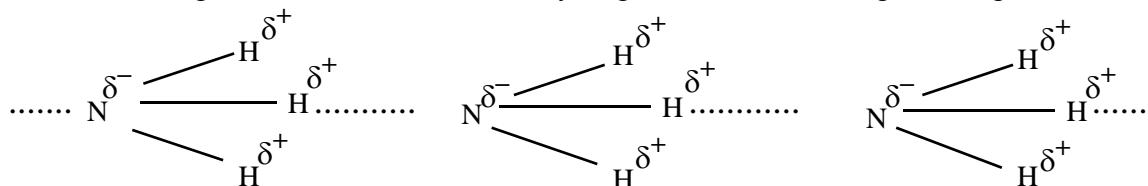
- (i) **Intermolecular hydrogen bonding :** The intermolecular hydrogen bonding results from the electrostatic forces of attraction between the positive and negative poles of different molecules of the same substance.

The following compounds show this type of hydrogen bonding.

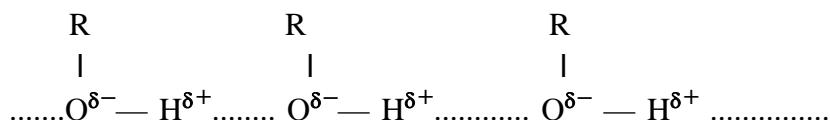
- (a) **In water :** Oxygen being more electronegative than hydrogen, in the water molecule, intermolecular hydrogen bonding is established involving the oxygen atom of one with the hydrogen atom of the other molecule.



- (b) **In ammonia :** Due to the polarity in the molecule, a hydrogen bond is established using the nitrogen atoms of one and the hydrogen atom of the neighbouring molecule.

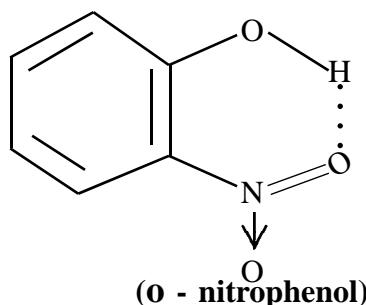


- (c) **In alcohol ($\text{R} - \text{OH}$) :** Association in alcohol molecules takes place due to the intermolecular hydrogen bonding.

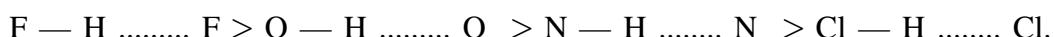


- (ii) **Intramolecular hydrogen bonding :** The intramolecular hydrogen bonding involve the electrostatic forces of attraction between hydrogen and an electronegative element both present in the same molecule.

For example, ortho-nitrophenol shows intramolecular hydrogen bonding.



Strength of hydrogen bond : A hydrogen bond is a much weaker bond and requires only 5 - 10 kcal per mole of energy to break. The bond strength depends on the electronegativity of the element with which a hydrogen bond is established. The decreasing strength of a hydrogen bond takes up the following pattern.



A chlorine atom has approximately the same electronegativity (3.0) value as that of a nitrogen atom , but due to its smaller size the nitrogen atom shows a stronger hydrogen bonding than the chlorine atom. Hydrogen bond strength of some molecules are given below.

Hydrogen bond	Strength (kcal/mole)
H.....F	10.0
H.....O	6.0
H.....N	3.0

Consequences of hydrogen bonding :

- (i) Compounds showing the property of hydrogen bonding have high melting and boiling points.
- (ii) Compounds showing the property of hydrogen bonding are highly soluble in water. Alcohol and ammonia are soluble in water, as these molecules form hydrogen bonding with water molecule.

CHAPTER (5) AT A GLANCE

1. **Atomic orbital :** It is a region around the nucleus in a single atom where the probability of finding the electron is maximum.
2. **Chemical bond :** It is defined as the force of attraction which holds the constituent atoms in a molecule.
3. **Co-ordinate bond :** This type of bond is formed by one side contribution and equal sharing of valence shell electron between the constituent atoms.
4. **Covalent bond :** It is defined as the the force of attraction which arises by the process of mutual sharing of valence electrons between the constituent atoms.
5. **Dipole moment :** It is defined as the product of the net positive or negative charge on one of the atoms and the distance between the two charges.
6. **Hybridisation :** It is the intermixing of the orbitals of an atom having nearly the same energy which result in the redistribution of energy to form an equal number of new orbitals of equivalent energy.
7. **Hydrogen bond :** It is defined as the force of attraction which binds hydrogen atom of one molecule with highly electronegative atom of another molecule of the same or different substance.
8. **Ionic bond :** It is formed by the transference of one or more electrons from one atom to the other resulting in the formation of ions which get attracted by the force of attraction.
9. **Molecular orbital :** They exist around the nuclei of all the bonded atoms in a molecule.
10. **Sigma bond :** This bond is formed by the overlapping of half-filled atomic orbitals of two atoms along their internuclear axis.
11. **Pi-bond :** This bond is formed by the lateral or sidewise overlapping of half-filled atomic orbitals above and below the internuclear axis.

QUESTIONS

Very short Answer Questions (1 mark each)

1. State whether SiO_2 is an ionic or a covalent compound.
2. Between KF and CHCl_3 , which is likely to have a higher melting point ?
3. Write the structural formula of nitric acid.
4. Name a monoatomic gas. What is its valency ?
5. Why ammonia gas is not collected over water ?
6. (a) What is the shape of C_2H_2 molecule ?
 (b) What type of hybridisation is found in acetylene ?

7. How many σ and π bonds are there in a molecule of ethylene ?
8. What is the angle between the C – H bonds of methane ?
9. Why is CCl_4 immiscible in water ?
10. What type of hybridisation exists in the central atom of BCl_3 molecule ?
11. What is the shape of ammonia molecule ?
12. Find out the total number of electrons in a water molecule.
13. What is the shape of BCl_3 molecule ?
14. What is the bond angle between O – H bonds of a water molecule ?
15. What type of hybridisation takes place in carbon atom for the formation of graphite ?
16. Between sigma and pi-bond, which bond is weaker ?
17. How do you account for the fact that H_2O is a liquid and H_2S is a gas at room temperature ?
18. Name the type of overlapping and type of bond in forming HF molecule.
19. (a) What is the shape of NH_3 molecule ?
 (b) What is the shape of NH_3 molecule ? What is the reason for it ?
20. What type of hybridisation takes place in carbon atom for the formation of diamond ?
21. Which of the halogens forms hydrogen bond ?
22. Why do H_2O molecules remain associated in liquid water ?
23. Why is sigma bond stronger than pi-bond ?
24. Which of the following contains a lone pair of electrons in the central atom ?
 $\text{NH}_3, \text{CH}_4, \text{CCl}_4$.
25. What is the shape of CO_2 molecule ?
26. What is the bond angle between two hybrid bonds in sp^2 hybridisation ?
27. How many sigma and pi-bonds are there in a molecule of acetylene ?
28. Among the compounds NH_3 , HF and CH_4 , in which hydrogen bonding is most prominent and why ?
29. What is the maximum number of electrons that can margin in a molecular orbital ?
30. In which of the following types of hybridisation the structure formed has maximum bond angle ?
 $\text{sp}^3, \text{sp}^2, \text{sp}$.
31. What is the shape of methane molecule ?
32. What is the bond angle in NH_4^+ ion ?

33. What are the overlapping orbitals of carbon and oxygen in CO ?
34. Mention the hybrid state of sulphur in H₂S molecule.
35. What is the hybridisation of carbon in CO₂ ?

Short Answer type questions. (2 marks each)

1. Give reasons, why ethanol is completely soluble in water but benzene is not.
2. Explain why H₂O is a polar molecule but CO₂ is not.
3. Give one example each of molecules with sp² and sp³ hybrid bonds.
4. Write the electronic structures of CO₃²⁻ and NH₄⁺ ions with lines and arrows.
5. Why covalent molecules have definite shape ?
6. Show the hybridisation process for the four valence electrons of carbon.
7. Why hydrofluoric acid is the weakest of all halogen acids ?
8. Describe two characteristics properties of electrovalent compounds.
9. What do you understand by hydrogen bond ?
10. What is co-ordinate bond ? Give one example.
11. Explain by an example what do you mean by polarity of a covalent bond.
12. The covalent compounds possess low melting and boiling point, why is it so ?
13. What are the conditions of hybridisation ?
14. Which of the following is an ionic compound ?

CO₂, KCl, CH₄, NH₃.

Short Answer type questions. (3 marks each)

1. Why three p-orbitals of each of two atoms cannot form more than one sigma bond ?
2. Explain the formation of co-ordinate bond in ammonium ion.
3. When is HF a liquid whereas other hydrides of halogens are gases ?
4. Why CO₂ is non-polar but SO₂ is polar ?
5. Differentiate between orbit and orbital.
6. Explain why oxygen molecule is paramagnetic
7. From the molecular orbital diagram of N₂, find out its bond order.
8. HF is a liquid, whereas HCl is a gas. Explain
9. Draw the orbital diagram of CO₂ and indicate the orbitals used by the elements.
10. What is the order of increasing bond angle (HxH) of the following ? What is the theory involved ?

CH₄, H₂O, NH₃

11. Why boron trifluoride is called electron deficient compound ? Explain
12. Why is sigma bond stronger than pi bond
13. Write the electron dot structure for hydronium ion.
14. Write the molecular orbital configuration of O_2 .

Long type questions. (7 marks each)

1. Explain the term hybridisation. What are the shapes of sp, sp^2 and sp^3 hybrid orbitals ? Give one example of a compounds of each.
2. State four physical properties that can be used to distinguish between covalent and ionic compounds. Discuss with examples.
3. Discuss with examples the directional properties of covalent bonds.
4. Explain with examples the term electrovalency, covalency and co-ordinate valency.
5. What is covalent bond ? Explain why the covalent bonds between oxygen and hydrogen atoms in water molecule are polar.
6. What is hydrogen bond ? How does it influence the properties of compounds ? Explain with two examples.
7. Write notes on Co-ordinate bond
8. What is hybridisation ? How does it explain the shapes of NH_3 and H_2O molecules ?
9. Explain the term hybridisation. Discuss the shape of CO_2 and PH_3 molecules.
10. Write a note on metallic bond
11. Write notes on (any two)
 - (a) Electrovalent bond (b) Covalent bond (c) Hydrogen bond [2002 (A), CHSE]

ADDITIONAL QUESTIONS

1. Define an electrovalent linkage. What are the necessary conditions for the formation of ionic bond ? Give two examples of such compounds.
2. What is lattice energy ? How the lattice energy of solid NaCl can be calculated.
3. Write short notes on :
 - (a) hydrogen bond.
 - (b) sigma and π -bond.
4. Explain why oxygen molecule is paramagnetic and nitrogen molecule is diamagnetic. Draw the molecular orbital energy level diagram of nitrogen molecule. (OJEE - 1991).
5. Using valence shell electron pair repulsion (VSEPR) theory predict the structure of the following compounds and write whether the bond angles are likely to be distorted from theoretical values.
 - (a) CH_4
 - (b) H_2O
 - (c) NH_3 .

Multiple Choice Questions

1. The polar molecule among the following is :
 - (a) CCl_4
 - (b) CO_2
 - (c) CH_2Cl_2
 - (d) $\text{CH}_2 = \text{CH}_2$
2. How many s (sigma) and π (pi) bonds are there in tetracyanoethylene $[\text{C}_2(\text{CN})_4]$ molecule ?
 - (a) Five s and nine π bonds
 - (b) Nine s and nine π bonds
 - (c) Six s and eight π bonds
 - (d) Nine s and seven π bonds.
3. Which of the following gases does not have eight electrons in the outermost orbit ?
 - (a) Kr
 - (b) Ne
 - (c) He
 - (d) Ar
4. On hybridisation of one s and one p-orbital, we get,
 - (a) Two mutually perpendicular orbitals
 - (b) Two orbitals at 180°
 - (c) Four orbitals directed tetrahedrally
 - (d) Three orbitals in a plane
5. Which of the following compounds has zero dipole moment.
 - (a) CCl_4 ,
 - (b) CHCl_3 ,
 - (c) HF
 - (d) NH_3 .
6. The species in which the central atom uses sp^2 hybrid orbitals in its bonding is
 - (a) PH_3
 - (b) NH_3
 - (c) SO_2
 - (d) SiO_2
7. The molecule that has linear structure is :
 - (a) CO_2
 - (b) NO_2
 - (c) SO_2
 - (d) SiO_2^-
8. Which is planar molecule ?
 - (a) H_2O
 - (b) NH_3
 - (c) BF_3
 - (d) CH_2Cl_2 .
9. The nature of hybridisation in carbon atoms in the ethylene ($\text{CH}_2 = \text{CH}_2$) molecule is,
 - (a) sp, and sp
 - (b) sp and sp^2
 - (c) sp and sp^3
 - (d) sp^2 and sp^2
10. Octet rule is not followed in
 - (a) CO_2
 - (b) H_2O
 - (c) O_2
 - (d) CO

11. CO_2 is isostructural with
 (a) HgCl_2 (b) SnCl_2
 (c) C_2H_2 (d) NO_2
12. The hybridisation of sulphur atom in SO_2 is
 (a) sp, (b) sp^3
 (c) sp^2 (d) dsp^2
13. Which one of the following has a dipolemoment ?
 (a) CH_4 (b) BCl_3
 (c) CO_2 (d) H_2O
14. A species which is formed by co-ordinate covalency is
 (a) NH_4^+ (b) NH_3
 (c) BF_3 (d) PCl_5
15. The hydrogen bond is strongest in
 (a) O – H S (b) F – H F
 (c) S – H O (d) F – H O
16. Out of the following which is least ionic
 (a) P - F (b) F - F
 (c) S – F (d) Cl - H
17. An example of a co-ordinate compound is
 (a) NH_3 (b) HCl
 (c) CaCl_2 (d) NaNO_3
18. The angle between two odjacent sp^2 hybridized orbital is
 (a) 90° (b) 104.3°
 (c) 120° (d) $109. 28$
19. Covalent bond formation is favoured by
 (a) Small cation and large anion
 (b) Small cation and small anion.
 (c) Large anion and large cation
 (d) Large cation and small anion
20. Which of the following liquid is completely miscible with water ?
 (a) CHCl_3 (b) CCl_4
 (c) CH_3OH (d) CS_2

ANSWERS TO MULTIPLE QUESTIONS

- | | | | | | |
|------|-------|-------|-------|-------|-------|
| 1. c | 7. a | 13. d | 19. a | 25. c | 31. b |
| 2. b | 8. c | 14. a | 20. c | 26. c | 32. b |
| 3. c | 9. d | 15. b | 21. a | 27. b | |
| 4. b | 10. b | 16. b | 22. c | 28. d | |
| 5. a | 11. a | 17. d | 23. a | 29. a | |
| 6. c | 12. c | 18. c | 24. d | 30. c | |



UNIT – V

STATES OF MATTER : GASES AND LIQUIDS

GENERAL INTRODUCTION :

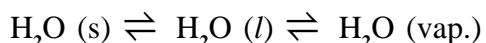
Three States of Matter : Matter is defined as something which has mass and occupies some space. Examples are iron, copper, chair, table, ice, water, air etc. Matter exists in three states: solid liquid and gas. The chemical properties of a substance do not change with the change of its physical state, but the rate of chemical reactions depends upon the physical state. This is because of the physical laws which govern the behaviour of matter in different states. Therefore, it is necessary to know about the nature of intermolecular forces, molecular interactions and effect of heat energy on the motion of the particles.

Solid state : Matter in the solid state has definite shape and volume. The constituent atoms, ions or molecules are held together by strong force of attraction. They have high melting, boiling points and density. Examples are copper, iron, gold, sand, sugar etc.

Liquid state : Matter in the liquid state has no definite shape but have definite volume. They have melting points, boiling points less than those of solids. Since the constituent atoms or molecules are held together by weak forces of interaction, they can flow from higher level to lower level. Their densities are also less than those of solids.

Gaseous state : Gases have neither definite shape or definite volume. They assume the shape of the container and spread throughout. Weak forces of interaction exist between the constituent atoms or molecules. Due to this reason gases can be compressed. The volume of gases are greatly affected by change of temperature and pressure.

The above three states of matter are interconvertible. For example, by increasing temperature and pressure solid ice can be converted into liquid water. In turn by further increasing temperature at constant pressure liquid water can be converted to water vapour.



Similarly by going in the reverse way i.e. by decreasing temperature and increasing pressure water vapour can be converted to liquid water. By further lowering the temperature liquid water can be converted into solid ice.

Intermolecular Interactions :

In matter forces of attraction and repulsion exist among the constituent atoms and molecules. Attractive intermolecular forces are known as van der Waals forces. These forces

vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces and dipole-induced dipole forces. Hydrogen bonding is a particular type of strong dipole-dipole interaction. All these forces are responsible for the different physical states of matter.

The constituent atoms or molecules of matter also experience repulsive forces among one another. When two particles are brought into close contact with each other the repulsion between the electron clouds and that between the nuclei produce repulsive force. The magnitude of the repulsion rises very rapidly as the distance of separation between the nuclei produce repulsive force. The magnitude of the repulsion rises very rapidly as the distance of separation between the particles decreases. Due to this reason liquids and solids do not change their volume on compression, but gases do. In gases the distance of separation between the approaching particles is large so that they experience less repulsive force at a given temperature and pressure.

Types of Bonds : As discussed above, in case of solids the constituent atoms or molecules experience different types of interactions as compared to liquids and gases. Metals except Mercury are solids and the bond type is metallic bond. Electron pool theory suggests that positively charged metallic kernels are fixed in the pool of valence electrons. In liquids the molecules are held together by van der Waals forces of attraction, dipole-dipole forces and hydrogen bond. Hydrogen bond is due to the coulombic force of attraction between the lone pair of electrons of the electronegative atom of one molecule and the hydrogen atom of same or other atom. The former is intramolecular hydrogen bond and latter is intermolecular hydrogen bond. In case of gases the molecules are mostly held together by van der Waals force of attraction.

When molecular attractions are very weak, molecules do not come closer on application of pressure unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only unless the thermal energy of molecules is not reduced.

Melting point and Boiling point : The melting point and boiling point of solid, liquid and gas depend upon the type of interactions involved among their constituent atoms and molecules. Solids have high melting points due to the strong forces of interaction among the constituent particles. The amount of energy required to separate them is high. In case of liquids the forces of interaction between the constituent atoms or molecules are less than that of the solids, hence less amount of energy is required to overcome these forces. They boil at temperatures at which the vapour pressure of the liquid become equal to the atmospheric pressure.

CHAPTER - 6

THE GASEOUS STATE

Physical classification indicates that matter exists in three different states namely solid, liquid and gas. This classification is more obvious since in our day-to-day life we have come across solid ice, liquid water and gaseous steam. Under suitable conditions of temperature and pressure almost all substances exist in three different states. The gaseous state is the simplest of all the three states of matter.

6.1 CHARACTERISTIC PROPERTIES OF GASES

1. **No definite shape or volume :** A gas has neither definite volume nor definite shape. It has no bounding surface due to random motion of the molecules. It acquires the shape and volume of the container in which it is filled.
2. **Expansibility :** A gas can occupy all the available space. It spreads uniformly throughout the container. It can be expanded to a desired volume by lowering the pressure or by raising the temperature.
3. **Compressibility :** A gas can be compressed to any desired volume by the application of pressure.
4. **Diffusion :** When two or more gases are introduced in to the same vessel, they intermix with each other and form a homogeneous mixture. This property is known as diffusion. The pleasant smell of kitchen and the pungent smell of laboratory are the common examples of diffusion.
5. **Density :** A gas has low density. This is because the intermolecular distance between the molecules of the gas is very large and the number of molecules per unit volume is lower than that in case of solids and liquids. For example, density of air is 0.00120 gm/cm^3 .
6. **Pressure :** A gas when enclosed in a vessel exerts pressure. The pressure is due to the collision of gas molecules on the walls of the container.
7. **Homogeneity :** When a gas is introduced into a container it fills the container uniformly. This property is known as homogeneity.
8. **Liquefaction :** A gas can be liquefied when subjected to high pressure below its critical temperature.
9. **Colour :** All gases are transparent. Most of the gases are colourless. Only a few are coloured e.g. chlorine is greenish yellow whereas bromine is reddish brown and iodine is violet.

6.2 STATE VARIABLES OF GASES

There are four measurable properties of a gas. These are : (i) mass , (ii) volume , (iii) pressure and (iv) temperature.

- (i) **Mass :** Mass of the gas is expressed in grams and kilograms. Also the mass is related to the number of moles by the equation

$$n = \frac{m}{M} \quad \text{where } n = \text{no. of moles}$$

m = mass of the gas in grams
 M = molecular mass of the gas.

- (ii) **Volume :** The volume of the gas is equal to that of the container in which the gas is kept. The units in which volume is expressed are litre (ℓ), cubic metre (m^3). The smaller units are cubic decimetre (dm^3) and cubic centimetre (cm^3). The conversion factors are $1m^3 = 10^3 dm^3 = 10^6 cm^3$.

However the units of litre(ℓ) and millilitre(ml) are more commonly used.

Litre is defined as volume of 1kg. of pure water at 1 atmospheric pressure and $3.98^\circ C$. For all practical purposes cm^3 and ml are taken to be equal.

$$1l = 1dm^3 = 10^3 cm^3$$

- (iii) **Pressure :** A gas when enclosed in a vessel exerts pressure. A gas consists of small particles known as molecules. The molecules of a gas are always in a state of constant rapid zigzag motion in all possible directions with different velocities. During motion the molecules may collide among themselves or with the walls of the container. As a result of collisions on the walls, the molecules exert force on the walls. The total force exerted by the collisions of molecules on the walls of the container per unit area determines the gas pressure.

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

The common units in which pressure is expressed are (a) atmosphere (b) cm of Hg (c) mm of Hg (d) Torr (Torricellie)

$$1 \text{ atmosphere} = 76 \text{ cm of Hg} = 760 \text{ mm Hg.}$$

$$1 \text{ mm Hg} = 1 \text{ torr}$$

The SI Unit of pressure is **pascal**. It is defined as the pressure exerted when a force of 1N (Newton) acts on an $1m^2$ area. $1 \text{ atm} = 101.325 \text{ KPa}$

For all practical purposes $1 \text{ atm} = 10^2 \text{ K Pa} = 10^5 \text{ Pa}$.

One standard atmospheric pressure is the pressure exerted on one cm^2 area by 76 cm Hg at $0^\circ C$ and standard gravity ($g = 980.665 \text{ cm/sec}^2$)

- (iv) **Temperature :** It indicates the intensity of heat or hotness with respect to a standard. It is an indicator of the average kinetic energy possessed by molecule. With increase in temperature the kinetic energy increases.

The units to represent temperature are (a) celsius temperature ($^\circ C$) (b) Kelvin temp (K)
 $[K = (^\circ C) + 273]$

In the celsius or centigrade scale the freezing point of water ($0^\circ C$) and boiling point of water ($100^\circ C$) at one atmospheric pressure are taken as the reference points.

6.3 GAS LAWS

BOYLE'S LAW (Relationship between Pressure and Volume)

Robert Boyle in 1662 proposed a relationship between pressure of the gas and the volume occupied by it. He found that at constant temperature the volume of a given mass of gas goes on decreasing with increase in pressure. The behaviour was generalised and was named **Boyle's law** after his name.

Statement : Temperature remaining constant, the volume of a given mass of gas is inversely proportional to its pressure.

Derivation : Let a given mass of gas occupy volume 'V' at pressure 'P' and constant temperature 'T'. According to Boyle's law,

$$\begin{aligned} V &\propto \frac{1}{P} \quad [T \text{ is constant}] \\ \Rightarrow V &= \text{Const.} \times \frac{1}{P} \\ \Rightarrow PV &= \text{Const.} ('K' \text{ say}) \end{aligned}$$

'K' is the proportionality constant. It depends upon the mass of the gas and the temperature at which the measurements are made.

If the volume of the same mass of gas be changed to V_1 , then pressure will change to P_1 and under such condition

$$P_1 V_1 = \text{Const.} (K_1 \text{ say})$$

If the pressure is changed to P_2 and volume to V_2 then

$$P_2 V_2 = \text{Const.} (K_2) \text{ at the same temperature } T$$

Since the constants K , K_1 and K_2 depend upon the mass of the gas and temperature and here both are kept constant, we can conclude

$$\begin{aligned} K &= K_1 = K_2 \\ \text{and hence } &PV = P_1 V_1 = P_2 V_2 = K \text{ (Constant)} \end{aligned}$$

Another statement of Boyle's law

"The product of pressure and volume of a given mass of gas at constant temperature is constant."

If pressure is doubled, volume will be reduced to half and vice versa. Similarly when pressure becomes three times its original value, volume is reduced to one third of its value.

Validity of Boyle's law

- (i) It is possible to demonstrate the validity of the law by determining the values of volume of a given mass of gas at different pressures and at constant temperature. The product PV remains constant in all the cases as given in table 6.1

Table 6.1 Changes in volume of a fixed mass of gas at different pressure and constant temperature.

Expt.No	Press. 'P' in atm	Vol. 'V' in litres	PV (lit-atm)
1.	0.20	112.0	22.4
2.	0.25	89.2	22.3
3.	0.35	64.2	22.47
4.	0.40	56.25	22.50
5.	0.60	37.40	22.44
6.	0.80	28.1	22.48
7.	1.00	22.4	22.40

- (ii) The validity can be tested by plotting a graph between volume in cm^3 and pressure in atmosphere of a given mass of gas at constant temperature.

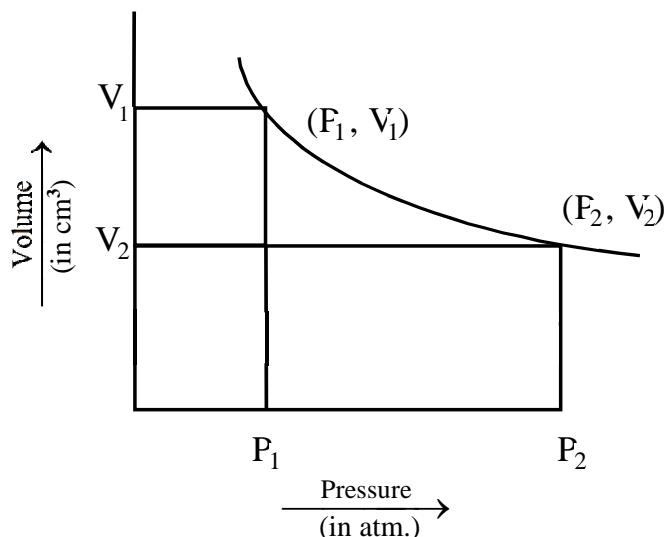


Fig. 6.1 Plot of 'V' in cm^3 against 'P' in atm.

- (iii) Validity may also be tested by plotting a graph between PV in lit-atm against 'P' in atmosphere. We get a horizontal line parallel to pressure axis.

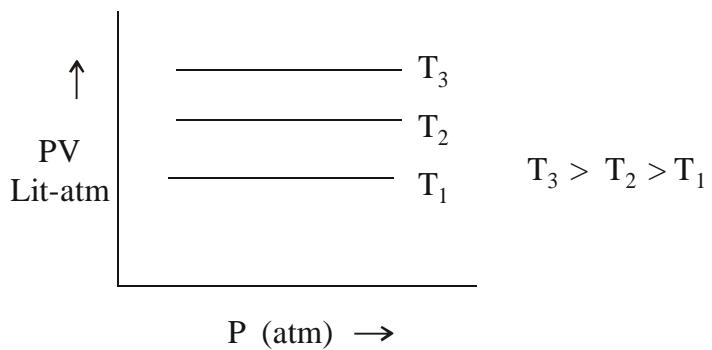


Fig. 6.2 Plot of 'PV' versus 'P'

- (iv) Boyle's law can be illustrated by plotting 'P' in atmosphere against $\frac{1}{V}$ in lit^{-1} . A straight line passing through the origin is formed.

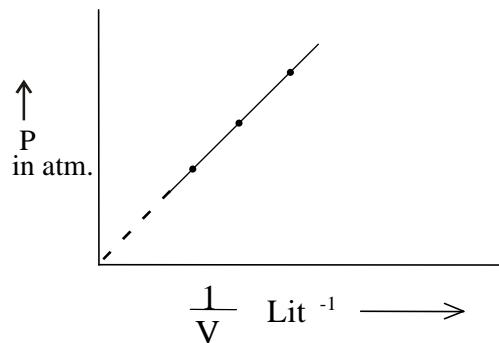


Fig. 6.3 Plot of 'P' versus $\frac{1}{V}$

Utility of the law :

It helps in determining

- (a) The volume of the gas at a given pressure if its volume at some other pressure and at constant temperature is known.
- (b) The value of pressure corresponding to any volume if the pressure at some other volume and at constant temperature is known.

NUMERICAL PROBLEMS

Example 1. 400 ml of air at 700 mm pressure were compressed to 200 ml. What will be the new pressure, if the temperature remains constant ?

<i>Solution :-</i>	Given conditions	Final conditions
	$P_1 = 700 \text{ mm}$	$P_2 = ?$
	$V_1 = 400 \text{ ml}$	$V_2 = 200 \text{ ml.}$

By applying Boyle's law

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ 700 \times 400 &= P_2 \times 200 \\ \Rightarrow P_2 &= \frac{700 \times 400}{200} = 1400 \text{ mm or } 140 \text{ cm.} \end{aligned}$$

Example 2. What is the volume of a sample of oxygen at a pressure of 3 atmosphere and 27°C , if its volume is 4.5 litres at 1 atmosphere and same temperature.

<i>Solution :-</i>	Given conditions	Final conditions
	$P_1 = 1 \text{ atm}$	$P_2 = 3 \text{ atm}$
	$V_1 = 4.5 \text{ litres}$	$V_2 = ?$

Applying Boyle's law

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ 1 \times 4.5 &= 3 \times V_2 \\ \Rightarrow V_2 &= \frac{1 \times 4.5}{3} = \frac{4.5}{3} = 1.5 \text{ litres.} \end{aligned}$$

Example 3. A certain volume of the gas was found to be at a pressure of 1000 mm of mercury. When the pressure was decreased by 500 mm, the gas occupied a volume of 2000 cm^3 . Calculate the initial volume occupied by the gas if the change was done at a constant temperature.

<i>Solution :-</i>	Initial conditions	Final conditions
	$P_1 = 1000 \text{ mm}$	$P_2 = 1000 - 500 = 500 \text{ mm}$
	$V_1 = ??$	$V_2 = 2000 \text{ cm}^3$

Applying Boyle's law

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \\ 1000 \times V_1 &= 500 \times 2000 \\ \Rightarrow V_1 &= \frac{500 \times 2000}{1000} = 1000 \text{ cm}^3. \end{aligned}$$

Example 4. For use in a certain industrial process the volume of a particular gas had to be reduced by 50% of its present volume. The original pressure of the gas was measured and found to be 5 atmospheres. Find the final pressure of the gas if the temperature of the gas was constant throughout the process.

Solution :-	Initial conditions	Final conditions
	$\text{Vol} = V_1$	Volume $V_2 = V_1 - 0.5V_1 = 0.5 V_1$
	Pressure $= P_1 = 5 \text{ atm.}$	Pressure $P_2 = ??$

Applying Boyle's law

$$\Rightarrow P_2 = \frac{5 \times V_1}{0.5 V_1} = \frac{5}{0.5} = 10 \text{ atm.}$$

CHARLE'S LAW (Relationship between Volume & Temperature)

Jacques Charles in 1787 studied the relationship between temperature of a gas and the volume occupied by it at constant pressure. He observed that at constant pressure the volume of a given mass of gas expands or contracts by $\frac{1}{273}$ of its value at 0°C for every degree celsius rise or fall in the temperature. This was later on confirmed by Joseph Gay-Lussac.

Statement :- "Pressure remaining constant the volume of a given mass of gas increases or decreases by $\frac{1}{273}$ of its value at 0°C for each 1°C rise or fall in temperature."

Derivation :

Let ' V_0 ' be the volume of a given mass of gas at 0°C and at constant pressure.

$$\text{Volume of the gas at } 1^\circ\text{C} = V_o + \frac{V_o \times 1}{273} = V_o + \frac{V_o}{273} = V_o \left(1 + \frac{1}{273}\right)$$

$$\text{Volume of the gas at } 2^\circ\text{C} = V_o + \frac{2V_o}{273} = V_o \left(1 + \frac{2}{273}\right)$$

$$\text{Volume of the gas at } t^{\circ}\text{C} = V_o + \frac{tV_o}{273} = V_o \left(1 + \frac{t}{273}\right)$$

When $t = -273^{\circ}\text{C}$

$$V_{-273} = V_o \left(1 - \frac{273}{273}\right) = V_o \times 0 = 0 \text{ (Zero)}$$

Thus, gases have no volume at -273°C . This temperature is known as **Absolute zero** of temperature.

Absolute zero :

The temperature at which a gas ceases to exist or at which volume of the gas becomes zero is called **Absolute Zero**. Thus, -273°C is the absolute zero of temperature. This temperature has no physical significance. Reduction of volume of a gas to zero cc is only a theoretical concept. Practically all gases get liquefied or solidified before reaching this temperature.

Absolute scale of Temperature :

The scale of temperature with -273°C as its Zero (0K) is called Absolute scale of temperature.

$$\text{Thus, } -273^{\circ}\text{C} = 0\text{K}$$

$$\text{or } (-273 + 273)^{\circ}\text{C} = (0 + 273) \text{ K}$$

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

$$\Rightarrow t^{\circ}\text{C} = (t + 273) \text{ K.}$$

The effect of temperature on volume of gas can be graphically represented as

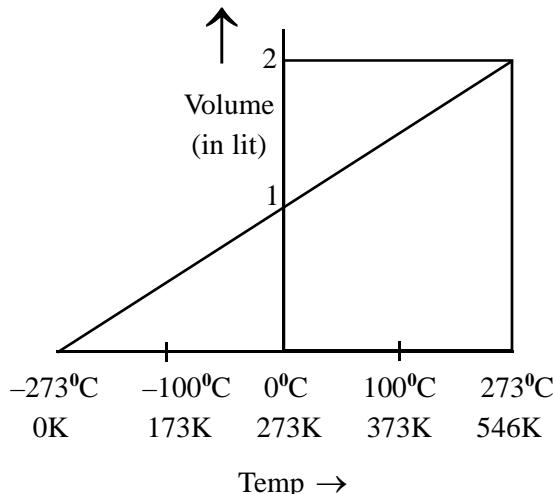


Fig. 6.4 Plot of V against T

Again let us assume that V_1 ml & V_2 ml be the volume of a given mass of gas at $t_1^{\circ}\text{C}$ and $t_2^{\circ}\text{C}$ respectively and at constant pressure.

$$V_1 = V_0 + \frac{V_0 \times t_1}{273} = V_0 \left(1 + \frac{t_1}{273}\right) = V_0 \left(\frac{273 + t_1}{273}\right) = \frac{V_0 T_1}{273}$$

$$V_2 = V_0 + \frac{V_0 t_2}{273} = V_0 \left(1 + \frac{t_2}{273}\right) = V_0 \left(\frac{273 + t_2}{273}\right) = \frac{V_0 T_2}{273}$$

where T_1 & T_2 are the temperatures in the absolute scale.

Dividing V_1 by V_2 we have,

$$\frac{V_1}{V_2} = \frac{V_0 T_1}{273} \times \frac{273}{V_0 T_2} = \frac{T_1}{T_2},$$

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \frac{V}{T} = \text{constant, at constant pressure.}$$

Thus, $V \propto T$, at constant pressure.

Another definition of CHARLE'S LAW :

"Pressure remaining constant, the volume of a given mass of gas is directly proportional to absolute temperature."

Validity of the law :

- It is possible to demonstrate the validity of the law by determining the volume of a given mass of gas at different temperatures and at constant pressure. The constancy of value $\frac{V}{T}$ in each case proves the validity as is evident from the following table 6.2.

Table-6.2 Changes in volume of a given mass of gas with temperature at constant pressure.

No. of Experiments	Temp in deg. centigrade ($^{\circ}\text{C}$)	Temp in Kelvin (K)	Volume in cm^3	$\frac{V}{T}$
1.	-50	223	223	1
2.	-0	273	273	1
3.	50	323	323	1
4.	100	373	373	1
5.	150	423	423	1

- The validity of the law can also be tested by plotting a graph (Fig 6.5) between volume and temperature of a given mass of gas at constant pressure. A straight line is formed which shows that $\frac{V}{T}$ is constant. At different pressures the straight lines formed in the graph meet at the same point '0' upon extension.

This point refers to zero volume and absolute zero of temperature.

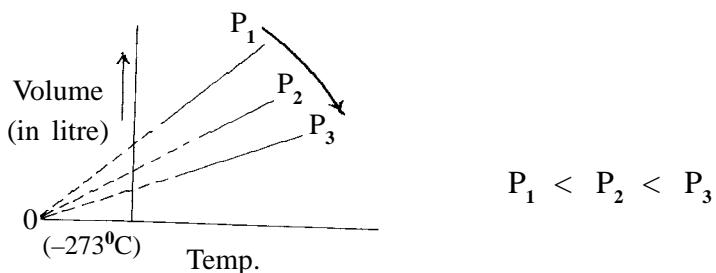


Fig 6.5 Volume - Temp. relationship

Utility of the law :

The law can be used in determining the volume of a given mass of gas at a certain temperature provided the volume at some other temperature is known keeping the pressure constant.

GAY - LUSSAC'S LAW

Statement : At constant volume, the pressure of the given mass of gas is directly proportional to its absolute temperature.

i.e. $P \propto T$ at constant volume.

If P_1 & P_2 be the pressure of the gas at temperature T_1 & T_2 respectively,

$$\text{Then, } \frac{P_1}{P_2} = \frac{T_1}{T_2} \text{ at constant volume.}$$

NUMERICAL PROBLEMS

Example 1. A certain volume of gas is kept at 67°C . When the temperature is decreased by 17°C the gas occupies a volume of 800 ml. What was the initial volume of the gas ? Assume that the pressure of the gas remains constant.

<i>Solution :</i>	Initial condition	Final condition
	$V_1 = ?$	$V_2 = 800 \text{ ml}$
	$T_1 = 273 + 67$	$T_2 = 273 + (67 - 17)$
	$= 340 \text{ K.}$	$= 273 + 50 = 323 \text{ K.}$

$$\begin{aligned} \text{According to Charle's Law} \quad & \frac{V_1}{T_1} = \frac{V_2}{T_2} \\ \Rightarrow \quad & \frac{V_1}{340} = \frac{800}{323} \\ \Rightarrow \quad & V_1 = \frac{800 \times 340}{323} = 842.10 \text{ ml} \end{aligned}$$

Example 2. A sample of hydrogen gas is found to occupy 900 cm^3 at 37°C . Calculate the temperature at which it will occupy 500 cm^3 .

<i>Solution :</i>	Given $V_1 = 900 \text{ cm}^3$
	$T_1 = 37^{\circ}\text{C} = (273 + 37) = 310 \text{ K}$
	$V_2 = 500 \text{ cm}^3$
	$T_2 = ??$
Applying Charle's Law	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
$\Rightarrow \frac{900}{310} = \frac{500}{T_2}$	
$\Rightarrow T_2 = \frac{500 \times 310}{900} = 172 \text{ K} (\text{or} - 101^{\circ}\text{C})$	

Example 3. 500 ml of Oxygen is collected at 27°C . If the volume is reduced to $\frac{1}{4}$ th its original volume, find the temperature to which the gas has to be cooled ?

<i>Solution :</i>	Given $V_1 = 500 \text{ ml}$
	$T_1 = 273 + 27 = 300 \text{ K}$
	$V_2 = \frac{1}{4} V_1 = \frac{1}{4} \times 500 = 125 \text{ ml}$
	$T_2 = ??$

$$\begin{aligned} \text{Applying Charle's Law} \quad & \frac{V_1}{T_1} = \frac{V_2}{T_2} \\ \Rightarrow \quad & \frac{500}{300} = \frac{125}{T_2} \\ \Rightarrow \quad & T_2 = \frac{300 \times 125}{500} = 75 \text{ K (or } -198^\circ\text{C}) \end{aligned}$$

Example 4. 3000cc of a gas is heated from 27°C to 127°C . What will be the new volume of the gas at constant pressure ?

$$\begin{aligned} \text{Solution :} \quad & \text{Given } V_1 = 3000 \text{ cc} \quad V_2 = ?? \\ & T_1 = 273 + 27 = 300 \text{ K} \quad T_2 = 127 + 273 = 400 \text{ K} \\ \text{Applying Charle's Law,} \quad & \frac{V_1}{T_1} = \frac{V_2}{T_2} \\ \Rightarrow \quad & \frac{3000}{300} = \frac{V_2}{400} \\ \Rightarrow \quad & V_2 = \frac{3000 \times 400}{300} = 4000 \text{ cc.} \end{aligned}$$

Example 5. A given mass of oxygen gas occupies 300 cm^3 at 27°C . What is the volume at 0°C , the pressure remains constant ?

$$\begin{aligned} \text{Solution :} \quad & \text{Given } V_1 = 300 \text{ cm}^3 \\ & T_1 = 27^\circ\text{C} = 273 + 27 = 300 \text{ K} \\ & V_2 = ?? \\ & T_2 = 0^\circ\text{C} = 273 \text{ K} \\ \text{Applying Charle's Law,} \quad & \frac{V_1}{T_1} = \frac{V_2}{T_2} \\ \Rightarrow \quad & \frac{300}{300} = \frac{V_2}{273} \\ \Rightarrow \quad & V_2 = \frac{300 \times 273}{300} = 273 \text{ cm}^3 \end{aligned}$$

COMBINED GAS EQUATION

The gas equation deals with the simultaneous effect of change of temperature and pressure on the volume of a given mass of gas. It is derived on the combination of both Boyle's law and Charle's law.

Derivation : Let us suppose that a given mass of gas occupies a volume ' V_1 ' at a pressure P_1 and temperature T_1

(i) **Apply Boyle's law :**

Keep Temp ' T_1 ' to be constant. When pressure changes from P_1 to P_2 , let the volume change from V_1 to v .

$$\text{So, } V_1 \propto \frac{1}{P_1} \text{ and } v \propto \frac{1}{P},$$

Thus, $P_1 V_1 = P_2 y$

(ii) **Apply Charle's law :**

Keep Pressure ' P_2 ' constant. When temperature changes from T_1 to T_2 , let the volume change from y to V_2 .

So $y \propto T_1$ and $V_2 \propto T_2$

$$\text{Thus } \frac{v}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow v = \frac{V_2 T_1}{T_2} \dots \dots \dots \quad (2)$$

Comparing (1) & (2) we have

$$\Rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = K \text{ [constant]}$$

Utility of the gas equation :

The volume of a given mass of gas at a certain temperature and pressure can be determined provided its value at some other temperature and pressure is known.

Standard Temperature and Pressure (STP or NTP) :

The volume of a given mass of gas varies with temperature and pressure. Hence a standard reference condition is chosen to compare the measurable properties P, V, T of gases.

Standard Temperatures	= 0°C = 273 K.
Standard Pressure	= 760 mm Hg.
	= 76 cm Hg.
	= 1 atmos. pressure.

NUMERICAL PROBLEMS

Example 1. A flask contains 300 ml of gas at 17°C and 50 cm of Hg. Find the final pressure when it is transferred to another flask of 100 ml. capacity at a temperature of 37°C.

Solution :

Initial condition	Final condition
$P_1 = 50 \text{ cm Hg}$	$P_2 = ?$

$$T_1 = 273 + 17 = 290 \text{ K}$$

$$V_1 = 300 \text{ ml}$$

$$T_2 = 273 + 37 = 310 \text{ K}$$

$$V_2 = 100 \text{ ml}$$

$$\text{Using the gas equation, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Substituting the values, } \frac{50 \times 300}{290} = \frac{P_2 \times 100}{310}$$

$$\Rightarrow P_2 = \frac{50 \times 300 \times 310}{290 \times 100} = 160.34 \text{ cm.}$$

Example 2. A gas occupies 500 ml at STP. Find the volume of the gas when its pressure is 200 mm of Hg and its temp 20°C .

Solution :

Initial condition (STP)

$$P_1 = 760 \text{ mm Hg}$$

$$V_1 = 500 \text{ ml}$$

$$T_1 = 273 \text{ K}$$

Final Condition

$$P_2 = 200 \text{ mm Hg}$$

$$V_2 = ?$$

$$T_2 = 273 + 20 = 293 \text{ K}$$

$$\text{Applying gas equation, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Substituting the values, } \frac{760 \times 500}{273} = \frac{200 \times V_2}{293}$$

$$\Rightarrow V_2 = \frac{760 \times 500 \times 293}{273 \times 200} = 2039.19 \text{ ml.}$$

Example 3. At a given temperature the pressure of the gas reduces to 60 % of its initial value and volume increases by 45% of its original value. Find this temperature if the initial temperature was -20°C .

Solution :

Initial condition

$$P_1 = P_1$$

Final condition

$$P_2 = \frac{60}{100} P_1 = \frac{3P_1}{5}$$

$$V_1 = V_1$$

$$V_2 = \left(V_1 + \frac{45V_1}{100} \right) = \frac{145}{100} V_1$$

$$T_1 = -20 + 273 = 253 \text{ K}$$

$$T_2 = ?$$

$$\text{Applying gas equation, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\Rightarrow \frac{P_1 V_1}{253} = \frac{3P_1 \times 145V_1}{5 \times 100 \times T_1}$$

$$\Rightarrow T_2 = \frac{3 \times 145 \times 253}{5 \times 100} = 220.11 \text{ K.}$$

Example 4. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm and 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.

Solution :

Initial condition	Final condition
$V_1 = 2.82 \text{ l}$	$V_2 = ?$
$T_1 = 27^\circ\text{C} = 300 \text{ K}$	$T_2 = 273 \text{ K}$
$P_1 = 20 \text{ atm}$	$P_2 = 1 \text{ atm}$
Applying gas equation	$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
$\Rightarrow \frac{20 \times 2.82}{300} = \frac{1 \times V_2}{273}$	
$\Rightarrow V_2 = \frac{20 \times 2.82 \times 273}{300} = 51.324 \text{ l} = 51324 \text{ ml.}$	

The volume of spherical balloon

$$= \frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times \left(\frac{21}{2}\right)^3 = 4847 \text{ ml.}$$

The capacity of the cylinder = 2.82 l = 2820 ml.

The amount of gas to be filled into balloons = 51324 – 2820 = 48504 ml.

$$\begin{aligned} L \text{ No of balloons} &= \frac{\text{Vol. of gas transferred}}{\text{Vol. of balloon}} \\ &= \frac{48504}{4847} \approx 10 \end{aligned}$$

Example 5. If the density of a gas at 27°C and 1 atmospheric pressure is 1.5 gms / litre, find the density at 127°C and 4 atm. pressure

Solution :

$$\text{According to combined gas equation, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V \propto \frac{1}{d} \text{ (at constant temp)}$$

$$\text{The equation may be expressed as } \frac{P_1}{d_1 T_1} = \frac{P_2}{d_2 T_2}$$

$$P_1 = 1 \text{ atm} \quad P_2 = 4 \text{ atm}$$

$$d_1 = 1.5 \text{ gms/lit} \quad d_2 = ??$$

$$T_1 = 27 + 273 = 300 \text{ K} \quad T_2 = 127 + 273 = 400 \text{ K}$$

From the above equation

$$d_2 = \frac{P_2 d_1 T_1}{P_1 T_2} = \frac{4 \times 1.5 \times 300}{1 \times 400} = 4.5 \text{ gms/lit.}$$

Example 6. The pressure of a given mass of gas becomes half the original pressure and simultaneously the volume becomes four times the original volume. What should have happened to the temperature?

Solution :

Let the initial pressure and volume be P_1 & V_1 respectively.

$$\text{Final pressure } P_2 = \frac{P_1}{2}$$

$$\text{Final volume } V_2 = 4 V_1$$

$$\text{We know } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\Rightarrow \frac{P_1 V_1}{T_1} = \frac{\frac{P_1}{2} \times 4 V_1}{T_2} = \frac{2 P_1 V_1}{T_2}$$

$$\Rightarrow T_2 = 2 T_1$$

i.e. the temperature is doubled.

IDEAL GAS EQUATION

Ideal gas equation can be derived on the basis of Boyle's law, Charle's law and Avogadro's law. The equation gives the general relationship between pressure, volume, temperature and no. of moles of the gas.

According to Boyle's Law :

$$V \propto \frac{1}{P} \text{ when temp 'T' and no. of moles 'n' are kept constant.}$$

According to Charle's Law :

$$V \propto T \text{ when pressure 'P' and no. of moles 'n' are kept constant.}$$

According to Avogadro's Law :

$$V \propto n \text{ when press. 'P' and Temp. 'T' are kept constant.}$$

[Equal volumes of all gases under similar conditions of temperature and pressure contain equal no. of molecules]

Combining all the three laws,

$$V \propto n \times \frac{1}{P} \times T$$

$$\text{or, } V = \text{const} \times \frac{nT}{P}$$

$$\text{or, } PV = nRT \rightarrow \text{Ideal gas equation.}$$

where R is a constant known as **Universal gas constant**.

If $W \rightarrow$ Mass of the gas

$M \rightarrow$ Molecular mass

$$n = \frac{W}{M}$$

$$\text{Then, } PV = nRT = \frac{W}{M} RT$$

$$\text{or } M = \frac{WRT}{PV} = \frac{d}{P} RT \text{ (where } d = \text{density of gas} = \frac{W}{V})$$

SIGNIFICANCE OF R

The ideal gas equation is $PV = nRT$

$$\text{So, } R = \frac{P \times V}{n \times T}$$

$$= \frac{\text{Press.} \times \text{Volume}}{\text{No. of moles} \times \text{Abs. temp.}}$$

$$= \frac{(\text{Force/Area}) \times \text{Volume}}{\text{No. of moles} \times \text{Abs. temp.}}$$

$$= \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{No. of moles} \times \text{Abs. temp.}}$$

$$= \frac{(\text{Force} \times \text{Length})}{\text{No. of moles} \times \text{Abs. temp.}}$$

$$= \frac{\text{Work}}{\text{No. of moles} \times \text{Abs. temp.}}$$

Thus, 'R' may be represented in the units of work per mole per degree.

NUMERICAL VALUE OF 'R'

(i) **In litre - atmosphere / cm³ – atm/lit – mm**

When Pressure is in atmosphere and volume is in litres, 'R' is represented in litre atmosphere

For 1 mole of gas at NTP, we have

$$P = 1 \text{ atm}, T = 273 \text{ K}$$

$$V = 22.4 \text{ litres}$$

$$\therefore R = \frac{P \times V}{n \times T} = \frac{1 \times 22.4}{1 \times 273} = 0.0821 \text{ lit. atm deg}^{-1} \text{ mole}^{-1}$$

$$R = 82.1 \text{ cm}^3 \cdot \text{atm K}^{-1} \text{ mole}^{-1} \text{ (When 'P' is in atm. and 'V' is in cm}^3)$$

$$= 62.39 \text{ litre. mm K}^{-1} \text{ mole}^{-1} \text{ (When 'P' is in mm and 'V' is in litre.)}$$

(ii) In ergs / calorie :

When Pressure is expressed in dynes per square centimetre and volume in cubic centimetre, 'R' is represented in terms of ergs/Joules /Calories.

For 1 mole of gas at STP

$$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes/cm}^2$$

$$V = 22.4 \text{ litres} = 22,400 \text{ cm}^3$$

$$T = 273 \text{ K}$$

$$\therefore R = \frac{P \times V}{n \times T} = \frac{76 \times 13.6 \times 981 \times 22,400}{1 \times 273}$$

$$= 8.31 \times 10^7 \text{ ergs K}^{-1} \text{ mole}^{-1}$$

$$\text{Since } 1 \text{ Joule} = 10^7 \text{ ergs}$$

$$R = 8.31 \text{ Joules K}^{-1} \text{ mol}^{-1} \text{ (SI Unit)}$$

Again we know, 1 calorie = 4.182×10^7 ergs

$$\text{So, } R = \frac{8.314 \times 10^7}{4.182 \times 10^7} = 1.99 \text{ Cal K}^{-1} \text{ mol}^{-1}$$

(iii) (SI Unit of Work) R in Joule

Pressure is expressed in pascals or Nm^{-2} and volume in m^3

For 1 mole of gas at STP

$$P = 1 \text{ atm} = 1.013 \times 10^5 \text{ pa} = 1.013 \times 10^5 \text{ Nm}^{-2}$$

$$V = 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ m}^3$$

$$T = 273 \text{ K}$$

$$\therefore R = \frac{PV}{nT} = \frac{1.013 \times 10^5 \times \text{Nm}^{-2} \times 22.4 \times 10^{-3} (\text{m}^3)}{1 \times 273}$$

$$= 8.31 \text{ Nm K}^{-1} \text{ mol}^{-1} = 8.31 \text{ pa m}^3 \text{ K}^{-1} \text{ mole}^{-1}$$

$$= 8.31 \text{ K Pa Dm}^3 \text{ K}^{-1} \text{ mole}^{-1}$$

$$= 8.31 \text{ Joule K}^{-1} \text{ mole}^{-1} \quad (\Theta 1\text{Nm} = 1\text{J})$$

NUMERICAL PROBLEMS

Example 1. Calculate the volume occupied by 7 gms of N_2 at 27°C and 750 mm Hg.

Solution :

$$\text{Given } W = 7 \text{ gms}, T = 300 \text{ K}, P = \frac{750}{760} \text{ atm}, M = 28$$

$$\begin{aligned} PV &= nRT = \frac{W}{M} RT = \frac{7}{28} \times 0.82 \times 300 \\ \Rightarrow \frac{750}{760} \times V &= \frac{7 \times 0.082 \times 300}{28} \\ \therefore V &= \frac{760 \times 7 \times 0.082 \times 300}{750 \times 28} = 6.239 \text{ litres.} \end{aligned}$$

Example 2. Calculate the weight of methane in a 9 litre cylinder at 16 atm and 27°C
(R = 0.08 l atm.K⁻¹)

Solution :

$$\begin{aligned} \text{Given} \quad P &= 16 \text{ atm} \\ V &= 9 \text{ litres} \\ T &= 273 + 27 = 300 \text{ K} \\ M &= 12 + 4 = 16 \end{aligned}$$

$$\text{We know } PV = nRT = \frac{W}{M} RT$$

Substituting the values,

$$\begin{aligned} 16 \times 9 &= \frac{W}{16} \times 0.08 \times 300 \\ \Rightarrow W &= \frac{16 \times 9 \times 16}{0.08 \times 300} = 96 \text{ gms.} \end{aligned}$$

Example 3. Calculate the temperature at which 28 gms of N₂ occupies a volume of 10 litres at 2.46 atm.

Solution :

$$\begin{aligned} \text{Given} \quad W &= 28 \text{ gms} \\ V &= 10 \text{ litres} \\ P &= 2.46 \text{ atm} \\ M &= 28 \end{aligned}$$

The ideal gas equation is

$$PV = nRT = \frac{W}{M} RT$$

Substituting the values,

$$\begin{aligned} 2.46 \times 10 &= \frac{28}{28} \times 0.082 \times T \\ \Rightarrow T &= \frac{2.46 \times 10}{0.082} = 299.64 \text{ K.} \end{aligned}$$

Example 4. O₂ is present in one litre flask at a pressure of 7.6 × 10⁻¹⁰ mm of Hg. Calculate the no. of O₂ molecules at 0°C

Solution :

$$\begin{aligned} \text{Given} \quad P &= 7.6 \times 10^{-10} \text{ mm} = \frac{7.6 \times 10^{-10}}{760} \text{ atm.} \\ V &= 1 \text{ litre,} \\ T &= 273 \text{ K} \end{aligned}$$

The ideal gas equation is $PV = nRT$

Substituting the values,

$$\begin{aligned} \frac{7.6 \times 10^{-10}}{760} \times 1 &= n \times 0.0821 \times 273 \\ \Rightarrow n &= \frac{7.6 \times 10^{-10}}{760 \times 0.0821 \times 273} = 4.46 \times 10^{-14} \text{ moles.} \\ 1 \text{ mole of O}_2 &\text{ contains Avogadro no. } (6.02 \times 10^{23}) \text{ of molecules} \\ \therefore 4.46 \times 10^{-14} \text{ moles} &\text{ contain } 4.46 \times 10^{-14} \times 6.02 \times 10^{23} \\ &= 2.68 \times 10^{10} \text{ no. of molecules.} \end{aligned}$$

Example 5. Calculate the density of CO_2 at 100°C and 800 mm Hg pressure.

Solution :

$$\begin{aligned} \text{Given } P &= \frac{800}{760} \text{ atm.} \\ T &= 273 + 100 = 373 \text{ K} \end{aligned}$$

The ideal gas equation is $PV = nRT$

$$\begin{aligned} \text{or, } PV &= \frac{W}{M} RT \\ \text{or, } P &= \frac{W}{M \times V} RT \\ \text{or, } P &= \frac{d}{M} RT \quad (\mid \frac{W}{V} = \frac{\text{mass of CO}_2}{\text{volume}} = \text{density}) \end{aligned}$$

Substituting the values

$$\begin{aligned} \frac{800}{760} &= \frac{d}{44} \times 0.082 \times 373 \quad (\text{1 mol mass of CO}_2 = 12 + 32 = 44) \\ \Rightarrow d &= \frac{800 \times 44}{760 \times 0.082 \times 373} = 1.5124 \text{ gl}^{-1} \end{aligned}$$

DALTON'S LAW OF PARTIAL PRESSURE

The behaviour of a mixture of gases that do not react chemically with each other is frequently of interest. A law dealing with such behaviour was stated by John Dalton in 1801.

Statement :

The total pressure of the mixture of gases that do not react chemically with each other is equal to the sum of partial pressures of all the gases present.

If the total pressure be P_{Total} and partial pressures of gases present be P_A , P_B etc.

$$P_{\text{Total}} = P_A + P_B + \dots$$

Partial Pressure :

It is defined as the pressure which each gas would exert if it is separately confined in the whole volume occupied by the mixture of gases

$$\text{Partial Pressure} = \text{mole fraction} \times \text{Total Pressure.}$$

Mathematical deduction :

Let there be two chemically non-reacting gases A and B. Let us suppose that n_A moles of gas A are mixed with n_B moles of gas B.

$$\text{Total no. of moles in the reaction mixture} = (n_A + n_B)$$

The ratio of no. of moles of A to the total no. of moles present is known as the molefraction of 'A'. It is represented by X_A .

$$\text{Thus, } X_A = \frac{n_A}{(n_A + n_B)}$$

$$\text{Similarly, mole fraction of 'B', } X_B = \frac{n_B}{(n_A + n_B)}$$

Let P_{Total} be the total pressure exerted by the mixture and P_A, P_B be partial pressures of A and B respectively.

Partial pressure of gas 'A' will be its mole fraction times the total pressure .

$$\text{i.e. } P_A = X_A P_{\text{Total}} = \frac{n_A}{(n_A + n_B)} \times P_{\text{Total}}$$

Similarly, partial pressure of gas 'B' will be its molefraction times the total pressure

$$\text{i.e. } P_B = X_B P_{\text{Total}} = \frac{n_B}{(n_A + n_B)} \times P_{\text{Total}}$$

$$\text{Thus } P_A + P_B = \frac{n_A}{(n_A + n_B)} P_{\text{Total}} + \frac{n_B}{(n_A + n_B)} P_{\text{Total}}$$

$$= P_{\text{Total}} \left[\frac{n_A}{(n_A + n_B)} + \frac{n_B}{(n_A + n_B)} \right]$$

$$= P_{\text{Total}} \left[\frac{n_A + n_B}{n_A + n_B} \right]$$

$$= P_{\text{Total}}$$

i.e.	$P_{\text{Total}} = P_A + P_B$
------	--------------------------------

So, if a mixture contains 1 mole of A and 4 moles of B, then total no. of moles is $(1 + 4) = 5$. The mole fraction of A = $\frac{1}{5}$ and that of B = $\frac{4}{5}$. The Partial pressure of 'A' is $\frac{1}{5}$ th of total Pressure whereas that of B is $\frac{4}{5}$ th of total pressure.

APPLICATIONS OF DALTON'S LAW

1. Determination of Total Pressure :

The law is used to determine the total pressure exerted by a mixture of chemically non-reacting gases. The total pressure is the sum of partial pressures of individual gases.

2. Determination of Pressure of dry gas :

When a gas is collected over water it is associated with some water vapour since at all temperatures there is a conversion of water into its vapour. So the pressure we measure of a moist gas is the sum of the partial pressure of dry gas and the pressure of water vapour at that temperature.

$$\text{Thus, } P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapour}}$$

The partial pressure of water vapour is known as "**Aqueous Tension**".

$$\text{So, } P_{\text{moist gas}} = P_{\text{dry gas}} + \text{Aqueous Tension}$$

$$\text{or, } P_{\text{dry gas}} = P_{\text{moist gas}} - \text{Aqueous Tension}$$

So, by knowing the aqueous tension at that particular temperature, the pressure of dry gas can be found out.

NUMERICAL PROBLEMS

Example 1. O₂ is collected over water at 28°C. The pressure inside the gas is 745 mm of Hg. What is the pressure due to O₂ alone if vapour pressure of H₂O is 15 mm at 28°C ?

Solution :

$$P_{\text{moist O}_2} = 745 \text{ mm}, P_{\text{H}_2\text{O}} = 15 \text{ mm}$$

$$\text{or, } P_{\text{moist O}_2} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$\text{or, } 745 = P_{\text{O}_2} + 15$$

$$\text{or, } P_{\text{O}_2} = 745 - 15 = 730 \text{ mm.}$$

Example 2. A container of 2.461 litre at 27°C has a mixture of 0.3 moles of N₂, 0.5 moles of He and 6.2 moles of O₂. What will be the partial pressure of gases ?

Solution :

Given V = 2.461 litres, T = 273 + 27 = 300 K

No. of moles of N₂ = 0.3

No. of moles of He = 0.5

No. of moles of O₂ = 6.2

Total No. of moles = 0.3 + 0.5 + 6.2 = 7

Apply the equation PV = nRT

$$P = \frac{nRT}{V} = \frac{7 \times 0.082 \times 300}{2.461} = 70.06 \text{ atm.}$$

We know that partial press. = molefraction × Total Press.

$$\text{molefraction of N}_2 = \frac{0.3}{7}$$

$$\text{molefraction of He} = \frac{0.5}{7}$$

$$\text{molefraction of O}_2 = \frac{6.2}{7}$$

$$\text{partial press. of N}_2 = \frac{0.3}{7} \times 70.06 = 3.003 \text{ atm.}$$

$$\text{partial press. of He} = \frac{0.5}{7} \times 70.06 = 5.004 \text{ atm.}$$

$$\text{partial press. of O}_2 = \frac{6.2}{7} \times 70.06 = 62.053 \text{ atm.}$$

Example 3. 300 ml of nitrogen at a pressure of 740 mm and 350 ml of oxygen at a pressure of 600 mm are put together in a one litre flask. If the temp. is kept constant what will be the total pressure ?

Solution :

(i) **Calculate Partial pressure of N₂ as follows :**

$$V_1 = \text{Vol. of Nitrogen} = 300 \text{ ml}$$

$$P_1 = \text{Press. of Nitrogen} = 740 \text{ mm}$$

$$V_2 = 1 \text{ litre} = 1000 \text{ ml}$$

$$P_2 = ??$$

Apply $P_1V_1 = P_2V_2$ (Θ temp. is kept constant)

$$740 \times 300 = P_2 \times 1000$$

$$\therefore P_2 = \frac{740 \times 300}{1000} = 222 \text{ mm.}$$

∴ Partial pressure of N₂ i.e. P_{N₂} = 222 mm.

(ii) **Calculate Partial pressure of O₂ :**

$$V_1 = 350 \text{ ml}$$

$$P_1 = 600 \text{ ml}$$

$$V_1 = 1000 \text{ ml}$$

$$P_2 = ??$$

Applying $P_1V_1 = P_2V_2$

$$600 \times 350 = P_2 \times 1000$$

$$\therefore P_2 = \frac{600 \times 350}{1000} = 210 \text{ mm.}$$

i.e. Partial pressure of O₂, P_{O₂} = 210 mm.

∴ Total pressure = P_{N₂} + P_{O₂} = 222 mm. + 210 mm = 432 mm.

Example 4. Two gases A and B having molecular mass 60 and 45 respectively are enclosed in a vessel. The weight of A is 0.50gms and that of B is 0.2gms. The total pressure of mixture is 750 mm. Calculate the partial pressure of each gas.

Solution :

Given wt of A = 0.50 gms

molecular mass of A = 60

$$\therefore \text{No. of moles of A} = \frac{0.5}{60}$$

$$\begin{aligned} \text{wt. of B} &= 0.2 \text{ gms} \\ \text{mol. mass of B} &= 45 \\ \therefore \text{No. of moles of B} &= \frac{0.2}{45} \\ \text{Total Pressure} &= 750 \text{ mm.} \end{aligned}$$

$$\text{Total no. of moles} = \left(\frac{0.5}{60} + \frac{0.2}{45} \right)$$

$$\text{Partial pressure of A} = \frac{0.5/60}{\left(\frac{0.5+0.2}{60+45} \right)}$$

Applying the formula Partial pressure = Total pressure \times molefraction

$$\text{Partial pressure of A} = 750 \times \frac{0.5/60}{\left(\frac{0.5+0.2}{60+45} \right)} = 489.23 \text{ mm}$$

$$\text{Partial pressure of B} = 750 - 489.23 = 260.77 \text{ mm.}$$

Example 5. A mixture of gases in a gas cylinder at 760 mm pressure contains 70% nitrogen, 20% oxygen and 10% CO₂ by volume. What is the partial pressure of each gas in mm. ?

Solution :

Combining Dalton's law and Avogadro's law we may conclude that

$$\% \text{ of each gas} = \frac{\text{Partial Pressure}}{\text{Total Pressure}} \times 100$$

i.e. volume fraction will correspond to mole fraction.

$$\text{So, Partial pressure} = \frac{\text{Total Press} \times \% \text{ of each gas}}{100}$$

$$\text{Partial pressure of N}_2 = \frac{760 \times 70}{100} = 532 \text{ mm}$$

$$\text{Partial pressure of O}_2 = \frac{760 \times 20}{100} = 152 \text{ mm}$$

$$\text{Partial pressure of CO}_2 = \frac{760 \times 10}{100} = 76 \text{ mm}$$

DIFFUSION OF GASES

Gases possess the property of diffusion ie. they can intermix with each other irrespective of their densities. This is due to the fact that there are intermolecular spaces or voids between the molecules and the molecules of a gas are always in a state of constant rapid motion. The molecules of a gas can be easily accommodated within the spaces between the molecules of other gas. For example,

- (i) In a closed room if a bottle of conc. NH₄OH is opened at one corner, the smell of NH₃ can be perceived at the other end.
- (ii) If a jar full of air is inverted over a jar of bromine gas, it is observed that bromine gas rises up, mixes with air forming a homogeneous mixture. This is revealed from the colour (i.e. reddish brown). Bromine is a heavier gas. Yet it rises up against the forces of gravity. This is possible only due to random perpetual motion of gas molecules.

This property, by virtue of which gases can intermix with each other forming a homogeneous mixture irrespective of gravitational force is known as **diffusion**.

GRAHAM'S LAW OF DIFFUSION

In 1869, Thomas Graham studied the effect of rates of diffusion of gases on their densities and expressed his experimental findings in the form of a law known as Graham's Law.

Statement : Under similar conditions of temperature and pressure, the rates of diffusion of gases are inversely proportional to the square root of their densities.

Mathematically it can be represented as follows :

Let us take two gases with rates of diffusion r_1 and r_2 and densities d_1 and d_2 .

According to Graham's law

$$r_1 \propto \frac{1}{\sqrt{d_1}}, r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$\text{So, } \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad (\text{at same temp. and pressure})$$

Again we know that molecular mass is twice the vapour density. Therefore, the above expression may be written as :

$$\frac{r_1}{r_2} = \sqrt{\frac{2d_2}{2d_1}} = \sqrt{\frac{M_2}{M_1}} \quad \text{where } M_1 \text{ and } M_2 \text{ are the molecular masses of gases having densities } d_1 \text{ and } d_2 \text{ respectively.}$$

Another statement of the Law :

From the above expression the law may also be stated as :

" The rates of diffusion of gases are inversely proportional to the square root of their molecular masses."

Again the rate of diffusion is the volume of gas that diffuses in unit time.

i.e. Rate of diffusion ' r ' = $\frac{\text{Vol. of gas diffused 'v'}}{\text{Time taken for diffusion 't'}}$

If V cc of two gases take t_1 and t_2 seconds respectively to diffuse then

$$r_1 = \frac{V}{t_1} \text{ and } r_2 = \frac{V}{t_2}$$

$$\text{So, } \frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \frac{t_2}{t_1}$$

i.e. Rate of diffusion of gas is inversely related to time of diffusion. If different volumes of two gases diffuse in the same time, the relationship between volume and density of the gas can be derived.

Let V_1 & V_2 be the volumes of two different gases that diffuse in the same time i.e.'t' secs.

$$\text{Then } r_1 = \text{Rate of diffusion of 1st gas} = \frac{V_1}{t}$$

$$r_2 = \text{Rate of diffusion of 2nd gas} = \frac{V_2}{t}$$

$$\text{and } \frac{r_1}{r_2} = \frac{V_1/t}{V_2/t} = \frac{V_1}{t} \times \frac{t}{V_2} = \frac{V_1}{V_2}, \text{ Thus, } \frac{r_1}{r_2} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}}$$

Thus the volumes of gases that diffuse in the same period of time are inversely proportional to the square root of their densities under similar conditions of temperature and pressure.

From the above discussion we may write

$$\boxed{\frac{r_1}{r_2} = \frac{V_1}{V_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}}$$

So, we may conclude that a gas with lower molecular mass will diffuse faster than that with higher molecular mass.

Applications of Gaseous Diffusion :

- When there are two gases having different rates of diffusion it can be applied to separate these two gases.
- A gas detector, which works on the principle of diffusion, can be used in mines for detecting the presence of poisonous gases.
- Law of diffusion helps us in calculating the molecular mass of gases and their relative densities.
- The effect of poisonous or foul gases can be diluted by diffusion into the air.
- The homogeneity of atmospheric air is maintained due to diffusion of its constituent gases.

Effusion : When a gas under pressure is allowed to pass through a small orifice into a region of low pressure, the process is called **Effusion**. So effusion is a special case of diffusion.

Graham's law also holds good in case of Effusion. The law may be stated as "The relative rates of effusion of different gases are in the inverse ratio of square root of their densities."

NUMERICAL PROBLEMS

Example 1. 150 ml of a certain gas diffuse in the same time as 125 ml of Chlorine under the same condition. Calculate the molecular mass of the gas.

Solution : Given

$$\text{Volume of gas (V}_1\text{)} = 150 \text{ ml}$$

$$\text{Volume of Chlorine (V}_2\text{)} = 125 \text{ ml}$$

$$\text{Molecular mass of chlorine, M}_2 = 71$$

$$\text{Molecular mass of the gas, M}_1 = ??$$

$$\text{By Graham's law, } \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Substituting the values we have

$$\begin{aligned}\frac{150}{125} &= \sqrt{\frac{71}{M_1}} \\ \Rightarrow \frac{71}{M_1} &= \frac{150 \times 150}{125 \times 125} \\ \Rightarrow M_1 &= \frac{71 \times 125 \times 125}{150 \times 150} = 49.30\end{aligned}$$

Example 2. 130 volumes of Hydrogen take 25 minutes to diffuse out of a vessel. How long will 100 volumes of Oxygen take to diffuse out from the same vessel under the same condition ?

Solution :

$$r_1 = \text{Rate of diffusion of } H_2 = \frac{130}{25}$$

$$r_2 = \text{Rate of diffusion of } O_2 = \frac{100}{t}$$

$$\text{Mol. wt of } H_2 = 2$$

$$\text{Mol. wt of } O_2 = 32$$

$$\text{By Graham's law, } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or, } \frac{130}{25} \times \frac{t}{100} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

$$\text{or, } \frac{13t}{250} = 4$$

$$\text{or, } t = \frac{250 \times 4}{13} = 76.92 \text{ minutes}$$

Example 3. Calculate the molecular mass of the gas X which diffuses twice as fast as another gas Y, which in turn diffuses thrice as fast as another gas Z. Given, molecular mass of the gas Z is 144.

Solution :

Let the rate of diffusion of gas Z (r_z) be 1.

So rate of diffusion of gas Y (r_y) be 3

and that of gas X (r_x) be 6

$$\text{According to Graham's law } \frac{r_y}{r_z} = \sqrt{\frac{M_z}{M_y}} = \frac{144}{M_y}$$

$$\text{or, } \frac{3}{1} = \sqrt{\frac{144}{M_y}}$$

$$\Rightarrow \frac{3 \times 3}{1 \times 1} = \frac{144}{M_y}$$

$$\Rightarrow M_y = \frac{144}{3 \times 3} = 16$$

$$\text{Again } \frac{r_y}{r_x} = \sqrt{\frac{M_x}{M_y}}$$

$$\text{or, } \frac{3}{6} = \sqrt{\frac{M_x}{M_y}}$$

$$\text{or, } \frac{M_x}{16} = \frac{3 \times 3}{6 \times 6}$$

$$\text{or, } M_x = \frac{16 \times 3 \times 3}{6 \times 6} = 4$$

Example 4. The rates of diffusion of an unknown gas and chlorine are in the ratio of 6:5. Assuming the density of chlorine to be 36, calculate the molecular wt of unknown gas.

Solution : According to Graham's law

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{when } r_1 \rightarrow \text{rate of diffusion of unknown gas,}$$

$r_2 \rightarrow$ rate of diffusion of chlorine,

$d_1 \rightarrow$ density of unknown gas,

$d_2 \rightarrow$ density of chlorine.

$$\therefore \frac{6}{5} = \sqrt{\frac{36}{d_1}}$$

$$\Rightarrow \frac{36}{25} = \frac{36}{d_1}$$

$$\Rightarrow d_1 = 25$$

$$\therefore \text{Molecular mass} = 2 \times \text{V.D} = 2 \times 25 = 50$$

Example 5. The relative ratio of diffusion of two gases A & B are found to be 0.3 and 0.2 respectively. If the density of 'A' is 4, find the relative density of B.

Solution : According to Graham's law

$$\frac{r_1}{r_2} = \sqrt{\frac{d_B}{d_A}}$$

$$\text{or } \frac{0.3}{0.2} = \sqrt{\frac{d_B}{4}}$$

$$\text{or } \frac{d_B}{4} = \frac{9}{4}$$

$$\text{or } d_B = 9$$

Example 6. 180 ml of a hydrocarbon diffuses through a porous membrane in 15 minutes, while 120 ml of SO_2 under identical condition diffuse in 20 minutes. What is the molecular wt of hydrocarbon ?

Solution :

$$\text{Volume of hydrocarbon diffuse} = 180 \text{ ml}$$

$$\text{Time taken for diffusion} = 15 \text{ minutes}$$

$$\therefore \text{Rate of diffusion } (r_1) = \frac{180}{15}$$

$$\text{Similarly rate of diffusion of } \text{SO}_2 \text{ } (r_2) = \frac{120}{20}$$

$$\text{Molecular mass of hydrocarbon } (M_1) = ??$$

$$\text{Molecular mass of } \text{SO}_2 \text{ } (M_2) = 64$$

$$\text{From Graham's law } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Substituting the values

$$\frac{\frac{180}{15}}{\frac{120}{20}} = \sqrt{\frac{64}{M_1}}$$

$$\text{or } \frac{180}{15} \times \frac{20}{120} = \sqrt{\frac{64}{M_1}}$$

$$\text{or } \sqrt{\frac{64}{M_1}} = 2$$

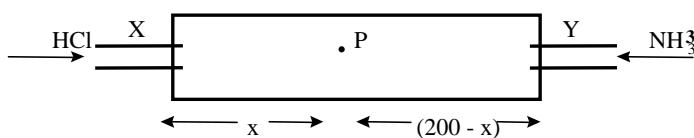
$$\text{or } \frac{64}{M_1} = 4$$

$$\text{or } M_1 = \frac{64}{4} = 16$$

i.e. Molecular wt of hydrocarbon is 16.

Example 7. A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through the inlet tube X and NH_3 gas through the inlet tube Y are allowed to enter into the tube at the same time. White fumes appeared at a point P. Find the distance of 'P' from X.

Solution :



Let the distance of 'P' from 'X' be x cm.

$$\text{So, } P_y = (200 - x)$$

Time taken by HCl to move x cm. must be equal to time taken by NH_3 to move $(200 - x)$ cm.

$$\frac{\text{Rate of diffusion of HCl}}{\text{Rate of diffusion of NH}_3} = \frac{\text{distance P}_x}{\text{distance P}_y} = \sqrt{\frac{M_{NH_3}}{M_{HCl}}}$$

$$\therefore \frac{x}{200-x} = \sqrt{\frac{17}{36.5}} = 0.68$$

$$\text{or, } x = 0.68 (200 - x)$$

$$\text{or, } x = 80 \text{ cm.}$$

6.4 KINETIC THEORY OF GASES

In all the three states of matter the molecules exhibit some sort of motion. In solid state only vibratory motion, in liquid state both vibratory and rotatory and in gaseous state all the three types, namely vibratory, rotatory and translatory motions are conspicuous. By virtue of these different types of motion the molecules acquire some energy. Such energy is called energy of motion or kinetic energy. Thus the theory that explains the behaviour of gases is known as kinetic theory of gases.

This theory was put forth by Bernoulli in 1728 and later on developed by Clausius, Kronig, Maxwell, Boltzmann and Waterson. The theory is applicable to **perfect or an ideal gas**.

6.4.1 POSTULATES OF KINETIC THEORY OF GASES :

1. Every gas consists of minute particles called molecules. The molecules have free existence.
2. The molecules of a gas are similar in shape, size and mass, but they are very much different from those of the other gases.
3. The actual volume occupied by the molecules is negligible compared to the total volume of the gas.
4. The molecules of a gas are always in a state of constant, rapid, zig-zag motion in all possible directions with different velocities. They travel in straight lines. The direction of motion is changed either on collision with other molecules or with the walls of the containing vessel.
5. The period during which the collision occurs is negligible compared to the time taken to traverse the distance between two successive collisions.
6. The molecules are supposed to be spherical in shape and perfectly elastic. As a result no energy is lost during their collisions with one another or with the walls of the containing vessel.
7. Unequal bombardments of molecules on the walls of the container give rise to pressure of the gas. The pressure is the average force per unit area which the molecules exert during their impacts on the walls per unit time. More the number of collisions, more will be the pressure.
8. At relatively low pressure the average distance between the molecules is large compared to molecular diametre. The forces of attraction between the molecules are therefore negligible. The molecules can then be considered as point masses.
9. The gravitational force on the molecules is negligible.
10. The average kinetic energy of gas molecules is a direct measure of absolute temperature.
i.e. Average K.E \propto Absolute temperature.

Basing on the above postulates of Kinetic theory of gases it is possible to derive an expression for the pressure of an ideal gas which is known as "**Kinetic gas equation**".

6.4.2 DERIVATION OF KINETIC GAS EQUATION

Consider a certain quantity of ideal gas to be enclosed in a cubical vessel ABCDEFGH.

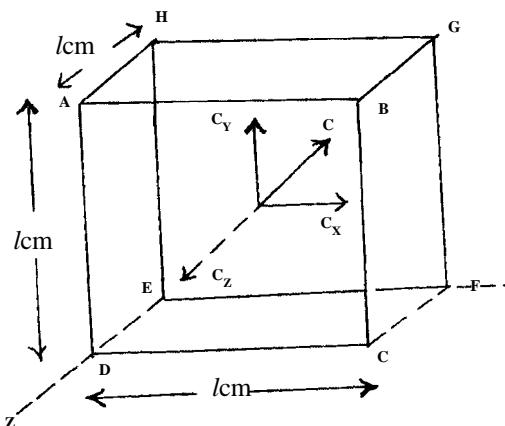


Fig. 6.6 Cubical vessel and resolution of molecular velocity

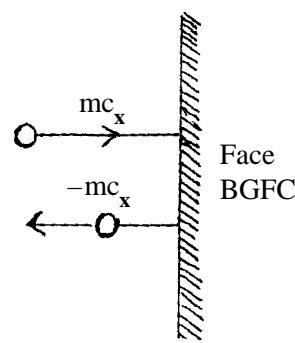


Fig. 6.7 Transfer of momentum to the wall of the vessel

Let us suppose :-

l cm → Length of each side of the cube.

n → Number of molecules present.

m → Mass of each molecule.

Consider a molecule moving with a velocity 'C' cm/sec. This velocity vector can be resolved into three components C_x , C_y and C_z along three axes x, y and z respectively. These components are at right angles to each other and parallel to three sides of the cube. The components will be related to velocity 'C' by the relation.

$$\mathbf{C}^2 = \mathbf{C}_x^2 + \mathbf{C}_y^2 + \mathbf{C}_z^2 \dots \dots \dots \quad (1)$$

Consider the motion of the molecule along X-axis striking the face BGFC. Its momentum will be $m.C_x$ (mass X velocity). As the molecule is perfectly elastic, on striking the wall it will rebound with same velocity but opposite sign. Principle of conservation of momentum is assumed to hold good.

Thus the momentum of the molecule after striking the wall in opposite direction = $-mc$.

∴ Change in momentum for one impact

$$= mC_x - (-mC_x) = 2mC_x$$

After striking the face BGFC the molecule moves ' l ' cm towards left and then ' l ' cm towards right to strike the same face again. In other words the molecule has to traverse a distance of $2l$ cm for each successive collision on the same face.

Since C_x is the velocity of the molecule along X-axis, the time taken to traverse a distance of $2l$ cm = $\frac{2l}{C_x}$ secs.

So the time taken by a molecule for one collision is $\frac{2l}{C_x}$ secs.

and the no. of impacts per sec on the same face = $\frac{C_x}{2l}$

For one impact the change of momentum = $2 mC_x$.

So for $\frac{C_x}{2l}$ impacts the change of momentum = $2 m C_x \times \frac{C_x}{2l} = \frac{m C_x^2}{l}$.

The cube has two opposite faces on the X-axis. Hence the total change in momentum per second due to impact of molecules on the two opposite faces of the cube along X-axis = $\frac{2mC_x^2}{l}$

Similarly the total change in momentum per second on the two opposite faces along Y-axis and Z-axis are $\frac{2mC_y^2}{l}$ and $\frac{2mC_z^2}{l}$ respectively.

If there are 'n' molecules having velocities $C_1, C_2, C_3 \dots \dots \dots C_n$, the total change in momentum per second due to 'n' molecules

(multiplying both numerator and denominator by n)

But $(C_1^2 + C_2^2 + \dots + C_n^2)$ is mean square velocity and let it be represented by \bar{C}^2
 Thus the total change in momentum per second due to 'n' number of molecules $= \frac{2mn\bar{C}^2}{l}$ (4)

Again according to Newton's second law, the change in momentum per second or the rate of change of momentum is the Force.

$$\text{Gas pressure } 'P' = \frac{\text{Force}}{\text{Area}} =$$

(l The area of six faces of cubical vessel = $6l^2$)

Thus $PV = \frac{1}{3} m \bar{v}^2$, where \bar{v} = Root mean square velocity (6)

This equation (6) is called the **kinetic gas equation**. The equation is valid for a vessel of any shape since such vessels may be considered to be made up of a large number of small cubes.

6.4.3 RELATIONSHIP BETWEEN AVERAGE KINETIC ENERGY AND ABSOLUTE TEMPERATURE

The kinetic gas equation is

$$PV = \frac{1}{3} mnC^2$$

where,

P → Pressure of the gas

$V \rightarrow$ Volume occupied by the gas

$m \rightarrow$ Mass of each molecule

$n \rightarrow$ Number of molecules present

$\bar{C} \rightarrow$ Root mean square velocity (RMS velocity)

Suppose one mole of gas is under consideration.

One mole of gas contains Avogadro number i.e. 'N' number of molecules.

$$\text{Hence , } PV = \frac{1}{3} mN \bar{C}^2$$

Comparing this equation with ideal gas equation

$PV = RT$, we have

$$\frac{1}{3} m N \bar{C}^2 = RT$$

$$\text{or, } \frac{2}{3} \times \frac{1}{2} mN\bar{C}^2 = RT$$

$$\text{or, } \frac{1}{2} m N \bar{C}^2 = \frac{3}{2} RT$$

$$(\Theta - \frac{1}{2} m N \bar{C}^2 = \text{K.E. of one mole of ideal gas})$$

$$\therefore \text{Kinetic energy per molecule} = \frac{3}{2} \frac{R}{N} T$$

or $\boxed{\text{Average Kinetic Energy} = \frac{3}{2} KT}$ (7)

where , K = Boltzmann Constant

$$= \frac{R}{N} = \frac{8.314}{6.02 \times 10^{23}} = 1.38 \times 10^{-23} \text{ J deg}^{-1} \cdot \text{mole}^{-1}$$

or Average K.E \propto T

Thus, Average Kinetic Energy of every gas is directly proportional to the absolute temperature.

From equation (7) it is evident that average kinetic energy of all gases is the same at the same temperatures. From equation (7) we can write

$$T = \frac{2}{3} \frac{Av \cdot KE}{K}$$

It follows that at absolute zero, the Kinetic energy is zero i.e. the molecules cease to move at absolute zero of temperature.

6.4.4 EXPLANATION OF GAS LAWS IN THE LIGHT OF KINETIC MOLECULAR THEORY**1. Boyle's law :**

According to Kinetic molecular theory, the pressure of a gas is due to the collision of gas molecules on the walls of the containing vessel. The total force exerted by the molecules on the walls per unit area gives the pressure of the gas.

At constant temperature there is a definite no. of collisions made by the gas molecules on the walls of the containing vessel. If the volume of the container is increased the no. of collisions decrease since the molecules get more space for movement. So the pressure exerted by the gas decreases. On the other hand when the volume decreases the no. of collisions made on the walls increases and therefore pressure increases. Thus, keeping temperature constant the pressure and volume become inversely related. This is what is Boyle's law.

2. Charle's law :

According to Kinetic molecular theory the average kinetic energy is a direct measure of absolute temperature. So when temperature increases, the molecules gain kinetic energy. As a result the molecular velocity increases and the molecules strike the walls harder. Thus the pressure of the gas becomes more. So in order to keep the pressure constant, the volume has to increase. In other words it can be concluded that with increase of temperature there will be proportionate increase in volume if pressure is kept constant. This is how Charle's law can be explained.

3. Avogadro's law :

Consider equal volumes of two gases at the same temperature and pressure. The pressure of the gas depends upon two factors

- (i) The no. of molecules present per unit volume.
- (ii) Average kinetic energy

Since the temperature remains same, the average kinetic energy of two gases remains constant. The two gases are also having the same pressure. This is possible if they possess same no. of molecules. In otherwords it can be said that equal volumes of all gases at the same temperature and pressure contain equal no. of molecules. This is how Avogadro's law can be explained.

4. Dalton's law of Partial pressure :

According to Kinetic theory, the intermolecular forces of attraction are almost negligible in case of a gas. So if a mixture of chemically non-reacting gases is taken in a container, then their molecules do not exert any force of attraction on each other. The pressure of each gas (partial pressure) is due to hits recorded by its molecules on the walls of the container. Since the total pressure is due to the total no. of collisions made by the molecules of all the gases present we may conclude that the total pressure is the sum of the partial pressures. This is how Dalton's law can be explained.

6.4.5 DEDUCTION OF GAS LAWS FROM KINETIC GAS EQUATION

1. Boyle's Law :

The Kinetic gas equation is

$$PV = \frac{1}{3} mn \bar{C}^2 = \frac{2}{3} \times \frac{1}{2} mn \bar{C}^2$$

According to Kinetic molecular theory the average kinetic energy remains constant at constant temperature i.e. at constant temperature KE, $\frac{1}{2} m \bar{C}^2$ is constant.

Further, if a definite mass of gas is considered, the no. of molecules 'n' will remain unchanged and hence $\frac{1}{2} m n \bar{C}^2$ is constant at constant temperature.

So, $\frac{2}{3} \times \frac{1}{2} mn \bar{C}^2$ is a constant at constant temperature.

or, $PV = \text{Constant}$ (at constant temperature).

which is Boyle's law.

2. Charle's Law :

The Kinetic gas equation is

$$PV = \frac{1}{3} mn \bar{C}^2 = \frac{2}{3} \times \frac{1}{2} mn \bar{C}^2$$

$$\text{But } \frac{1}{2} m n \bar{C}^2 \propto T$$

$$\Rightarrow \frac{1}{2} m n \bar{C}^2 = K T, \text{ where } K = \text{Proportionality constant}$$

$$\text{So, } PV = \frac{2}{3} KT$$

If pressure is kept constant, the R.H.S of above equation (8) is constant

$\Rightarrow \frac{V}{T} = \text{Constant}$ at constant pressure, which is Charle's law.

3. Avogadro's law :

Let us consider two gases I and II

For gas I, the kinetic gas equation is $P_1 V_1 = \frac{1}{3} m_1 n_1 \bar{C}_1^2$

For gas II, the kinetic gas equation is $P_2 V_2 = \frac{1}{3} m_2 n_2 \bar{C}_2^2$

If the two gases are at the same pressure and they occupy the same volume

i.e. $P_1 = P_2$, and $V_1 = V_2$

$$\text{Then, } P_1 V_1 = P_2 V_2$$

$$\Rightarrow \frac{1}{3} m_1 n_1 \bar{C}_1^2 = \frac{1}{3} m_2 n_2 \bar{C}_2^2$$

$$\text{or, } \frac{2}{3} \times \frac{1}{2} m_1 n_1 \bar{C}_1^2 = \frac{2}{3} \times \frac{1}{2} m_2 n_2 \bar{C}_2^2$$

$$\text{or, } \frac{1}{2} m_1 n_1 \bar{C}_1^2 = \frac{1}{2} m_2 n_2 \bar{C}_2^2 \dots \dots \dots (9)$$

If both the gases are at same temperature, then mean K.E. of both the gases are same.

$$\text{i.e. } \frac{1}{2} m_1 \bar{C}_1^2 = \frac{1}{2} m_2 \bar{C}_2^2 \dots\dots\dots(10)$$

From equation (9) and (10) we can write

$$\boxed{n_1 = n_2}$$

i.e. the no. of molecules of Gas I = No. of molecules of Gas II

This is how Avogadro's law can be derived.

4. Dalton's law of Partial pressure :

Partial pressure of a gas is defined as the pressure exerted by it when it occupies the whole volume of the container at that temperature.

$$\begin{aligned} \text{The kinetic gas equation is } PV &= \frac{1}{3} m \bar{C}^2 \\ &= \frac{2}{3} \times \frac{1}{2} m n \bar{C}^2 \\ &= \frac{2}{3} \text{ K.E} \quad (\therefore \frac{1}{2} m n \bar{C}^2 = \text{K.E}) \end{aligned}$$

$$\text{or Kinetic energy} = \frac{3}{2} PV$$

If a number of gases are under consideration then the total kinetic energy of the gaseous mixture must be equal to the sum of kinetic energy of individual gases.

i.e. For a gaseous mixture –

$$(KE)_{\text{Total}} = (KE)_1 + (KE)_2 + (KE)_3 + \dots\dots\dots$$

where $(KE)_1, (KE)_2, (KE)_3$ are the kinetic energies of individual gases 1, 2, 3..... respectively.

$$\text{or, } \frac{3}{2} PV = \frac{3}{2} P_1 V + \frac{3}{2} P_2 V + \frac{3}{2} P_3 V + \dots\dots\dots$$

Where P_1, P_2, P_3 are the Partial pressures of gases 1, 2, 3.....respectively.

$$\text{or, } \frac{3}{2} PV = \frac{3}{2} V (P_1 + P_2 + P_3 + \dots\dots\dots)$$

$$\text{or, } \boxed{P = P_1 + P_2 + P_3 \dots\dots\dots} \text{ This is Dalton's law of partial pressure.}$$

5. Graham's law of diffusion :

$$\text{The kinetic gas equation is } PV = \frac{1}{3} m \bar{C}^2 = \frac{1}{3} M \bar{C}^2$$

where, M = mass of 'n' number of molecules

m = mass of individual molecule

$$\text{or, } \bar{c}^2 = \frac{3PV}{M} = \frac{3P}{M/V} = \frac{3P}{d} \quad \text{Where } d = \text{Density of gas}$$

$$\text{or, } \bar{c}^2 \propto \frac{1}{d} \text{ at constant pressure}$$

$$\bar{c} \propto \frac{1}{\sqrt{d}} \text{ at constant pressure}$$

But root mean square velocity $\bar{c} \approx \text{Mean velocity } 'C'$

$$\therefore C \propto \frac{1}{\sqrt{d}} \text{ at constant pressure} \dots\dots\dots(11)$$

The rate of diffusion of gas evidently depends upon the velocity of the molecules.

$$\text{i.e. } r \propto 'C' \dots \dots \dots \quad (12)$$

From equations (11) and (12), we have

$r \propto \frac{1}{\sqrt{d}}$ which is Graham's law of diffusion.

6. Combined gas law (Gas equation) :

$$\begin{aligned}
 \text{The kinetic gas equation is } PV &= \frac{1}{3} mn \bar{c}^2 \\
 &= \frac{2}{3} \times \frac{1}{2} mn \bar{c}^2 \\
 &= \frac{2}{3} KT \quad (\Theta = \frac{1}{2} mn \bar{c}^2 \propto T) \\
 \text{or } \boxed{\frac{PV}{T} = \frac{2}{3} K \text{ (a constant)}} \rightarrow \text{ Combined Gas law.}
 \end{aligned}$$

For 1 gm molecule of the ideal gas, this constant is denoted by R (Universal gas constant)

$$\therefore \frac{PV}{T} = R$$

$$\text{or, } PV = RT$$

For 'n' moles of an ideal gas,

$PV = nRT$ → Ideal gas equation.

6.4.6 | MOLECULAR VELOCITIES AND THEIR CALCULATION

There are three types of molecular velocities.

(i) Most Probable Velocity (C_p) :

The velocity possessed by the maximum fraction of molecules of a gas at a particular temperature is known as most probable velocity (C_p).

(ii) Average Velocity (C_a) :

The arithmetic mean of different velocities of molecules present in a given sample of gas at a particular temperature represents the average velocity (C_a).

Suppose there are 'n' number of molecules having velocities $V_1, V_2, V_3, \dots, V_n$.

The average velocity , $C_a = \frac{V_1 + V_2 + V_3 + \dots + V_n}{n}$

(iii) Root mean square Velocity (C_r or \bar{C}) :

The square root of the mean value of the square of velocities of the molecules in a given sample of gas at a particular temperature represents the root mean square velocity or RMS velocity.

$$\bar{C} = \sqrt{\frac{V_1^2 + V_2^2 + \dots + V_n^2}{n}}$$

where V_1, V_2, \dots, V_n are the individual molecular velocities.

Calculation of RMS Velocity :

$$\text{The Kinetic gas equation is } PV = \frac{1}{3} mn \bar{C}^2$$

$$\text{or, } \bar{C}^2 = \frac{3PV}{mn}$$

$$\text{or, } \bar{C} = \sqrt{\frac{3PV}{mn}}$$

If we consider one mole of the gas, the number of molecules involved will be N (ie. Avogadro's number)

So, for 1 mole of the gas $n = N$

and $mN = M$ = Molecular mass of the gas

$$\therefore \bar{C} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{D}} \quad \text{where } D \rightarrow \text{ Density of the gas.}$$

$$\text{From detailed calculation, } C_a = \sqrt{\frac{8RT}{\pi M}} \quad \text{and} \quad C_p = \sqrt{\frac{2RT}{M}}$$

Relationship between various types of velocities :

Average velocity (C_a) = $0.9213 \times$ RMS velocity (C_r or \bar{C})

Most probable velocity (C_p) = $0.8164 \times$ RMS velocity

From the above relation, the ratio of three kinds of velocities

$$C_p : C_a : \bar{C} = 1 : 1.128 : 1.224$$

NUMERICAL PROBLEMS

Example 1. Calculate the average velocity of oxygen molecule at 27°C .

$$\begin{aligned} \text{Solution : We know } \bar{C} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}} \quad (\Theta T = 27 + 273 = 300 \text{ K} \\ &\quad \text{and } M = 32 \text{ for Oxygen}) \\ &= 4.835 \times 10^4 \text{ cm/sec.} \end{aligned}$$

$$\begin{aligned} \text{Average Velocity} &= (0.9213 \times 4.835 \times 10^4) \text{ cm/sec} \\ &= 44544.8 \text{ cm sec}^{-1}. \end{aligned}$$

Example 2. Calculate the average velocity of hydrogen at NTP.

$$\begin{aligned}
 \text{Solution : } \bar{c} &= \sqrt{\frac{3RT}{M}} \\
 &= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 273}{2}} = 18.45 \times 10^4 \text{ cm/sec.} \\
 \text{Average velocity} &= 0.9213 \times 18.45 \times 10^4 = 169979.85 \text{ cm/sec.}
 \end{aligned}$$

Example 3. Calculate the RMS velocity of nitrogen at 30°C and 75cm pressure.

Solution :

Given condition	at NTP
$P_1 = 75 \text{ cm}$	$P_2 = 76 \text{ cm}$
$V_1 = ?$	$V_2 = 22,400 \text{ ml}$
$T_1 = 30 + 273 = 303 \text{ K}$	$T_2 = 273 \text{ K}$

$$\begin{aligned}
 \text{We know that } \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\
 \Rightarrow V_1 &= \frac{P_2 V_2 T_1}{P_1 T_2} = \frac{76 \times 22,400 \times 303}{75 \times 273} = 25193.02 \text{ ml} \\
 \text{RMS velocity } \bar{c} &= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 75 \times 13.6 \times 981 \times 25193.02}{28}} \\
 &= 51978.64 \text{ cm/sec.}
 \end{aligned}$$

$$[\Theta P = 75 \text{ cm} = (75 \times 13.6 \times 981) \text{ dynes / cm}^2.]$$

Example 4. At what temperature will the RMS velocity of hydrogen be the same as that of oxygen at 30°C ?

Solution :

Let the RMS velocities of hydrogen and oxygen be \bar{c}_1 & \bar{c}_2 respectively

$$\bar{c}_1 = \sqrt{\frac{3RT_1}{M_1}}, \quad \bar{c}_2 = \sqrt{\frac{3RT_2}{M_2}}$$

$$\text{When } \bar{c}_1 = \bar{c}_2$$

$$\text{or } \sqrt{\frac{3RT_1}{M_1}} = \sqrt{\frac{3RT_2}{M_2}}$$

$$\text{or } \frac{T_1}{M_1} = \frac{T_2}{M_2}$$

$$M_1 = \text{molecular mass of hydrogen} = 2$$

$$M_2 = \text{molecular mass of oxygen} = 32$$

$$T_1 = ?$$

$$T_2 = 30 + 273 = 303 \text{ K}$$

$$\text{So, } \frac{T_1}{2} = \frac{303}{32}$$

$$\text{or } T_1 = \frac{303 \times 2}{32} = 18.93 \text{ K.}$$

$$= 18.93 - 273 = -254.07^\circ\text{C.}$$

Example 5.

The density of H_2 at 0°C and 760 mm pressure is 0.00009 gms/ml. Find the RMS velocity of H_2 molecule.

Solution :

We know that

$$\bar{c} = \sqrt{\frac{3P}{D}}, P = 760 \text{ mm} = 76 \text{ cm} (76 \times 13.6 \times 981) \text{ dyne/cm}^2$$

$$\bar{c} = \sqrt{\frac{76 \times 13.6 \times 981 \times 3}{0.00009}} = 183,100 \text{ cm/sec.}$$

BEHAVIOUR OF REAL GASES**What is an ideal gas ?**

A perfect or an ideal gas is one which obeys the gas laws i.e. Boyle's law, Charle's law etc for all values of temperature and pressure. In other words. a gas that obeys the equation of state $PV = nRT$ is said to be an ideal gas since both the gas laws are contained in it . The chief characteristics of an ideal gas are as follows :

- (i) If PV is plotted against ' P ' at constant temperature, a straight line is obtained which is parallel to the pressure axis. This shows that the product of P and V at constant temperature for a given mass of gas is constant.
- (ii) One mole of the gas at NTP occupies 22.4 litres.
- (iii) The volume of a given mass of gas decreases uniformly with decrease in temperature at constant pressure. At -273°C , the volume becomes zero.

DEVIATION OF REAL GASES

In actual practice no gas is 100 % ideal or perfect. The word ideal is purely hypothetical. Careful experiments have shown that the real gases obey the ideal gas equation only approximately, particularly when the **pressure is low** and the **temperature is high**. The higher the pressure and lower the temperature the more will be the deviation from ideal behaviour.

With a view to explaining the deviation of real gases from ideal behaviour, scientists like Regnault, Rayleigh, Amagat had studied the effect of change of pressure on PV of several gases at 0°C .

Deviation from gas laws :

(i) Deviation from Boyle's law

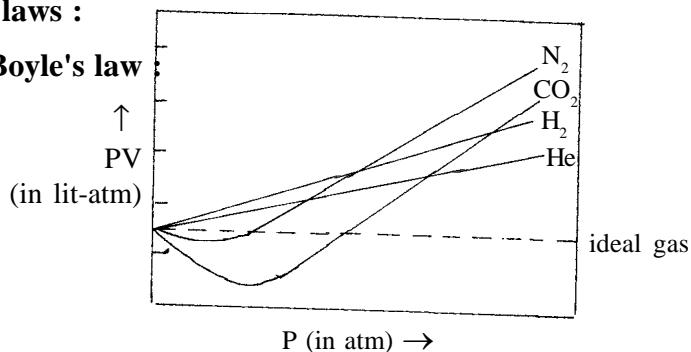


Fig 6.8 Plot of PV against P

From the above graph it can be seen that for H_2 and He there is continuous rise of PV value with increase of pressure. For N_2 and CO_2 , PV value gradually decreases, passes through a minimum and then continuously rise with increase in pressure. In other words for N_2 and CO_2 at low pressure the PV value decreases from that of ideal gases, but at high pressure there will be marked deviation from ideal behaviour.

The horizontal dotted line is for an ideal gas. If the gases behave ideally i.e. if Boyle's law is obeyed then the value of PV would remain constant over all ranges of pressure and the curves for CO_2 , N_2 , etc. would be straight horizontal lines.

Thus PV – P plots for several gases give us an indication about the deviation of real gases from Boyle's law i.e. from ideal behaviour.

(ii) Deviation from Charle's law :

According to Charle's law the volume of a given mass of gas increases or decreases by $\frac{1}{273}$ of its value at constant pressure and at $0^\circ C$ for each one degree rise or fall in temperature. In other words the coefficient of increase or decrease in volume should be $\frac{1}{273}$ for almost all gases. But in actual practice this is a fact only at low pressure. As the pressure increases there will be marked deviation.

The deviation of real gases from Charle's law was successfully explained by scientists like Amagat and others.

(iii) Deviation from Avogadro's law :

According to Avogadro's law the volume occupied by 1 mole of an ideal gas should be 22.4 litres. But in actual practice it has been found that the volume occupied by 1 mole of different gases is not exactly 22.4 litres but deviate from that.

TABLE 6.3

Gas	Gram molecular volume at NTP. (in litres)
1. H_2	22.427
2. O_2	22.393
3. N_2	22.401
4. NH_3	22.084

Effect of temperature on deviation from ideal behaviour :

The following figure depicts the PV-P plots of N₂ at various temperature. It is quite evident that with the increase of temperature the dip in the curves gradually diminish and at high

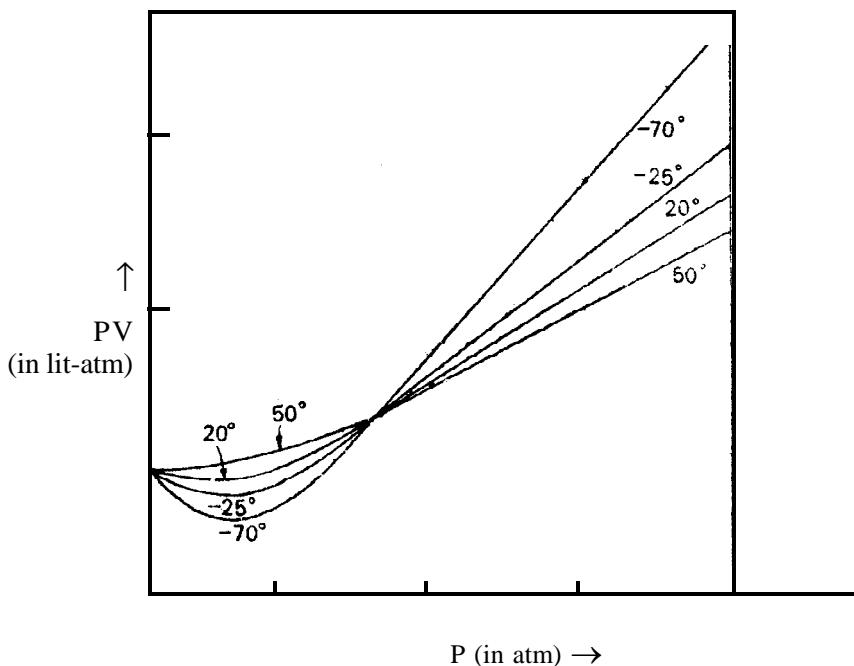


Fig 6.9 PV - P Plot of N₂ at various temperature

temperature the curves almost become straight approaching the ideal behaviour. For N₂ at 50° the curve becomes almost horizontal for an appreciable change of pressure. This temperature is called the Boyle Temperature for N₂.

From the above discussion we may come to a conclusion that the real gases behave ideally only approximately that too under conditions of **low pressure and high temperature**.

It has been found that easily liquefiable and highly soluble gases show larger deviation. So, gases like CO₂, SO₂ and NH₃ show larger deviations than H₂, N₂, O₂ etc.

Compressibility factor (Z) and deviation

Compressibility factor (Z) is defined as

$$Z = \frac{PV}{(PV)_{\text{ideal}}} = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

where V_m is the molar volume ie volume occupied by 1 mole of the gas = $\left(\frac{V}{n}\right)$.

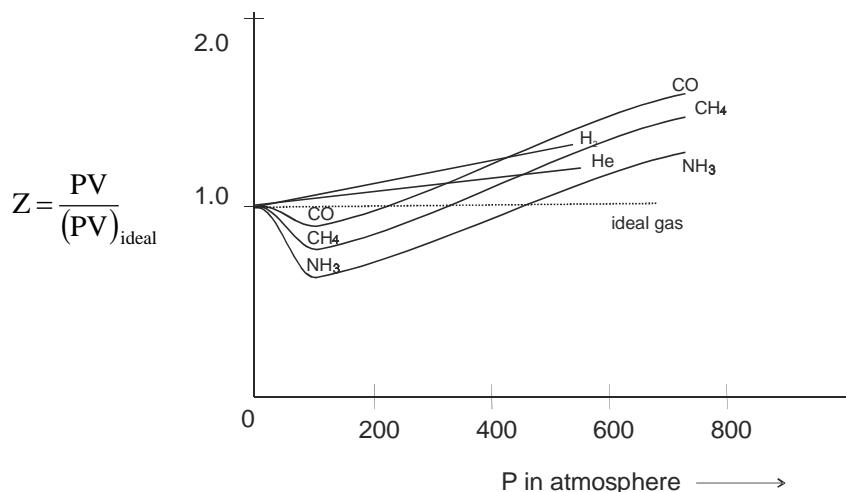
Z = 1, for an ideal gas under all conditions of temperature and pressure (Since $\frac{PV}{nRT} = 1$).

So, PV = nRT which is equation of state for 'n' moles of an ideal gas)

The deviation of Z from unity is thus a measure of imperfection of the gas under consideration. Thus, compressibility factor successfully explains the deviation of real gases from ideal behaviour.

Effect of change of Pressure on deviation

The compressibility factors are determined for a number of gases over a wide range of pressures at a constant temperature i.e. 0°C . A graph plotted between compressibility factors and pressures is shown below (Fig. 6.10)



(Fig : 6.10)

- (i) At extremely low pressure 'Z' is very close to unity which indicates that all gases behave almost ideally.
- (ii) At very high pressure 'Z' is more than unity which indicates that the gases are less compressible than the ideal gas. This is due to dominance of molecular repulsive forces.
- (iii) At moderately low pressure the gases are more compressible than the ideal gas. PV is less than PV_{ideal} and $Z < 1$. This is due to dominance of long range attractive forces at low pressure which favour compression.

The value of 'Z' goes on decreasing with increase in pressure, passes through the minimum and then begins to increase with further increase in pressure.

(iv) For H_2 and He , $Z > 1$. These gases are seen to be less compressible than ideal gas at all pressure and at 0°C . However, if the temperature is sufficiently low (i.e. below -165°C for H_2 and below -240°C for He) then same type of $Z - P$ plots are shown by both these gases as for other gases.

On the other hand, if the temperature is sufficiently high then other gases show $Z - P$ plots similar to those given by H_2 and He .

CAUSES FOR THE DEVIATION

A simple and logical explanation for these deviation was given by a Dutch scientist vanderWaals. He pointed out two faulty assumptions of kinetic theory of gases.

1. The actual volume of the molecule is negligible compared to the total volume of the gas.

vanderWaals, showed that this assumption is valid so long as the pressure is low and temperature is high. However the assumption does not hold good at high pressure. When pressure

is too high, the volume of the gas decreases to an appreciable amount. But as the molecules are treated as incompressible, the volume of the molecule is not affected. And under such condition the volume of the molecule cannot be neglected compared to the total volume of the gas. The same thing happens for lowering of temperature.

2. The intermolecular forces of attraction are almost negligible in case of gases.

This is another faulty assumption of kinetic theory of gases that vanderWaals could point out. According to vanderWaals, the above assumption holds good only at low pressure and high temperature. If the pressure becomes sufficiently high the volume occupied by the given amount of gas becomes low and as a result a definite number of gas molecules will be confined within a small volume. Under such condition the molecules come closer to each other and hence the molecular forces of attraction between them cannot be completely ignored.

At low temperature also the velocity of gas molecule decreases as a result of which each molecule exerts appreciable attractive force on the other.

Thus vanderWaals gave satisfactory explanation for the deviation of real gases from ideal behaviour.

6.4.7 EQUATION OF STATE FOR REAL GASES

To explain the behaviour of real gases a number of equations have been suggested by various scientists. But the best one amongst all is the equation suggested by vanderWaals.

vanderWaals' Equation of state :

vanderWaals deduced a modified equation of state for real gases by just introducing two correction factors, one for volume and other for pressure into the ideal gas equation in order to rectify the error for neglecting (i) the intermolecular forces of attraction (ii) individual molecular volume.

(a) Volume Correction :

Consider the motion of the gas molecule 'A' in a closed space CDEF having volume 'V'.

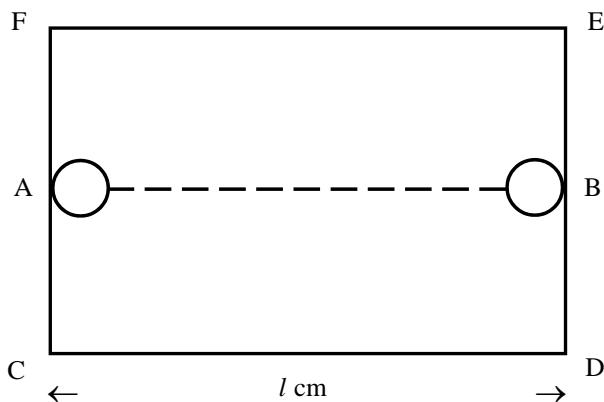


Fig : 6.11 Motion of a particle in a closed space

Let $l \text{ cm} \rightarrow$ Length of side CD

The molecule 'A' moves along a straight line parallel to CD and strike the face ED at B. As the molecule is perfectly elastic it will come back to its original position after striking the face. Now the distance traversed by the molecule is not ' $2l$ ' but $(2l-d)$ where 'd' is the diameter of the molecule.

If the motion of all the particles present in the container is considered in a similar way, we will find that the actual volume available for the movement of molecules is less than the original volume.

According to kinetic molecular theory the molecules are nothing but point masses. They occupy no volume and move in the free space equal to volume 'V' of the container. But at high pressure the volume occupied by the molecules becomes a considerable fraction of the total volume occupied by the gas and hence can no longer be neglected. Under such condition the molecules are assumed to have finite size. The space occupied by a molecule at a given instant will not be available to other molecules at the same instant for movement. Thus each molecule excludes certain volume for the movement of other molecules.

Since molecules are considered to be noncompressible and spherical particles of radius 'r' (say) the closest approach of two molecules may be represented as given below in figure 6.12.

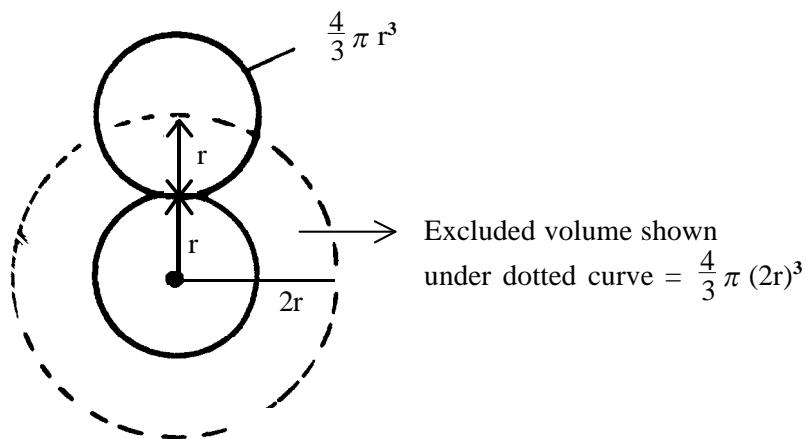


Fig 6.12 Closest approach of two molecule

The upper molecule excludes a volume of $\frac{4}{3} \pi (2r)^3$ i.e. $8 \times \frac{4}{3} \pi r^3$ to the lower molecule for movement. The lower molecule excludes a volume of $8 \times \frac{4}{3} \pi r^3$ to the upper molecule for movement. The two molecules mutually exclude $8 \times \frac{4}{3} \pi r^3$ volume for the movement of each other. So the excluded volume for each molecule will be $4 \times \frac{4}{3} \pi r^3$ i.e 4 times its molecular volume.

The excluded volume per mole of gas = $4N (\frac{4}{3} \pi r^3) = 'b'$ (vanderWaals' constant)

It can be concluded that the actual free space available for movement of the molecules is not 'V' but something less than 'V'. vander Waal suggested a correction factor 'b' for 1 mole of gas where 'b' is called the excluded volume or co-volume.

$$\begin{aligned}\therefore \text{Ideal volume} &= \text{Actual volume} - b \\ &= (V-b) \text{ per mole of gas}\end{aligned}$$

Thus in the ideal gas equation we will write $(V-b)$ in place of ' V ' for real gases.

(b) Pressure correction

Another faulty assumption in Kinetic theory of gases is the absence of intermolecular force of attraction. Forces of attraction between the molecules, however weak, are always present. This is much pronounced particularly when the pressure is made high or volume small i.e. when the molecules are brought closer to each other.

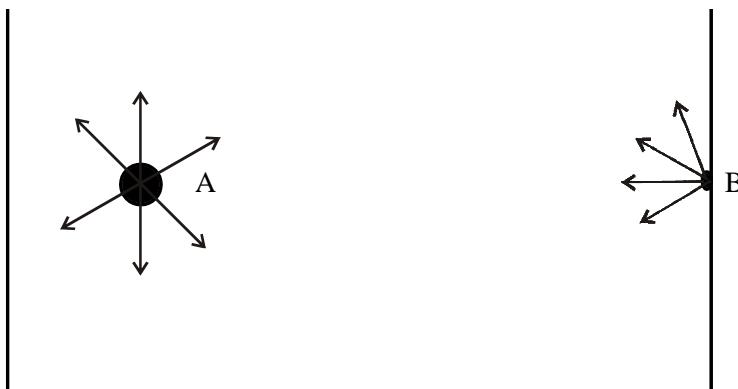


Fig 6.13 Pressure correction

Consider a molecule 'A' lying somewhere inside the vessel. The net force of attraction on this molecule is zero. This is because this molecule is uniformly attracted from all sides by the other molecules present in the neighbourhood. As a result the forces of attraction on this molecule mutually neutralise each other.

However, the molecule 'B' which is about to strike the wall of the vessel is subjected to an inward pull from the bulk of the molecules. Hence the molecule strikes the wall with a low velocity and will exert a low pressure. The observed pressure is thus less than the ideal pressure. It becomes necessary, therefore, to add a certain quantity to the observed pressure ' P ' of the gas in order to get the ideal pressure. vander Waal introduced a correction factor ' p ' for pressure.

Thus, the corrected pressure = $(P + p)$

$$\begin{aligned}\text{i.e. Ideal Pressure} &= \text{observed pressure} + \text{pressure correction factor} \\ &= (P + p)\end{aligned}$$

Now two things are to be noted :

- (i) The inward pull which molecule 'B' experiences depends upon the number of molecules per unit volume ie. directly upon density of the gas.

- (ii) The number of molecules which are about to strike the wall also depends upon the density of the gas.

Thus the correction factor for pressure 'p' which is a direct consequence of the inward pull is proportional to the square of density of the gas.

$$\text{i.e. } p \propto d^2$$

$$\text{or, } p \propto \frac{1}{V^2} \quad (\Theta \text{ density} = \frac{\text{mass}}{\text{volume}})$$

$$\text{or, } p = \frac{a}{V^2}$$

where, $a =$ constant depending upon the nature of the gas — It is known as **vander Waal constant**.

$$\text{Hence, Ideal pressure} = (P + \frac{a}{V^2})$$

Incorporating necessary corrections for volume and pressure in the ideal gas equation we get

$$(P + \frac{a}{V^2})(V - b) = RT \quad \dots \dots \dots \quad (1)$$

This is vanderWaals' equation of state for 1 mole of real gas.

van derWaals' Equation of state for 'n' moles of real gas :

If 'n' moles of gas occupy the volume 'V', the free space available for their movement will be $(V - nb)$, where $nb \rightarrow$ excluded volume.

$$\text{Again, } p \propto n^2 d^2$$

$$\text{or, } p \propto \frac{n^2}{V^2}$$

$$\text{or, } p = \frac{an^2}{V^2}$$

Thus, van der Waals' equation of state for 'n' moles of the gas will be

$$(P + \frac{an^2}{V^2})(V - nb) = nRT \quad \dots \dots \dots \quad (2)$$

van der Waals' Constant

- (i) The constant 'a' is related to the intermolecular attractive forces. More the value of 'a', more is the strength of molecular interaction. If for a gas the value of 'a' is more, then the gas can liquify easily. This is due to greater attractive force operating between the molecules.

$$\text{We know that } p \text{ (pressure correction)} = \frac{an^2}{V^2}$$

$$\Rightarrow a = \frac{p \times v^2}{n^2} = \frac{\text{Pressure} \times (\text{volume})^2}{(\text{no. of moles})^2}$$

Thus, the unit of 'a' is atm. lit.² mole⁻²

- (ii) The constant 'b' is related to size of the molecule. Larger the size of the molecule larger is the value of 'b'.

'b' is incompressible or excluded volume per mole of the gas. Therefore, it has same unit as volume i.e. **lit. mole⁻¹**

EXPLANATION OF REAL GAS BEHAVIOUR ON THE BASIS OF VAN DER WAALS' EQUATION

The deviation of real gases from ideal gas behaviour at various ranges of temperature and pressure can be explained on the basis of van der Waals' equation.

(i) At low pressure :

The vanderWaals' equation for 1 mole of real gas is

$$(P + \frac{a}{V^2}) (V - b) = RT$$

When pressure is low, volume is sufficiently large. Then the term 'b' can be neglected as compared to 'V' in the above expression. Thus, we have

$$(P + \frac{a}{V^2}) V = RT$$

$$\text{or, } PV + \frac{a}{V} = RT$$

$$\text{or, } PV = RT - \frac{a}{V} \quad \dots \dots \dots \quad (3)$$

i.e. PV is less than RT by an amount $\frac{a}{V}$. In the fig.1.8 from the graph it is found that actually at low pressure PV is having a lower value than 'RT'. As pressure increases volume will decrease, so $\frac{a}{V}$ will increase. Thus PV value will become less and less with increase of pressure. The dip in the curve for N₂ and CO₂ can thus be explained.

(ii) At high pressure :

When the pressure is made high, the volume is small. Under such condition 'b' cannot be neglected compared to V. However, $\frac{a}{V^2}$ is neglected compared to pressure P. Hence equation of state can be written as : $P(V-b) = RT$

i.e the value of PV is greater than RT by an amount ' P_b '. Now it can be realised why after reaching a minima the PV value continuously increases with increase in pressure.

(iii) At high temperature :

When the temperature is high, the volume 'V' is large. Thus both the terms $\frac{a}{V^2}$ and 'b' can be neglected. Under such condition $PV = RT$ i.e. the gases behave ideally.

(iv) Exceptional behaviour of hydrogen and helium :

The mass of the molecules of such gases have small values. Consequently the forces of attraction between the molecules are negligible.

The correction factor $\frac{a}{V^2}$ is thus neglected. The equation reduces to the form.

$$PV = RT + Pb$$

This explains why the value of PV will continuously rise with increase of pressure in case of these two gases.

6.4.8 MAXWELL'S LAW OF DISTRIBUTION OF MOLECULAR VELOCITIES

1. Random movement of gas molecules :

In a gas assembly the molecules are always in a state of constant rapid motion in all possible directions with different molecular velocities. During their motion they collide amongst themselves and with the walls of the container. As a result, their direction of motion is changed, so also their velocities. Thus the variation of velocity of gas molecules is due to collision amongst themselves.

Let us consider two molecules A and B having the same velocity 'c' but moving in opposite directions. When they collide with each other, the velocity of both the molecules will become zero. But when they collide with each other at right angles (Fig.6.14) 'A' will be brought to rest while 'B' will move off with a velocity $\sqrt{2} c$ in a direction inclined at 45° to the original direction of motion.

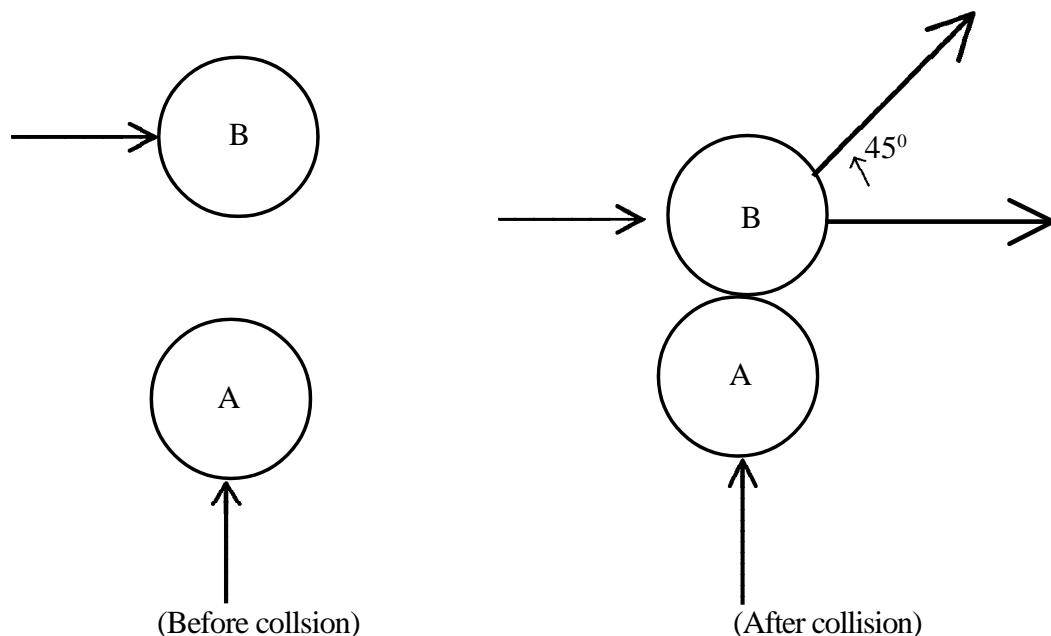


Fig 6.14 Collision among molecules

As a result of further collisions with other molecules present in the gas, 'A' will acquire momentum and begin to move again whereas 'B' will either lose or gain momentum depending upon the nature of subsequent impacts.

A gas contains a large number of molecules out of which only a few molecules have either low or high velocities but majority of molecules have an average velocity. The zig-zag motion of molecules in all directions with different velocities gives rise to random movement of molecules.

(2) Distribution of velocity :

From the above discussion it is very much clear that as a result of impacts, all the molecules of a gas cannot have same velocity. It is also interesting to know how between the molecules the velocities are distributed when a steady state is reached.

Distribution of velocity thus refers to steady state of the molecules. By steady state we do not mean that the velocity of individual molecule remains unaltered but rather the distribution of velocity remains unchanged.

The concept of distribution of molecular velocities between the molecules was first of all suggested by Maxwell. He worked out the same by simply applying probability considerations.

Assumptions made by Maxwell :

- The number of molecules per unit volume at any point is the same.
- The molecules are in chaotic motion even in a small volume. Distribution of velocity would equally apply to them. So far as molecular velocity is concerned isotropic (no change in physical properties) behaviour is assumed.
- The velocities of individual molecule are changing continuously but at any instant the fraction of total no. of molecules, possessing a given velocity, remains unaltered. This is sometimes referred to as **steady state** of the gas.

Basing on the above assumptions and applying probability considerations Maxwell showed that distribution of molecular velocity is given by the following expression :-

$$\frac{dn_c}{n} = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{Mc^2}{2RT}} c^2 dc \quad (1)$$

where dn_c = The number of molecules having velocities between c and $(c+dc)$

n = Total number of molecules

M =Molecular mass of the gas.

T = Temperature in the absolute scale.

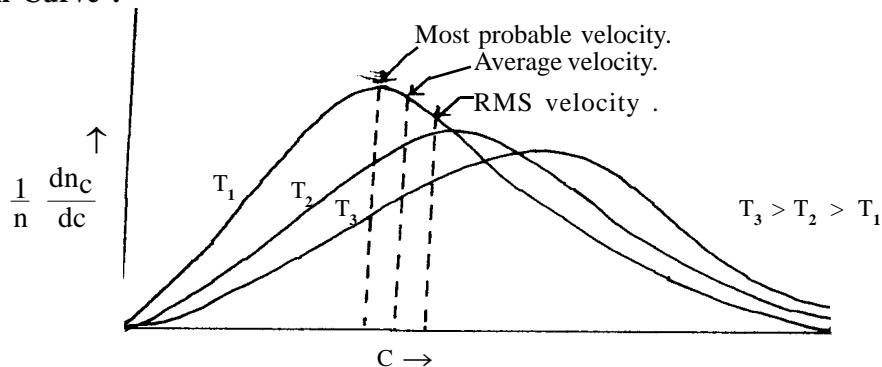
$\frac{dn_c}{n}$ Fraction of total number of molecules having velocity within the range c and $(c+dc)$

The above equation may be rewritten as :

$$\frac{1}{n} \frac{dn_c}{n} = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{Mc^2}{2RT}} c^2 \quad (2)$$

This is the usual form of Maxwell's law of distribution of velocities.

The left hand side of the above expression simply represents the probability of finding the fraction of molecules having velocity ' c '. If molecular mass of any gas is known, it is possible to calculate the fraction of molecules having any particular velocity ' c ' at any desired temperature.

Distribution Curve :**Fig 6.15 Maxwell's distribution of velocities**

For a given gas, the theoretical curves can be drawn at various temperatures by plotting $\frac{1}{n} \frac{dn_c}{dc}$ against 'c'. Three curves are drawn at various temperature T_1 , T_2 and T_3 in the above figure.

Nature of distribution curves :

An examination of above curves reveals the following :

- From the nature of the curve, it follows that the total molecules having velocity greater than zero goes on increasing, attains a maximum value and then again starts to fall towards zero for very high velocities.
- The fraction of the molecules having very small velocities ($c \rightarrow 0$) or very high velocities ($c \rightarrow \infty$) is practically zero
- The curve at one particular temperature has a maximum. The velocity corresponding to this maximum represents the speed possessed by majority number of molecules. This velocity is called the most probable velocity. We may represent this velocity by (C_p). Thus most probable velocity of a gas is defined as the velocity possessed by maximum number of molecules of gas at a given temperature.
- The areas under different curves drawn at different temperatures are the same because the area represents the total number of molecules.

Effect of Temperature on distribution of molecular velocities :

With variation of temperature, separate curves are obtained for every temperature (see Fig. 6.15) At high temperature there will be wider distribution of velocities. That is the no. of molecules having high speed is increased. The maxima, therefore, shifts to the right and becomes flattened. The value of most probable velocity also increases with increase in temperature. Thus the effect of temperature on the distribution of molecular velocities can be well explained by the graph.

The effect can also be well understood from the equation.(2) In this equation there is an exponential term $e^{-MC^2/2RT}$. Here 'e' is raised to a -ve power and T is in the denominator. If we raise the temperature the value of exponential term simply increases. Thus the fraction of molecules in the curve having high velocity increases.

LIQUEFACTION OF GASES

Increase of pressure and decrease of temperature are the main causes of liquefaction of a gas.

In a gas, the molecules are far apart from each other and are always in a state of constant rapid motion. The molecules have independent existence particularly when the pressure is low and temperature is high.

As the temperature decreases, the kinetic energy of gas molecules decreases. Also there is decrease in volume occupied by the gas. At a sufficiently low temperature the slow moving molecules come closer under forces of attraction and ultimately the gas is converted to liquid.

Again, as the pressure increases there is decrease in volume. The molecules of the gas come closer to each other. This becomes an additional helpful factor in changing the gas into liquid. For example, SO_2 can be liquefied at -8°C if the pressure is 1 atm.

From the concept of critical temperature it can be concluded that the gas is to be necessarily cooled below its critical temperature before it can be liquefied. Gases like NH_3 , SO_2 , CO_2 etc are gases which have fairly high critical temperature. Hence these gases can be easily liquefied only upon application of pressure. But gases like H_2 , O_2 , He , N_2 etc have very low value of critical temperature. Hence they can not be liquefied by this simple technique. These gases are to be cooled below their critical temperature before they are compressed to get liquefied.

There are two principles which are applied in cooling the gases below their critical temperature.

1. Joule-Thomson effect

According to Joule and Thomson, when a gas at certain pressure is allowed to expand adiabatically to a region of low pressure through a porous plug its temperature falls and the phenomenon is known as **Joule - Thomson effect**.

In a gas the molecules are held together by cohesive or attractive forces. When a gas expands the molecules fall apart from each other. So work has to be done with a view to overcoming the attractive forces operating between the molecules. Since the process is adiabatic, no heat is allowed to enter nor to leave the system. Hence work is done in this case at the expense of kinetic energy of gas molecules, Consequently, kinetic energy decreases and again since average kinetic energy is a direct measure of absolute temperature, the temperature of the gas decreases and cooling effect is caused.

It has been found from the experiment that the gases can be cooled by Joule-Thomson effect provided they are below a certain temperature known as **Inversion temperature** ' T_i '. Inversion temperature is characteristic of each gas which is related to vanderWaals constants 'a' and 'b' by the expression.

$$T_i = \frac{2a}{Rb}$$

2. Adiabatic expansion involving mechanical work

During the expansion of gas against a pressure as in case of an engine, it does some external work. This work is at the expense of its kinetic energy which decreases and consequently there is a fall in temperature.

Critical Temperature (T_c)

The critical temperature of a gas (T_c) is defined as the temperature above which the gas can not be liquefied however higher the pressure may be. For example, the critical temperature of CO₂ is 31.1°C. This means that CO₂ can not be liquefied by any means above 31.1°C. The critical temperatures of O₂ and H₂ are -118°C and -240°C respectively.

CHAPTER (6) AT A GLANCE

1. Expansibility, compressibility and diffusion are three important properties of a gas.
2. Mass, volume, pressure and temperature are the measurable properties of a gas.
3. **Boyle's law :-** Temperature remaining constant the volume of a given mass of any gas is inversely proportional to pressure.
4. **Charle's law :-** Pressure remaining constant the volume of a given mass of gas increases or decreases by $\frac{1}{273}$ of its value at 0°C for each 1°C rise or fall in temperature.
5. **Absolute Zero of Temperature :-** The temperature at which the gas ceases to exist i.e at which the volume of the gas becomes Zero. It is -273°C.
6. **Gay - Lussac's law :-** At constant volume, the pressure of the given mass of gas is directly proportional to its absolute temperature.
7. **STP - or NTP** (Standard Temp and Pressure) standard temp = 0°C = 273K, standard Press = 1 atm. = 760 mm Hg.
8. **Ideal gas equation** PV = n RT.
9. **Value of R :-**
 - (a) 0.0821 lit atm deg⁻¹ mole⁻¹.
 - (b) 82.1 cm³ atm K⁻¹ mole⁻¹.
 - (c) 62.39 lit mm K⁻¹ mole⁻¹.
 - (d) 8.31×10^7 ergs K⁻¹ mole⁻¹.
 - (e) 8.31 JK⁻¹ mole⁻¹.
 - (f) 1.99 Cal K⁻¹ mole⁻¹.
 - (g) 8.31 Nm K⁻¹ mole⁻¹.
 - (h) 8.31 Pa m³ K⁻¹ mole⁻¹.
 - (i) 8.31 K Pa dm³ K⁻¹ mole⁻¹.
10. **Dalton's law of Partial Pressure :-** The total pressure exerted by a mixture of chemically not reacting gases is equal to sum of partial pressures of individual gases.

QUESTIONS**A. Multiple choice type questions with answers (1 mark)**

1. For one mole of gas the total Kinetic energy at temperature T is equal to
(a) RT (b) $\frac{3}{2}RT$, (c) $\frac{2}{3}RT$ (d) $(C_p - C_v)RT$.
2. For a given mass of gas if pressure is reduced to half and the temperature is doubled, the volume will become
(a) $4V$ (b) $2V$ (c) $\frac{V}{4}$ (d) $8V$
3. The value of universal gas constant in litre atmosphere per degree per mole is
(a) 8.200 (b) 8.020 (c) 1.987 (d) 0.082
4. Volume of 20 grams of hydrogen gas at NTP is
(a) 224 litres (b) 22.4 litres (c) 2.24 litres (d) 112 litres
5. 1cc at NTP of a hydrocarbon vapour is as heavy as 4cc of oxygen. What quantity of hydrocarbon will occupy a volume of 22.4 litres ?
(a) 6.4 (b) 32 (c) 128 (d) 64
6. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is called the
(a) Critical temperature (b) Boyle temperature. (c) Inversion temperature (d) Reduced temperature.
7. A gas at constant temperature 250 K is contained in a closed vessel. If it is heated through 1°C , the percentage increase in its pressure is
(a) 0.4 % (b) 0.6 % (c) 0.8 % (d) 1.0 %
8. Equal weights of methane and oxygen are mixed in an empty container at 25°C . The fraction of total pressure exerted by oxygen is
(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3} \times \frac{273}{298}$
9. Equal weights of methane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is
(a) $\frac{1}{2}$ (b) $\frac{8}{9}$ (c) $\frac{1}{9}$ (d) $\frac{16}{17}$.
10. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16
11. In a closed room of 1000 m^3 a perfume bottle is opened up. The whole room develops smell. This is due to which property of the gases ?
(a) Viscosity (b) Density (c) diffusion (d) None

12. Helium diffuses twice as fast as another gas B. If the vapour density of He is 2, the molecular weight of B is
(a) 4 (b) 8 (c) 16 (d) 24
13. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of gas X is
(a) 64 (b) 32 (c) 4 (d) 8
14. 50ml of gas A diffuses through a membrane in the same time as taken for the diffusion of 40 ml of another gas B under identical pressure temperature conditions. If the molecular weight of A is 64 that of B would be
(a) 100 (b) 250 (c) 200 (d) 80
15. The internal energy of one mole of an ideal gas is given by
(a) $\frac{3}{2} RT$ (b) $\frac{1}{2} KT$ (c) $\frac{1}{2} RT$ (d) $\frac{3}{2} KT$.
16. Which is not true in case of an ideal gas ?
(a) It cannot be converted into a liquid.
(b) There is no interaction between the molecules
(c) All molecules of the gas move with same speed.
(d) At a given temperature PV is proportional to the amount of the gas.
17. An ideal gas cannot be liquefied because
(a) Its critical temperature is always above 0°C .
(b) Its molecules are relatively smaller in size.
(c) It solidifies before becoming a liquid.
(d) Forces operative between its molecules are negligible.
18. The vander Waals equation explains the behaviour of
(a) Ideal gas (b) Real gases (c) Vapours (d) Non - real gases
19. Real gases approximate to ideal behaviour only
(a) If temperature is lower
(b) If pressure is high
(c) If pressure is low and temperature is high
(d) If both temperature and pressure are low.
20. The deviation of behaviour of real gas from ideal gas will depend on
(a) Force acting between molecules
(b) Space occupied between molecules
(c) Mass of molecules only
(d) The force acting between molecules, space occupied by molecules and mass of molecules.

21. The pressure at which one mole of a gas at 0°C occupies a volume of one litre is :
 (a) 2.24 atm (b) 4.48 atm (c) 11.2 atm (d) 22.4 atm
22. At what temperature in the celsius scale, volume of certain mass of gas at 27°C will be doubled keeping the pressure constant.
 (a) 54° (b) 327°C (c) 427°C (d) 527°C .
23. Partial pressure of CO_2 in a mixture of CO_2 and N_2 is 1.25 atmosphere while the total pressure of the gas mixture is 5 atmosphere. Mole fraction of N_2 in the mixture is :
 (a) 0.82 (b) 0.75 (c) 0.80 (d) 0.65 (1988 OUAT)
24. A comparison of relative rates of diffusion of H_2 and O_2 at a given temperature shows that.
 (a) O_2 diffuses four times faster than H_2 .
 (b) H_2 diffuses two times faster than O_2 .
 (c) H_2 and O_2 diffuse at the same rate.
 (d) H_2 diffuses four times faster than oxygen
25. Two grams of hydrogen diffuse from a container in 10 minutes. How many grams of oxygen would diffuse through the same container.
 (a) 6 grams (b) 4 grams (c) 0.5 grams (d) 8 grams
26. The root mean square velocity is expressed as
 (a) $(\frac{3}{2} \text{RT})^{\frac{1}{2}}$ (b) $(\frac{3\text{RT}}{\text{M}})^{\frac{1}{2}}$ (c) $(\frac{2\text{RT}}{\text{M}})^{\frac{1}{2}}$ (d) $(\frac{3\text{RT}}{\text{M}})$
27. If 3 litre of oxygen is heated from 27°C to 100°C keeping the pressure constant, the new volume will be
 (a) 3.5 litres (b) 4.5 litres (c) 3.73 litres (d) 5.00 litres
28. In vanderwaals' equation of state for a non ideal gas, the term that accounts for intermolecular forces is
 (a) $(v - b)$ (b) RT (c) $(P + \frac{a}{V^2})$ (d) $(\text{RT})^{-1}$
29. A gas is initially at 1 atm pressure. To compress it to $\frac{1}{4}$ th its initial volume, pressure to be applied is :
 (a) 1 atm (b) 2 atm (c) 4 atm (d) $\frac{1}{4}$ atm
30. At what temperature will the average speed of CH_4 molecules have the same value as O_2 has at 300 K
 (a) 1200 K (b) 150 K (c) 600 K (d) 300 K

B (I). Very short answer type (one mark each)

1. What is the value of R in gas equation in calories ?
2. (a) Give vanderWaals' equation for 1 mole of a real gas ?
 (b) Write vander Waals equation for n moles of real gas

3. Define Boyle's law
4. At constant temperature the product of pressure and volume of a given mass of gas is constant. What is this law called ?
5. Real gas will approach the behaviour of ideal gas at _____
6. The temperature beyond which a gas cannot be liquified even by increase in pressure is called _____
7. What is the value of 'R' in gas equation when the volume is expressed in litres and pressure in atmospheres.
8. Between SO_2 and NH_3 , which gas will diffuse faster at STP
9. Define Charle's law
10. What is absolute zero of temperature ?
11. Between O_2 and NH_3 , which will diffuse faster at NTP ?
12. Rate of diffusion of $\text{SO}_2(\text{g}) < \text{CH}_4(\text{g})$.
Which is lighter ?
13. What is the relationship between average kinetic energy and temperature ?
14. Name the measurable properties of a gas
15. How is kinetic energy of a gas molecule related to the temperature ?
16. What is the temperature in absolute scale corresponding to -20°C
17. What is the relationship between density and temperature of a gas ?
18. "Rate of diffusion of Carbon dioxide is greater than that of Nitrous oxide." Whether the statement is correct or not ?
19. What is the order of ideality of following gases ? CO_2 , H_2 , O_2
20. The temperature above which a gas can not be liquefied even by increasing the pressure is called _____.
21. When pressure of a given mass of gas is tripled its volume becomes one third at constant temperature. What is this law called ?
22. Which of the following has the highest rate of diffusion ? $\text{O}_2, \text{CO}_2, \text{NH}_3, \text{N}_2$
23. What is the relationship between root mean square velocity and average velocity ?
24. What is absolute zero of temperatures ?
25. How Kinetic energy is related to absolute temperature ?
26. Under what condition the real gases behave ideally ?
27. Why does CO_2 diffuse rapidly as compared to chlorine ?
28. What is the value of 'R' in SI Units ?
29. What is aqueous tension ?
30. Write the vander Waals equation of state for 'n' moles of real gas.
31. What is most probable velocity ?
32. Which symbol represents the excluded volume in vander Waals equation of state for 1 mole of real gas ?

II. Fill in the blanks with answers : (One mark each)

1. The value of PV for 5.6 litres of an ideal gas is _____ RT at NTP
2. The total number of electrons present in 18 ml of water is _____
3. The $C_p - C_v$ for an ideal gas is _____
4. The total energy of one mole of an ideal monoatomic gas at 27°C is _____ calories
5. Under similar conditions of temperatures and pressure the rate of diffusion of gases vary _____ as the square roots of their _____ or _____.
6. At STP the order of mean square velocity of molecules of H_2 , N_2 , O_2 & HBr is _____
7. Eight grams each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of _____
8. The value of the gas constant 'R' in joules per mole per degree is _____.
9. Between CO_2 & NH_3 , _____ gas will diffuse faster.
10. Temperature remaining constant, the pressure of a gas is _____ proportional to volume.
11. Equal volumes of all gases under similar conditions of _____ and pressure contain equal number of _____.
12. Real gases behave ideally under the conditions of low pressure & _____ temperature.
13. The rate of diffusion of a gas is _____ proportional to the square root of its molecular weight.
14. The temperature at which the real gases obey the ideal gas laws is known as _____.
15. SO_3 diffuses _____ than SO_2 .
16. Average Kinetic energy of gas molecules is a measure of _____.
17. The vander Waals equation of state for 'n' moles of real gases is

$$(P + \frac{n^2}{V^2}) (V - nb) = nRT$$
18. The ratio between root mean square velocity, average velocity and most probable velocity is — : — : — : —.
19. The inter molecular forces between the molecules of an ideal gas are _____.
20. The molecules of a gas are always in a state of constant _____.

C. Short answer type : (Two marks each)

1. State and explain Boyle's law
2. Which of the two graphs will be a straight line at constant temperature, 'P' verses 'V' or 'P'
 verses $\frac{1}{V}$? Explain
3. Distinguish between ideal gas and real gas. Write an equation for one mole of an ideal gas
4. Why do N_2 and C_2H_4 diffuse at the same rate ?
5. State Graham's law of diffusion

6. State Dalton's law of partial pressure.
7. Explain absolute zero and absolute scale of temperature
8. Derive an equation for 'n' moles of an ideal gas.
9. At what conditions a real gas will behave as an ideal gas ? Explain in 5 sentences
10. What are the two reasons for relating the gas volumes to the temperature in Kelvin scale rather than Celsius scale ?
11. How does the real gas differ from ideal gas
12. Automobile tyres are inflated to less pressure in summer than winter. Give reasons.
13. If certain mass of dry gas at 27°C and 760 mm pressure has density 28, what will be its density at 7°C and 740 mm pressure ?
14. Under what conditions real gases obey ideal gas equation and why ?
15. Distinguish between diffusion and osmosis.
16. Derive Graham's law of diffusion from kinetic gas equation.
17. Distinguish between Diffusion & Effusion.
18. Liquid ammonia bottle is to be cooled before opening - Explain (I.I.T, 1983)
19. Write three important postulates of Kinetic theory of gas.
20. Deduce Charle's law from Kinetic gas equation.
21. Give units of vander Waals constants.
22. Offer an explanation to the exceptional behaviour of Hydrogen & Helium.
23. What are the two faulty assumptions in Kinetic theory of gases.
24. What is Critical temperature ? Discuss its importance.
25. How is real gas different from ideal gas ?
26. Explain Boyle's law in the light of Kinetic model of gas.
27. A gas collected over water appears to be exerting more pressure in comparison to when it is dry. Explain

D. Short answer type questions : (Three marks each)

1. If a given mass of gas, obeying Charle's law and Boyle's law has a volume of 30cc at 27°C and 10 atmosphere what will be its volume at NTP ?
2. What will be the volume at 450 K of a gas which occupies 200cc at 300K, the pressure remaining same throughout ? (Ans 300 cc)
3. If the pressure of a given mass of gas becomes half the original pressure and simultaneously the volume has become four times the original volume, what should have happened to the temperature. (Ans-double)
4. The atomic weight of Helium, oxygen and sulphur are 4,16 and 32 respectively. Helium and sulphur dioxide in equal volume are contained in a glass vessel. If the gases leak out through a pinhole, what will be the ratio of rate of escape of helium to that of SO_2 ?
5. 300 CC of a gas are heated from 27°C to 127°C . What will be the new volume of the gas at constant pressure ? (Ans - 400 CC)
6. The rates of diffusion of an unknown gas and chlorine are in the ratio of 6 : 5. Assuming the density of chlorine to be 36, calculate the molecular weight of the unknown gas ? (Ans - 50)

7. The volume of a gas sample is 100 ml at 100°C. If the pressure is held constant, what will be the temperature of the gas when the sample occupies a volume of 200 ml ?
8. The relative rates of diffusion of two gases A & B are found to be 0.3 and 0.2 respectively. If the density of 'A' is 4, find the relative density of gas B. (Ans - 9)
9. 180 ml of a hydrocarbon diffuse through a porous membrane in 15 minutes while 120 ml of SO₂ under identical condition diffuse in 20 minutes. Calculate molecular weight of hydrocarbon. (Ans - 19)
10. What is the root mean square velocity of CH₄ at 27°C ? At what temperature would ethane molecule have the same velocity as that of methane molecule ?

$$[C = 12, H=1, R=8.314 \text{ JK}^{-1} \text{ mole}^{-1}]$$

11. A hydrocarbon having the formula C_n H_{2n+2} diffuses twice as fast as SO₂ at the same temperature. Calculate the value of n. (Ans n=1)
12. A sample of pure gas at 27°C and 380 torr occupied a volume of 492 cm³. What was the number of moles of gas in this sample ?
13. A desiccator of internal volume of 1 litre and containing nitrogen at one atmospheric pressure is partially evacuated to a final pressure of 7.6 mm of Hg while the temperature remains constant. What is the volume of the gas at this stage ? (Ans-1 litre)
14. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode? (Ans 99.5°C)
15. What is the volume of 6 gms of Hydrogen at 1.5 atm and 273°C ? (Ans - 89.6 litres)
16. Calculate the density of NH₃ at 30°C and 5 atm pressure ? (Ans - 3.42 gms/lit)
17. Calculate the total number of electrons present in 1.6 gms of methane. (1985) (Roorkee)
18. An open vessel at 27°C is heated until three fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated ? (Ans - 477°C)
19. Oxygen is present in a litre flask at a pressure of 7.6 × 10⁻¹⁰ mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C. (Ans - 2.7 × 10¹⁰ molecules)
20. When 2 gms of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 gms of another gas B is added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molecularweights M_A : M_B (Ans M_A : M_B = 1 : 3)
21. 3.7 gms of a gas at 25°C occupied the same volume as 0.184 gms of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas ? (Ans. 41. 33)
22. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure, as that of H₂, is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas ? (Ans - 1088)
23. At room temperature, ammonia gas at one atmospheric pressure and hydrogen chloride gas at P atm pressure are allowed to effuse through identical pin-holes from opposite

- ends of a glass tube of one metre length and of uniform cross section. NH_4Cl is first formed at a distance of 60cm from the end through which HCl gas is sent in. What is the value of 'P' ? (Ans 2.197 atm)
24. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially ? (Ans - He : CH_4 = 8 :1)
25. The average velocity at T_1 K and the most probable velocity at T_2 K of CO_2 gas is 9.0×10^4 cm sec⁻¹. Calculate the value of T_1 and T_2 . (Ans $T_1 = 1682.5$ K $T_2 = 2143.4$ K)

E. Long answer type questions : (Seven marks)

1. State and explain Dalton's law of partial pressure.
500 ml of oxygen at a pressure of 700 mm, 300 ml of hydrogen at a pressure of 750 mm and 700 ml of Nitrogen at a pressure of 600 mm are enclosed in a vessel of 1 litre capacity at 25°C.
Calculate the total pressure of the gas mixture.
2. State and explain Graham's law of Diffusion.
3. State and explain Dalton's law of partial pressure. A certain quantity of gas occupies 50 ml when collected over water at 15°C and 750 mm. pressure. It occupies 49.95 ml in the dry state at NTP. Find the partial pressure of water at 15°C.
4. Derive the equation of state for an ideal gas. Why do real gases deviate from ideal gas behaviour ? What is vanderWaals modification ?
5. What are the postulates of Kinetic theory of gases ? How Boyle's law and Charle's law can be explained in the light of Kinetic model of gas ?
6. State and explain Boyle's law and Charle's law ? A gas occupies a volume of 200 ml at 27°C and 700 mm pressure. What volume will it occupy at 47°C and 600 mm pressure?
7. Define Boyle's law and Charle's law. Derive the combined gas equation from the two laws. Temperature remaining constant 100 ml of oxygen at 100 mm pressure is transferred to a container of 25 ml capacity. What is the pressure of oxygen in the new container ?
8. What are the main postulates of Kinetic theory of gases ? How does it explain the effect of temperature on the volume of a gas.
9. Define Boyle's law and Charle's law. Derive the gas equation from these laws.
What will be the volume of 3.2 gms of O_2 gas at 0°C and 760 mm pressure ?
10. State and explain the equation of state for an ideal gas. Why real gases deviate from the ideal behaviour ? What is vander Waals' modification of the gas equation.
11. Define Boyle's law and Charle's law. Derive the combined gas equation from the two laws. Find out the value of gas constant R.
12. (a) Derive the equation of state for an ideal gas
(b) What volume will be occupied by 48 gms of CO_2 at 27°C and 650 mm pressure ?
13. Write notes on :
(a) Dalton's law of Partial pressure
(b) Graham's law of Diffusion

14. Describe the kinetic model of gas and derive Boyle's law and Charle's law on this basis.
15. State and explain Graham's law of diffusion. Mention two of its applications. A hydrocarbon with molecular formula C_nH_{2n+2} diffuses twice as fast as SO_2 at the same temperature. Find out the molecular formula of the hydrocarbon (At mass of S = 32)
16. How Graham's law of diffusion can be explained in the light of kinetic theory of gases ? At STP 0.48g. of oxygen diffuses through the porous partition in 1200 seconds. What volume of carbon dioxide will diffuse in the same time under similar condition ?
17. State and explain Graham's law of diffusion. The rates of diffusion of SO_2 and an unknown gas are in the ratio 5:6.03. The density of SO_2 is 32. Calculate the molecular mass of the unknown gas ?
18. What are the postulates of kinetic theory of gases ? How are Boyle's law, Charle's law and Dalton's law of partial pressures explained in the light of Kinetic model of gas ?
19. Derive the kinetic equation for gases
20. State and explain Graham's law of diffusion. A given volume of oxygen containing 20% by volume of ozone required 175 seconds to diffuse, when an equal volume of oxygen took 167 seconds to diffuse under similar conditions. Find the density of ozone.
21. Derive an equation for 'n' moles of an ideal gas. How can Charles' law be explained in the light of kinetic theory of gases ? Under what condition a real gas shows ideal behaviour ?
22. State and explain Graham's law of Diffusion. Discuss its important application.
23. Derive vander Waals' equation of state and show how it explains the behaviour of real gases.
24. What is an ideal gas ? Why do real gases deviate from ideal behaviour. What are the causes of deviation.
25. (a) State and explain Graham's law of Diffusion
(b) 3 moles of a gas are present in a vessel at $27^\circ C$. What will be the value of 'R', the gas constant in terms of Kinetic energy of the molecules of the gas ?
26. What is numerical value (as obtained from consideration of dimension) of the molar gas constant 'R' ? How do you arrive at this value ? How do you arrive at different units ? (lit-atm, erg, cal, Joules) in which the molar gas constant is expressed ?
27. (a) Does a real gas at a very high pressure occupy more volume or less volume than that occupied by an ideal gas under identical conditions ?
(b) Does the temperature have any effect on the above ?
(c) Calculate the root mean square speed of a molecule of oxygen at NTP
28. What is vander Waals equation ? Under what conditions it will reduce itself to ideal gas equation ?
29. Write notes on
(a) Root mean square velocity.
(b) Deviation of real gas from ideal behaviour.
(c) Effusion.

30. State Maxwells' law of distribution of molecular velocities and explain its significance. How distribution of molecular velocities is affected by temperature.
31. Give an account of Kinetic theory of gases. Discuss the behaviour of real gases.
32. How are the gas laws explained on the basis of Kinetic theory of gases ? Calculate the root mean square velocity and average velocity in kms per second of H₂ molecule at 30°C.
33. State and explain Dalton's law of partial pressure. What are its applications ?

ANSWERS

(A) Multiple Choice Type Questions.

- | | | | | | |
|--------|---------|---------|---------|---------|---------|
| 1. (b) | 6. (b) | 11. (c) | 16. (c) | 21. (d) | 26. (b) |
| 2. (a) | 7. (b) | 12. (c) | 17. (d) | 22. (b) | 27. (c) |
| 3. (d) | 8. (a) | 13. (a) | 18. (b) | 23. (b) | 28. (c) |
| 4.(a) | 9. (b) | 14. (a) | 19. (c) | 24. (d) | 29. (c) |
| 5. (c) | 10. (d) | 15. (a) | 20. (d) | 25. (d) | 30. (b) |

B (II) FILL IN THE BLANKS

- | | | | |
|--------------------------|---|---------------------|-------------------------|
| 1. 0.25 | 6. H ₂ > N ₂ > O ₂ > HBr | 11. temp, molecules | 16. Absolute temp. |
| 2. 9 x 10 ²² | 7. 1 : 16 | 12. high | 17. $\frac{n^2 a}{V^2}$ |
| 3. R | 8. 8.314 | 13. inversely | 18. 1 : 1. 120 : 1.234 |
| 4. 900 | 9. NH ₃ | 14. Boyle Temp. | 19. Negligible |
| 5. Inversely, densities, | 10. Inversely
Molecular wt. | 15. Slower | 20. motion. |

□ □ □

CHAPTER - 7

LIQUID STATE

The intermolecular forces of attraction in a liquid is intermediate between the solid and the gas. In crystalline solid the constituent particles occupy fixed position, whereas the particles of the gases are in the state of random motion. But in the liquid state the particles are neither arranged in an orderly manner nor there is a complete disorder as in gases. As a result, the behaviour of the liquid is expected to be in between solids and gases.

7.1 CHARACTERISTIC PROPERTIES OF THE LIQUIDS

1. **Volume and shape :** Matter in liquid state has a definite volume but no definite geometrical shape. It takes up the shape of the container in which it is contained. The intermolecular forces between the molecules in the liquid state are just sufficient to hold the molecules together, but the forces are less than the forces required to fix the molecules at definite position.
2. **Compressibility :** Liquids are almost incompressible. It can be compressed to a small extent under extremely high pressure.
3. **Fluidity :** Liquid possesses the property of flowing. When a solid melts into a liquid, the intermolecular force of attraction decreases and the intermolecular distance increases. Consequently the molecules begin to slide over one another.
4. **Diffusion :** Gases undergo spontaneous intermixing irrespective of gravity, which is known as **diffusion**. Liquid also exhibits diffusion. When two miscible liquids like water and alcohol are kept together in a container, they diffuse into one another, but the rate of diffusion is much slower than that of gas. When a few drops of blue ink are added to water taken in a beaker, the coloured ink substances diffuse through water and turn the whole solution blue. The liquid molecules diffuse slowly because of the restricted movement of molecules due to less free space available.
5. **Evaporation :** The gaseous state of a liquid is known as the **vapour**. If a liquid is exposed to the atmosphere at room temperature, its volume decreases gradually and after sometime, the liquid disappears. The decrease in volume is due to the spontaneous change of liquid into its vapour. This process in which a liquid changes into the vapour state at the surface is known as **evaporation**. Evaporation of liquid is due to the fact that the molecules in a liquid possess different kinetic energy, since they move at different

velocities. When the K.E. is sufficient to overcome the attractive forces molecules pass into vapour state provided they are nearer to the surface. When the temperature of a liquid is raised, it evaporates more quickly, since the kinetic energy of the moving molecules of the liquid increases with the rise of temperature. However, when the temperature of a liquid is lowered sufficiently, the liquid changes its state to a solid, that means the liquid freezes to a solid. The lowering of temperature means a decrease in the K.E. of the molecules. When this decrease in energy is enough, the existing weak van der Waals forces between the molecules of the liquid hold the particles together in the fixed position converting it into a solid.

6. **Density :** The density of liquids is comparatively less than that of the solids but sufficiently greater than that of gases. The weak intermolecular force and relatively poor packing of the molecules account for the less density of a liquid.
7. **Structure :** In the solid state the lattice points are fixed which is not the case with the liquid state. The weak intermolecular force often acts as a barrier for the formation of a regular crystal lattice. Due to this reason liquids possess a distorted crystal lattice with a tendency to move in different direction. Such an arrangement leads to the semicrystalline state of liquids.

7.2. **VISCOSITY**

Some liquids like kerosene, alcohol, water etc. flow more rapidly, while a few such as oils, honey etc. flow very slowly. The variation in the flow rate of the liquids is due to some internal resistance possessed by all the liquids. This property of the liquids is known as **viscosity**. The resistance of flow is due to the intermolecular attractive forces in liquids.

Viscosity of a liquid is defined as its property by virtue of which it tends to oppose the relative motion between its different layers.

Viscosity of liquid is temperature dependent. When the temperature of a liquid increases the viscosity decreases because the kinetic energy of the molecules of the liquid increases which overpowers the attractive forces. High pressure also increases the viscosity of a liquid. The internal structure and the extent of vander Waals force generally controls viscosity. The viscosity of water is high due to greater hydrogen bonding. Viscosity increases with the increase in molecular mass of the same class of compounds. For this reason lower alcohols are mobile than the higher ones. Viscosity increases with the increase in the branching of carbon chain in case of organic liquids.

7.3. **SURFACE TENSION**

Let us consider two molecules A and B of a liquid kept in a beaker. The molecule A is well within the liquid and is attracted equally from all sides by the surrounding molecules. So the resultant force acting on A is zero.

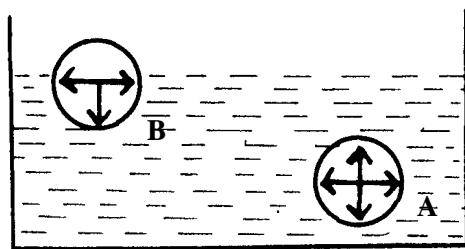


Fig 7.1 Surface tension

The molecule B is situated on the surface of the liquid and is pulled by the molecules below it and those lying on its sides. Since there is no molecule of liquid above B no force exists to balance the downward pull. Hence the molecule experiences a resultant pull downward. All the molecules at the surface of the liquid are bound together from something like a stretched membrane tending to compress the molecules below to the smallest possible volume. This force on a liquid is known as **surface tension**.

Surface tension is defined as "force in dynes acting at right angles to an imaginary line of unit length on the surface of a liquid". It is expressed in dynes per cm.

Examples :

- (i) The rise or fall of liquids in capillaries, the floating of a shaving blade, the spherical shape acquired by a drop of liquid are the common consequences of surface tension.
- (ii) The meniscus of a liquid in a glass tube is also due to surface tension. The surface of water is concave because glass - water adhesive force is greater than the intermolecular attraction in water (cohesive force).
- (iii) The surface of mercury is convex because the intermolecular force in mercury is more than glass – mercury adhesive force.

Surface tension decreases with the increase of temperature. Surface tension varies from liquid to liquid according to its nature and structure of molecules.

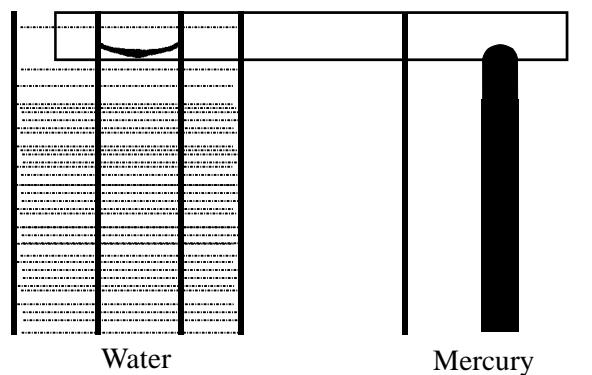


Fig 7.2 Meniscus of liquid in glass tube

7.4 VAPOUR PRESSURE

When a liquid is placed in an open vessel exposed to atmosphere, it gradually disappears. The change of liquid into gas is known as **evaporation**. At constant temperature, when the evaporation of a liquid takes place in a closed container, the molecule that escape from the surface of the liquid are trapped in the container and occupy the space above the surface of the liquid. The molecules collide with each other and with the walls of the container. A few of them may also hit the surface of the liquid and return to it resulting in condensation. The rate of return of molecules in vapour state (condensation) is proportional to the concentration of molecules in vapour state. Finally a stage reaches, when the rate of evaporation is equal to the rate of condensation.

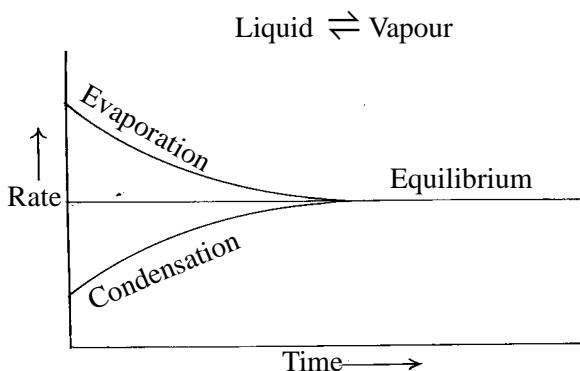


Fig. 7.3 Equilibrium curve for evaporation and condensation

Vapour pressure of the liquid at any given temperature is the pressure exerted by the vapour of a liquid when it is in equilibrium with the liquid.

Vapour pressure increases with the increase of temperature.

B.P. (Boiling point) : The temperature at which the vapour pressure of a liquid becomes equal to the prevailing atmospheric pressure, bubbles begin to form through out the liquid and finally boils. This temperature is called the **boiling point** of a liquid. Every liquid has a standard or normal boiling point.

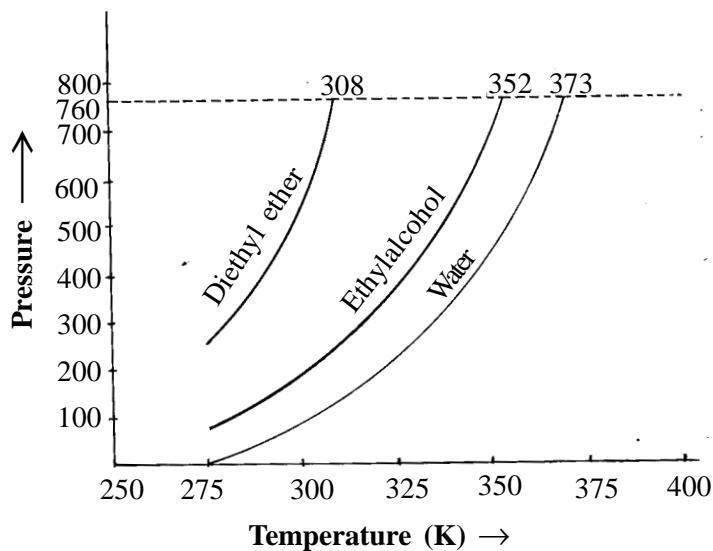


Fig 7.4 Plot showing variation of vapour pressure of liquids with temperature

Boiling point is defined as the temperature at which the vapour pressure becomes equal to the standard atmospheric pressure (760 mm). At a given temperature, the greater the vapour pressure of a liquid, the lesser would be its boiling temperature. The pressure cookers hasten the cooking process. In pressure cooker higher pressure is built up, consequently the boiling temperature of liquid increases.

Molar heat of vapourisation is the quantity of heat supplied to one mole of a liquid at its boiling point so as to change it into vapour state at the same temperature.

CHAPTER (7) AT A GLANCE

1. Liquids have definite volume but no definite shape. They are incompressible and they possess the property of flowing.
2. At any given temperature the pressure exerted by the vapour of a liquid when it is in equilibrium with the liquid is known as vapour pressure of the liquid.
3. Vapour pressure increases with increase of temperature.
4. Boiling point is the temperature at which the vapour pressure becomes equal to the atmospheric pressure.
5. Greater the vapour pressure of a liquid, the lesser would be its boiling point.
6. Viscosity of a liquid is its property by virtue of which it tends to oppose the relative motion between its different layers.
7. Viscosity decreases with increased in temperature and increases with increase in pressure.
8. Surface tension is the force in dynes acting at right angles to an imaginary line of unit length on the surface of a liquid.
9. Surface tension decreases with increase of temperature.

QUESTIONS**A. Multiple choice type questions : (one mark)**

1. Compared to Jalandhar, the vapour pressure of water at Simla is,
 - (a) Lower
 - (b) More
 - (c) Equal.
2. Viscosity of a liquid
 - (a) Increases with increase in temperature.
 - (b) Decreases with decrease in temperature.
 - (c) Independent of temperature.
 - (d) Decreases with decrease in pressure
3. With increase in temperature, the vapour pressure of a liquid.
 - (a) Decreases
 - (b) Does not change.
 - (c) Increases
4. Cleaning action of soap is due to.
 - (a) Viscosity of water.
 - (b) Surface tension of water.
 - (c) Polarity of water.
 - (d) high boiling point of water.
5. The unit of viscosity is poise which means
 - (a) Dyne Cm⁻²
 - (b) dyne
 - (c) dyne cm⁻² sec⁻¹
 - (d) dyne cm
6. The internal resistance to flow possessed by liquid is called its
 - (a) Surface tension
 - (b) Fluidity
 - (c) (n)
 - (d) Viscosity
7. A liquid in capillary tube rises due to
 - (a) Surface tension
 - (b) Vapour pressure
 - (c) Osmosis
 - (d) Viscosity
8. The vapour pressure of a liquid
 - (a) is directly proportional to the temperature.
 - (b) is inversely proportional to the temperature.
 - (c) increases only up to the boiling point.
 - (d) vary from liquid to liquid.

9. At high altitudes the water boils at low temperature because
 - (a) water molecules are bound with strong hydrogen bonds.
 - (b) low atmospheric pressure.
 - (c) high atmospheric pressure.
 - (d) at low altitude the fuel does not give sufficient energy.
10. When temperature increases, the surface tension of a liquid is
 - (a) increased
 - (b) decreased
 - (c) neither increased nor decreased
 - (d) depends on the nature of the liquid
11. The boiling point of water in a pressure cooker is
 - (a) below 100°C.
 - (b) above 100°C.
 - (c) 100°C.
 - (d) depends upon the size of pressure cooker.

B. Very short answer type questions : (one mark)

1. At 730 mm pressure, the boiling point of water is (more than 100°C, less than 100°C)
2. The boiling point of sea water at 760 mm pressure is (more than 100°C, less than 100°C).
3. The vapour pressure of a liquid is equal to the atmospheric pressure at its (boiling point, freezing point)
4. The viscosity of glycerol is more than that of water due to (hydrogen bonding, van der Waals forces)
5. Define the term surface tension and viscosity.
6. What is the freezing point of water at 1 atm. pressure in Kelvin scale ?
7. With the increase of temperature, the vapour pressure of a liquid
 - (a) Decreases, does not change, increases)
8. Between sea water and drinking water which will freeze at a lower temperature ?
9. What do you understand by viscosity of a liquid ?
10. Vapour pressure of a liquid _____ with rise of temperature.
11. How does boiling point of a liquid change with decrease in atmospheric pressure ?
12. What is the effect of pressure on the boiling point of a liquid ?
13. How does viscosity of a liquid vary with temperature ?
14. Between water and ether which has a higher vapour pressure ?
15. What is the SI unit of viscosity ?
16. What is the SI unit of surface tension ?
17. Which of the following has higher vapour pressure at the same temperature ?
 CH_3OH (BP = 64.5°C) $\text{C}_2\text{H}_5\text{OH}$ (BP = 78.3°C)

C. Short answer type questions : (two marks)

1. Write four important characteristics of liquids.
2. Define and explain the term "vapour pressure".
3. Describe the effect of temperature on the vapour pressure of a liquid.
4. Define the term 'boiling point'.
5. Explain the term freezing point.
6. Define surface tension.
7. (a) Define the terms (i) viscosity (ii) coefficient of viscosity.
(b) What do you understand by viscosity of a liquid ?
8. Explain why ?
 - (a) In summer, earthen pots are used to keep water cool.
 - (b) Liquid drops are spherical.
 - (c) The boiling point of water is more than that of ether.
 - (d) Ammonia is used as a refrigerant.
9. What do you understand by viscosity of a liquid ? (3 marks)
10. Why surface tension of a liquid decreases with increase in temperature ?
11. Between sea water and pure water, which will boil at a higher temperature ? Give reason.
12. Why glycerol is more viscous than water ?
13. What is the effect of temperature on the surface tension of a liquid ? Explain with reason. (3 marks)

D. Long answer type questions : (seven marks)

1. Describe the kinetic molecular theory of liquids.
2. Describe the characteristic properties of the liquids.
3. (a) Write a method for measuring the vapour pressure of a liquid.
(b) Write a note on boiling point.
4. Explain the term surface tension. What are the factors on which surface tension depends ?
5. Write short notes on :
 - (a) Viscosity
 - (b) Surface tension.
 - (c) Boiling point and freezing point.
6. Describe the characteristic properties of liquids and explain the following ;
 - (i) Evaporation causes cooling.
 - (ii) A drop of liquid assumes spherical shape.
 - (iii) The vapour pressure of a liquid increases with the increase in temperature.

- (iv) 'Like dissolves like.'
 - (v) "Liquid state" lies between solid and gaseous state."
 - (vi) Boiling point of a liquid depends on temperature.
7. What is viscosity ? How does it vary with rise of temperature ? Mention some applications of viscosity in everyday life.

A. ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS

- | | | |
|--------|--------|---------|
| 1. (b) | 5. (c) | 9. (b) |
| 2. (b) | 6. (d) | 10. (b) |
| 3. (c) | 7. (a) | 11. (a) |
| 4. (b) | 8. (c) | |



UNIT – VI

CHAPTER - 8

THERMODYNAMICS

Introduction

Thermodynamics is an important branch of physical chemistry that deals with the energy changes accompanying all physical and chemical processes. The word *thermodynamics* (*Thermo*-heat, *dynamics* - motion) refers to the flow of heat or heat motion. It is an exact mathematical science in which inter-relationships between various forms of energies have been fully described. It is not concerned with the total energy of the body rather with the energy changes accompanying a particular process of transformation. There are three fundamental laws of thermodynamics, namely 1st law, 2nd law and 3rd law of thermodynamics which are based on human experience.

Importance of Thermodynamics

- (i) The feasibility of physical and chemical processes is predicted by the laws of *thermodynamics*. This is its primary objective.
- (ii) The study of *thermodynamics* enables us to know whether a chemical reaction is possible under a given set of conditions.
- (iii) Various laws like Law of chemical equilibrium, gas laws, van't Hoff law of dilute solutions, Raoult's law of relative lowering of vapour pressure, Phase rule, Distribution law etc. can be deduced on the basis of the laws of *thermodynamics*.
- (iv) The extent to which a given reaction proceeds before attainment of equilibrium can be predicted by *thermodynamics*.

Limitations of Thermodynamics

- (i) The laws of *thermodynamics* do not apply to individual atoms or molecules. The laws apply to the matter in bulk only.
- (ii) The rate at which a given chemical reaction proceeds can not be predicted by *thermodynamics*.
- (iii) The systems away from equilibrium can not be explained by *thermodynamics*.

8.1 SOME BASIC TERMS USED IN CHEMICAL ENERGETICS

1. System and Surrounding : The entire universe may be imagined to be made up of two things : the **system** and **surrounding**. Any portion of the universe chosen for thermodynamic consideration is known as the **system**. The rest of the universe excluded from the system is known as the **surrounding**. The **system** can exchange energy with the **surrounding**.

The system is separated from the surrounding by well defined real or imaginary boundaries known as thermodynamic walls. This helps us to study the effect of certain variables like pressure, volume, temperature etc upon the contents present in the system.

2. Types of system :



Fig 8.1
Liquid in contact with vapour

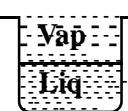


Fig 8.2
Liquid in contact with vapour in open vessel

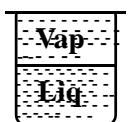


Fig 8.3
Liquid in contact with vapour in closed vessel

- (i) **Isolated system :** A system which can exchange neither energy nor matter with the surrounding is known as an **isolated system**.

e.g. - A liquid in contact with its vapour in an insulated closed vessel.

- (ii) **Open system :** A system which can exchange both energy and matter with the surrounding is known as an **open system**.

e.g. - A liquid in contact with its vapour in an open vessel. Here the liquid absorbs heat from the surrounding and gives out vapour to the surrounding.

- (iii) **Closed system :** A system which can exchange only energy and not matter with the surrounding is known as a **closed system**.

e.g. - A liquid in contact with its vapour in a closed vessel which is not insulated.

- (iv) **Homogeneous system :** The system which has uniform composition and identical properties throughout is known as a **homogeneous system**. The system consists of only one phase.

e.g. - A pure liquid, a solid, two miscible liquids etc. Air is a homogeneous mixture of all gases.

- (v) **Heterogeneous system :** The system which has neither uniform composition nor identical properties throughout is said to be a **heterogeneous system**. The system consists of two or more phases.

e.g. - A solid in contact with a liquid, two immiscible liquids, a liquid in contact with its vapour etc.

3. Macroscopic system and Macroscopic properties :

When there are a large number of particles (molecules, atoms, ions) the system is referred to as macroscopic system.

The properties associated with collective behaviour of particles are known as macroscopic properties e.g. temperature, pressure, volume, density etc.

4. State of a system :

A system is said to be in a particular state when it is in equilibrium under a given set of conditions i.e. when all its macroscopic properties have definite values. The system changes from one state to other when there is a change in one or more macroscopic properties.

5. State Variables or State Functions.

The macroscopic properties are the state variables since a change in any macroscopic property brings about a change in state of the system.

A state variable that depends on other variables is known as **dependent** variable whereas the variable which does not depend upon other variables is known as **independent** variable.

For example, in case of an ideal gas P, V or T can be calculated provided any two of these variables are known. These two are independent variables whereas the third one is dependent variable.

Again, since the state variables depend only upon the initial and final state of the system and not upon the path followed, these are called **state functions**. Some common state functions are internal energy (E), entropy (S), enthalpy (H), free energy (G), pressure (P), volume (V) etc.

It may be noted that heat (Q) and work (W) are not state functions because they are path dependent. They are rather known as **path functions**.

6. Properties of a system :

The properties of a system may be studied under two heads (i) Extensive property. (ii) Intensive property.

(i) **Extensive property** : The property which depends on the amount of substance present in the system is known as an **extensive property**.

e.g. - mass, volume, energy etc.

(ii) **Intensive property** : The property which is independent of the amount of substance present in the system is known as an **intensive property**.

e.g. - temperature, pressure, density, surface tension, viscosity etc.

It is of interest to note that when unit amount of substance is mentioned an extensive property becomes intensive.

e.g. - mass and volume both are extensive but mass per unit volume i.e. density and volume per unit mass i.e. specific volume are intensive.

7. Thermodynamic process :

A **thermodynamic process** is the operation which brings about change in the system. The processes are of different types.

(i) **Adiabatic process** : When heat is neither allowed to enter nor to leave the system, it is known as an **adiabatic process**.

(ii) **Isothermal process** : The process carried out at constant temperature is known as an **isothermal process**.

(iii) **Isochoric process** : The process carried out at constant volume is known as an **isochoric process**.

(iv) **Isobaric process** : The process carried out at constant pressure is known as an **isobaric process**.

- (v) **Cyclic process :** A process during which the system can be brought back to the initial state after undergoing a series of intermediate changes is known as a **cyclic process**.
- (vi) **Reversible process :** When the change is brought about infinitesimally slowly so that the system is always in equilibrium with the surrounding, the process is referred to as a **reversible process**. It takes place in both the direction and can never be carried to completion.
- (vii) **Irreversible process :** If the change is brought about rapidly and the system does not get proper scope to attain equilibrium, the process is referred to as an **irreversible process**. All the naturally occurring processes are irreversible. These are unidirectional and can be carried to completion.
- (viii) **Path :** The sequence of various steps involved in the process is known as the **path**. For the same process there may be more than one path.

8.2 CONCEPT OF INTERNAL ENERGY

A definite quantity of any substance, under a given set of conditions is associated with a fixed amount of energy. This amount of energy is different for different substances. The energy stored in the substance by virtue of its chemical nature is called its **internal energy**. It is denoted by the symbol U.

During a chemical reaction there is exchange of energy between the system and the surrounding. So the internal energy of the reactants very much differs from that of the product.

If $U_p \rightarrow$ Internal energy of the product

$U_r \rightarrow$ Internal energy of the reactant

$(U_p - U_r) = \Delta U$ = Change in Internal energy.

If the reaction is carried out in such a manner that there is no change in temperature and the system does not perform any work nor has work done upon it then in that case the energy exchange between the system and the surrounding represents the change in internal energy of the system. This is no doubt, a consequence of the law of conservation of energy. In actual practice energy exchange is in the form of heat and work is associated with change in volume against pressure. So change in internal energy of a system (ΔU) can be measured by carrying out the reaction at constant temperature and constant volume and measuring the heat exchange with the surrounding.

Matter, in all its forms, is associated with a certain amount of energy. We can not observe this energy, but we can certainly observe the energy change that appears in the form of heat, light, work etc. during the change of state of matter. Matter consists of molecules, which in turn consists of atoms and within the atoms there are subatomic particles like electrons, protons and neutrons. The origin of energy in matter, therefore, lies in position and motion of molecules, atoms and subatomic particles.

The total energy possessed by the molecules present in the substance is the **internal energy** (**U**) and it may be represented as :

$$U = U_r + U_v + U_t + U_e + U_n + U_{pe}$$

where,

U_r = Rotational energy which arises due to the rotation of molecule as a whole about an axis passing through the centre of gravity.

U_v = Vibrational energy which arises due to vibration of molecules to and fro about their mean position. (If vibrational energy exceeds bond energy, the atoms separate out.)

U_t = Translational energy which arises due to vibration of molecules from one point to the other.

U_e = Electronic energy which arises due to motion and position of electrons around the nucleus.

U_n = Nuclear energy which arises due to binding of the nucleons within the nucleus.

U_{pe} = Potential energy which is possessed by the molecules by virtue of their position.

Internal Energy '**U**' is a state function since its value depends only upon the state of the system and not upon the path followed by the system.

If U_1 = Internal energy of the system in the initial state.

U_2 = Internal energy of the system in the final state.

Then, ΔU = Change in Int. energy = $(U_2 - U_1)$

The absolute value of **U** can not be determined. However, the value of ΔU can be determined experimentally using a **bomb calorimeter**.

Factors on which '**U**' depends

Internal energy **U** depends upon

- (i) The quantity of the substance.
- (ii) The chemical nature of the substance.
- (iii) Temperature, pressure and volume.

Sign of ΔU and some important conclusions

- (i) For exothermic reactions $U_R > U_P$

So ΔU is -ve.

- (ii) For endothermic reactions $U_P > U_R$

So ΔU is + ve.

- (iii) In a cyclic process, the change in internal energy, ΔU is zero since **U** is a state function.

- (iv) The internal energy (U) of a given system is directly proportional to the absolute temperature.
- (v) During adiabatic expansion of a gas, work is done at the expense of internal energy. As a result internal energy decreases and cooling effect is caused.
- (vi) In an isochoric process, volume is kept constant. The quantity of heat supplied to the system is equal to the increase in its internal energy.

$$\text{i.e. } Q = \Delta U$$

8.3 CONCEPT OF ENTHALPY

Most of the chemical reactions are carried in open vessels. In an open vessel the reactants are in contact with the atmosphere, therefore the volume of the reactants may change but pressure remains constant i.e. equal to atmospheric pressure. Since atmospheric pressure is constant, the processes carried out in open vessel may be considered as taking place at constant pressure and not at constant volume.

There is exchange of energy between the system and the surrounding in every chemical reaction. The amount of heat exchanged between the system and the surrounding at constant pressure and constant temperature must differ from that at constant volume and constant temperature. The reason is obvious. When the process is carried out at constant temperature and constant pressure, its volume changes. If volume increases, the system has to expand against atmospheric pressure and energy is needed for this expansion. Thus heat exchange with the surrounding at constant pressure is less than that at constant volume since a portion of it is used in expansion of the system. On the other hand, in case of contraction, work is done on the system, so the heat exchange at constant pressure becomes greater than that at constant volume.

From the above discussion it is clear that energy changes in a reaction at constant pressure and constant temperature is not due to change in internal energy alone but it also includes energy contribution due to expansion or contraction. To explain this, another property called **enthalpy or heat content (H)** associated with every substance is necessary.

'H' is defined as, $H = U + PV$

Since, U, P and V are the properties of state of the system it follows that 'H' is also a **state function**.

If H_1 = Enthalpy of the system in the initial state.

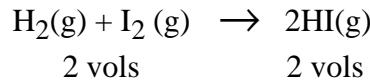
H_2 = Enthalpy of the system in the final state.

$$\begin{aligned}\Delta H &= (H_2 - H_1) = (U_2 + PV_2) - (U_1 + PV_1) \\ &= (U_2 - U_1) + P(V_2 - V_1) \\ &= \Delta U + P\Delta V.\end{aligned}$$

So, $\boxed{\Delta H = \Delta U + P\Delta V}$ - Relationship between Internal energy and Enthalpy.

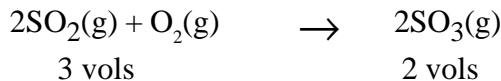
Sign of ΔH and some important conclusions :

- (i) For exothermic reactions $H_R > H_P$
So, $\Delta H = H_P - H_R = -ve.$ where, H_P = Heat content of products.
 H_R = Heat content of reactants.
- (ii) For endothermic reactions $H_P > H_R$
So, $\Delta H = H_P - H_R = +ve.$
- (iii) The quantity of heat supplied to a system at constant pressure i.e Q_p is equal to increase in its enthalpy value.
$$Q_p = \Delta H$$
- (iv) ΔH is more significant than ΔU since most of the reactions are carried out at constant pressure.
- (v) When no gaseous components are involved, the change in volume is almost negligible.
So, $\Delta V = 0$ and $\Delta H = \Delta U = Q$
- (vi) When gases are involved but the reaction proceeds with no change in volume as in case with



$$\Delta V = 2 - 2 = 0, \text{ and } \Delta H = \Delta U = Q$$

- (vii) When the reaction proceeds with change in gaseous volume,



the no. of moles of reactants and products also change.

We know, $PV = nRT$ (For 'n' moles of an ideal gas)

If n_1 and n_2 be the no. of moles in the initial and final states respectively, we have

$$PV_1 = n_1 RT$$

$$PV_2 = n_2 RT$$

$$\Rightarrow PV_2 - PV_1 = n_2 RT - n_1 RT$$

$$\Rightarrow P(V_2 - V_1) = (n_2 - n_1) RT$$

$$\Rightarrow P\Delta V = \Delta n RT$$

$$\text{So, } \Delta H = \Delta U + P\Delta V = \Delta U + \Delta n RT$$

8.4 FIRST LAW OF THERMODYNAMICS (CONSERVATION OF ENERGY)

The law was stated by **Meyer** and **Helmholtz** in 1840. Scientists like **Joule** in England and **Colding** in Denmark made significant contribution towards the development of the law. The law may be stated in a variety of ways.

1. This is simply the law of conservation of energy which states that “Energy can neither be created nor destroyed”. Only it can be transformed from one form to the other.
 2. “The total energy of an isolated system remains constant although one form of energy is convertible to the other form.”
 3. “It is impossible to construct a perpetual motion machine which could produce work without consuming energy.”
 4. “Whenever a given quantity of energy of the one kind disappears, an exactly equivalent amount of some other form of energy must appear in the system.”
 5. “The change in internal energy in a cyclic process is zero.”
 6. “The total mass and energy of an isolated system remains unchanged although these are interconvertible.” This is in accordance with Einstein’s mass-energy relationship $E = mc^2$.

Mathematical Formulation of the law :

Suppose a system absorbs Q amount of heat from the surroundings and undergoes a change from state 'A' to state 'B'.

In state 'A' - Let U_1 = Internal energy of the system

V_1 = Volume of the gas

n_1 = Number of moles of the gas

P = Pressure of the gas

and in state ‘B’—

Let U_2 = Internal energy of the system

V_2 - volume of the gas

n_2 = No. of moles of the gas

P = Pressure of the gas.

The amount of heat absorbed is used in two ways :

- (i) It changes the internal energy of the system from U_1 to U_2 , change of internal energy $\Delta U = U_2 - U_1$
 - (ii) It does some work by consuming rest amount of heat energy.

Hence, $Q = \text{change in internal energy} + \text{work done}$
 $\equiv \Delta U + W$

Since the pressure is constant, work done is work of expansion only which is $P(V_2 - V_1)$ i.e. $P\Delta V$

Hence, $Q = \Delta U + P\Delta V$ (1)

Equation (1) is the mathematical form of First law of thermodynamics.

Again, applying ideal gas equation to both the states 'A' & 'B',

i.e. $n_1 = n_2$, $\Delta n = (n_2 - n_1) = 0$

Thus, equation (3) is reduced to $Q = P\Delta V$

Case - VI In case of solid or liquid state, the change in volume is negligible, i.e.
 $\Delta V = 0$

So, work done $P\Delta V = 0$, and the heat supplied to the system is used only in changing the internal energy.

Significance of first law

- (i) It helps in establishing a direct relationship between the heat absorbed by the system and work done.
- (ii) Work can not be performed by the system without consuming heat energy.
- (iii) Work and energy can not be produced from nothing.

8.5 HEAT CAPACITY AND SPECIFIC HEAT OF A SYSTEM

Heat Capacity : The capacity of a system to absorb heat and preserve the same within is known as **heat capacity**. As a result of absorption of heat, the kinetic motion of the atoms and molecules present in the system increases. Thus the kinetic energy of the system increases which ultimately results in increasing the temperature of the system.

Heat capacity of a system between any two temperatures may be defined as the amount of heat required to raise the temperature of the system from lower to higher temperature divided by the temperature difference.

Specific heat : If the mass of the system is one gram, the heat capacity is referred to as the specific heat of the system.

Molar Heat Capacity : If the mass of the system is one mole, the heat capacity is referred to as **molar heat capacity**. It is represented by C. It is defined as the quantity of heat required to raise the temperature of one mole of the substance by 1 K.

Thus, $C = \frac{Q}{T_2 - T_1} = \frac{Q}{\Delta T}$ (When the system operates between two temperatures T_1 and T_2)

Since molar heat capacity varies with temperature, the true molar heat capacity is represented by the differential equation

$$C = \frac{dq}{dT} \dots\dots\dots (1)$$

Molar heat capacity at constant volume (C_v)

From 1st Law of thermodynamics

$$dq = du + Pdv$$

Substituting the value of dq in equation (1)

$$C = \frac{du + Pdv}{dT} \dots\dots\dots (2)$$

At constant volume, $dv = 0$,

$$\text{Thus, } C_v = \frac{du}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \quad \dots \dots \dots \quad (3)$$

So, molar heat capacity at constant volume is defined as the rate of change of internal energy with temperature

Molar heat capacity at constant pressure (C_p)

$$\text{From equation (2), } C = \frac{du + Pdv}{dT}$$

We know that enthalpy of the system $H = U + PV$

Differentiating at constant pressure,

$$dH = dU + PdV$$

$$\text{Equation (2) becomes } C_p = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \quad \dots \dots \dots \quad (4)$$

Thus, molar heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature.

Relationship between C_p and C_v in gaseous system.

Molar heat capacity at constant pressure is always greater than that at constant volume. This is because when the gas is heated at constant volume, the heat absorbed by the gas is used to increase the internal energy only without doing any external work. But heating the gas at constant pressure results in doing the external work and also raising the internal energy of the system.

The difference between C_p and C_v gives the work done by 1 mole of the gas during expansion when heated through 1°C at constant pressure.

$$C_p - C_v = \left[\frac{\partial H}{\partial T}\right]_P - \left[\frac{\partial U}{\partial T}\right]_V \quad \dots \dots \dots \quad (5)$$

We know, $H = U + PV$

Differentiating both the sides with respect to temperature at constant pressure, we have

$$\left[\frac{\partial H}{\partial T}\right]_P = \left[\frac{\partial U}{\partial T}\right]_P + P \left[\frac{\partial V}{\partial T}\right]_P \quad \dots \dots \dots \quad (6)$$

Substituting the value of $\left[\frac{\partial H}{\partial T}\right]_P$ from equation (6) in eqn. (5),

We have

$$C_p - C_v = \left[\frac{\partial U}{\partial T}\right]_P + P \left[\frac{\partial V}{\partial T}\right]_P - \left[\frac{\partial U}{\partial T}\right]_P \quad \dots \dots \dots \quad (7)$$

Again, we know that $U = f(T, V)$

$$\text{So, } dU = \left[\frac{\partial U}{\partial T} \right]_V dT + \left[\frac{\partial U}{\partial V} \right]_T dV$$

Dividing through out by dT and keeping pressure P constant.

We have

$$[\frac{\partial U}{\partial T}]_P = [\frac{\partial U}{\partial T}]_V + [\frac{\partial U}{\partial V}]_T [\frac{\partial V}{\partial T}]_P \dots \dots \dots (8)$$

Substituting the value of $\left[\frac{\partial U}{\partial T} \right]_P$ from eqn (8) in eqn. (7),

We have,

$$C_p - C_v = \left[\frac{\partial U}{\partial T} \right]_V + \left[\frac{\partial U}{\partial V} \right]_T \left[\frac{\partial V}{\partial T} \right]_P + P \left[\frac{\partial V}{\partial T} \right]_P - \left[\frac{\partial U}{\partial T} \right]_V \\ = \left[\frac{\partial U}{\partial V} \right]_T \left[\frac{\partial V}{\partial T} \right]_P + P \left[\frac{\partial V}{\partial T} \right]_P \quad \dots \dots \dots (9)$$

The term $\left[\frac{\partial U}{\partial V} \right]_T$ is zero for an ideal gas.

$$\text{So, } C_p - C_v = P \left[\frac{\partial V}{\partial T} \right]_P \dots \dots \dots \quad (10)$$

Again, for 1 mole of ideal gas, $PV = RT$

Differentiating this equation with respect to temperature at constant pressure, we have

$$P \left[\frac{\partial V}{\partial T} \right] P = R \dots \quad (11)$$

Thus, equation (10) becomes

$$C_P - C_V = R$$

Thus, the difference between molar heat capacity at constant pressure (C_p) and at constant volume (C_v) is equal to the gas constant R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Measurement of the Enthalpy change (ΔH) and change in Internal energy (ΔU)

In a chemical reaction, heat evolved or absorbed is measured by carrying out the reaction in an apparatus called **calorimeter**. The principle is based on the fact that the heat given out is equal to the heat taken in,

If Q = Amount of heat of reaction taken out

W = Water equivalent of the calorimeter

m = Mass of liquid taken the calorimeter

S = Specific heat

T_1 = Initial temperature and

T_2 = Final temperature

$$Q = (W + m) \times S \times (T_2 - T_1)$$

The common types of calorimeter used for the measurement are

- (i) Water calorimeter
- (ii) Bomb calorimeter

(i) Water calorimeter : This is the simple form of calorimeter normally used in physical laboratories (Fig. 8.4)

It consists of a large vessel in which the calorimeter is placed on cork. Packing material such as cotton wool separates the vessel from the calorimeter. There are holes inside the calorimeter through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken inside the calorimeter. Known amounts of reacting substances are taken in the boiling tube. The heat evolved during the reaction will be absorbed by water. The rise in temperature is recorded with the help of the thermometer. The heat evolved is then calculated using the formula mentioned above. It may be noted that the heat evolved is not lost since the calorimeter is separated from the large vessel with the help of insulating material like cotton wool.

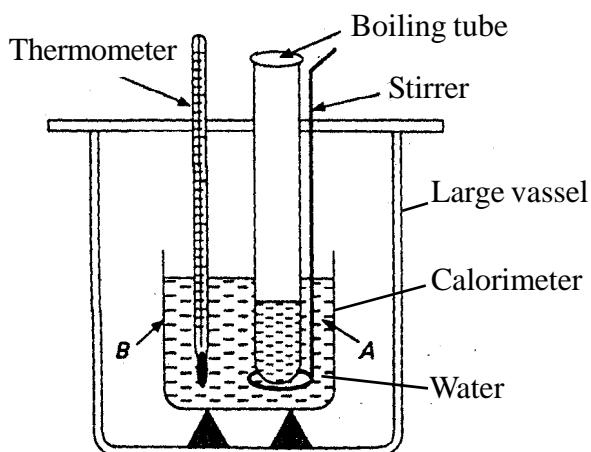


Fig. 8.4 Water calorimeter

(ii) Bomb Calorimeter : This is commonly used to determine the heat of combustion (enthalpy of combustion) of organic substances. The apparatus consists of a sealed combustion chamber called a bomb. A weighed amount of substance is taken in a dish with oxygen at about 20 atm. pressure is placed inside the bomb, which is taken inside the water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in Fig. 8.5

The temperature of water is noted and the substance is ignited by electric current. After combustion, the rise in temperature of the system is noted. From the heat gained by water and calorimeter, the enthalpy of combustion can be calculated.

The enthalpy of combustion measured is actually ΔU , since the reaction takes place at constant volume inside the bomb calorimeter

$$\Delta U = \frac{(W + m)(T_2 - T_1) \times S}{W_1} \times M \text{ kcal.}$$

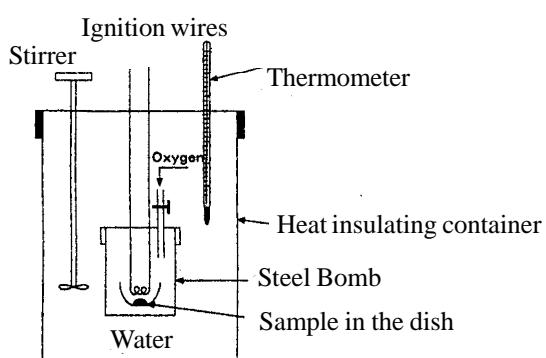


Fig. 8.5 The arrangement of Bomb calorimeter

Where M = Molecular mass of the substance

W_1 = Mass of the substance taken

ΔH can be calculated using the relationship

$$\Delta H = \Delta U + \Delta nRT$$

8.6 THERMOCHEMISTRY AND THERMOCHEMICAL REACTIONS

Thermochemistry is a branch of physical chemistry which deals with heat changes accompanying chemical reactions. The chemical reactions accompanied with evolution or absorption of heat energy are known as **thermochemical reactions**.

TYPE OF THERMOCHEMICAL REACTIONS :

(a) Exothermic reactions (Exoergic reactions)

- (i) Such reactions proceed with evolution of heat.
- (ii) The energy of the product is less than the energy of the reactants in $H_P < H_R$
- (iii) ΔH is -ve. The value of ΔH is written on the product side with a (+) sign.
- (iv) If heat content is plotted against extent of reaction, the nature of the graph will be as follows.

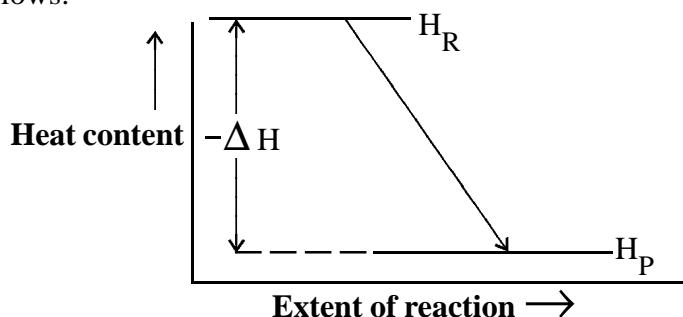
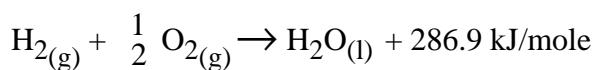
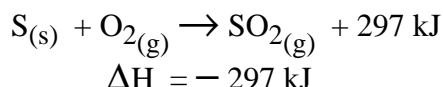
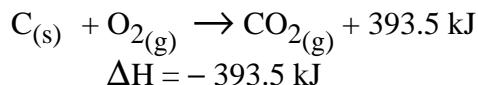


Fig 8.6. : Plot of Heat content against Extent of reaction for an exothermic reaction.

- (v) Examples of such type of reactions are



$$\Delta H = -286.9 \text{ kJ/mole}$$



(b) Endothermic reactions (Endoergic reactions):

- (i) Such reactions proceed with absorption of heat.
- (ii) The energy of the product is more than that of the reactant.
i.e. $H_P > H_R$

- (iii) ΔH is + ve. The value of ΔH is written on the product side with a (-) sign.
- (iv) If heat content is plotted against extent of reaction, the nature of the graph will be as follows.

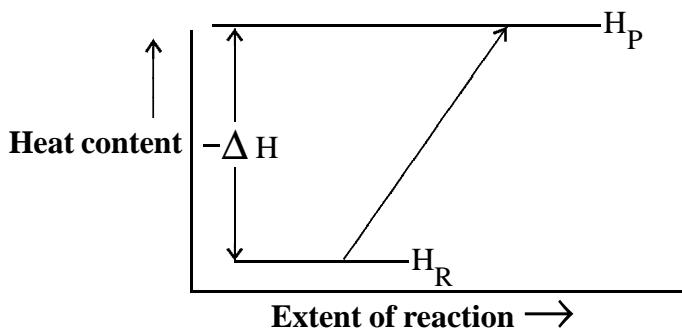


Fig 8.7 - Plot of heat content against extent of reaction for endothermic reaction.

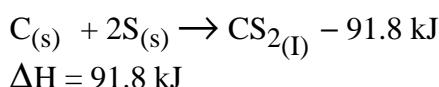
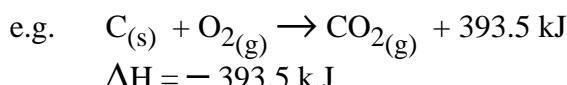
- (v) Examples of such reactions are :
- $$\text{NH}_4\text{Cl}_{(\text{S})} + \text{aq} \rightarrow \text{NH}_4\text{Cl}_{(\text{aq})} - 16.11 \text{ kJ}$$
- $$\Delta H = + 16.11 \text{ kJ}$$
- $$\text{Ice (1 gm)} \rightarrow \text{Water (1 gm)} - 334.7 \text{ kJ}$$
- $$\Delta H = + 334.7 \text{ kJ}$$

8.7 ENTHALPY CHANGES IN CHEMICAL REACTIONS (Heat of Reaction)

It is defined as the quantity of heat evolved or absorbed when the number of gram molecules of the substances taking part in the chemical reaction as indicated in the balanced thermochemical reaction have completely reacted giving the products. In otherwords it is the difference between the heat content of the products and that of the reactants.

i.e. Heat of reaction = (Heat content of the product) – (Heat content of the reactant)

$$\text{or, } \Delta H = \sum H_p - \sum H_r$$



Factors affecting Enthalpy of reaction : Enthalpy of reaction depends on the following factors.

- (i) **Amount of reactants :** More the amount of the reactants more is the heat evolved or absorbed as the case may be.
- (ii) **Physical state of the reactants and products :** The change of physical state is accompanied with heat change. So the value of ΔH depends on the physical state of the substances.
- (iii) **Temperature :** The value of ΔH for a reaction changes with change in temperature.

Enthalpy change of reaction at constant volume (Q_v)

Consider a chemical reaction taking place at constant temperature and at constant volume. In such a case, work done by the system ' W ' = 0

According to the 1st law of thermodynamics, $Q = \Delta U + W$,

$$\text{So, } \Delta U = Q_v \dots \quad (1)$$

Where Q_v is the heat or enthalpy of reaction at constant volume.

If U_p = Internal energy of the product

U_R = Internal energy of the reactant

$$\Delta U = U_B - U_{B'} = Q_V$$

Enthalpy change of reaction at constant pressure (Q_p)

Consider a chemical reaction taking place at constant pressure.

Let us suppose H_p = Enthalpy of reactants

H_p = Enthalpy of products.

Since $H = U + PV$

$$H_R = U_R + PV_1$$

$$H_p = U_p + PV,$$

$$\Delta H = H_p - H_R = (U_p - U_R) + P(V_2 - V_1) = \Delta U + P\Delta V \dots \dots (2)$$

If Q_p be the amount of heat exchanged in the above reaction i.e. the enthalpy change of the reaction at constant pressure,

Then, $Q_p = \Delta H = \Delta U + P\Delta V$ (3)

Relationship between Q_p and Q_v

We known that $\Delta H = \Delta U + P\Delta V$ (Eqn.2)

Also, $Q_v = \Delta U$ and $Q_p = \Delta H$ (Eqn. 1 & 3)

So, we may also write.

$$Q_p = Q_v + P\Delta V \dots \quad (4)$$

For 'n' moles of ideal gas, $PV = nRT$

Let n_1 = no. of moles of the reactants.

V_1 = volume occupied by the gaseous reactants

n_2 = no. of moles of the products.

V_g = volume occupied by the gaseous products

At constant temperature and pressure,

$$PV_1 = n_1 RT$$

$$PV_2 = n_2 RT$$

$$\text{So, } PV_2 - PV_1 = n_2 RT - n_1 RT$$

$$\text{Or, } P(V_2 - V_1) = (n_2 - n_1)RT$$

Substituting the value of $P\Delta V$ in eqn.(4)

$$Q_p = Q_v + \Delta n RT$$

where Δn = Difference between the number of moles of gaseous products and gaseous reactants.

Special cases :

- (i) When the reactants and products are in solid or liquid state, ΔV becomes almost negligible and under such condition $Q_p = Q_v$
 - (ii) When the number moles of gaseous reactants is same as those of gaseous products, i.e. $n_1 = n_2$.

Under such condition, $\Delta n = 0$ and $Q_p = Q_v$

Examples : 1. Dissociation of NH₃



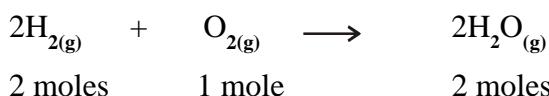
2 moles 1 mole 3 moles

In this case, $n_1 = 2$, $n_2 = 1+3 = 4$

$$\Delta n = 4 - 2 = 2$$

$$Q_p = Q_v + \Delta n RT = Q_v + 2RT$$

2. Combination of Hydrogen and Oxygen



In this case, $n_1 = 2+1 = 3$, $n_2 = 2$

$$\Delta n = n_2 - n_1 = 2 - 3 = -1$$

$$Q_p = Q_v + \Delta n RT = Q_v - RT$$

Standard Enthalpy (Heat) of reaction :

ΔH values are usually reported in a standard or reference state. This is because value of ΔH varies with temperature. The standard state is the most stable state of a substance under 1 atmospheric pressure and 298 K.

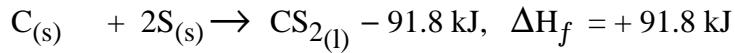
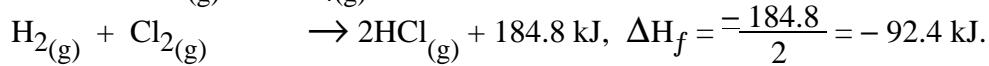
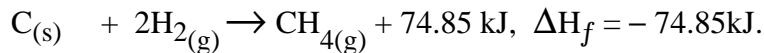
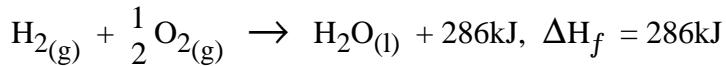
So, when a process is carried out at 298 K and 1 atmospheric pressure the enthalpy change ΔH of a reaction is called the **standard enthalpy change** and it is represented as ΔH° .

8.8 TYPES OF ENTHALPIES OF REACTIONS

1. Enthalpy of formation (ΔH_f) :

It is the quantity of heat evolved or absorbed (change in enthalpy) when 1 mole of the substance is formed from its constituent elements under given conditions of temperature and pressure.

For example –



Standard enthalpy of formation (ΔH_f^0)

When all the substances involved are in their standard states (1 atm. pressure and 298 K) the enthalpy change accompanying the formation of 1 mole of the compound from its elements is known as **standard enthalpy of formation (ΔH_f^0)**. The values of standard heat of formation of elementary substances are taken to be zero.

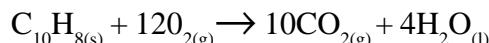
Importance of enthalpy of formation.

The enthalpy of reaction can be calculated by the help of heat of formation values.

$$\Delta H^\circ = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$$

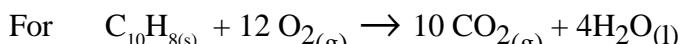
Example - 1

The enthalpy of reaction for



at constant volume is 4345.1 kJ at 25°C. Calculate the heat of reaction at constant pressure at 25°C

Solution :



Given $\Delta n = 10 - 12 = -2$ (only in gaseous phase)

$$T = 298 \text{ K}$$

$$\Delta U = 4345.1 \times 10^3 \text{ Joules}$$

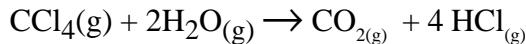
$$R = 8.3143 \text{ Joules K}^{-1} \text{ mole}^{-1}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\begin{aligned}
 &= 4345.1 \times 10^3 + (-2) (8.3143) (298) \\
 &= -4350055.3 \text{ Joules} \\
 &= -4350.055 \text{ kJ}
 \end{aligned}$$

Example - 2

The standard heats of formation for $\text{CCl}_4(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -25.5 , -57.8 , -94.1 and -22.1 kcal respectively. Calculate $\Delta H_{(298)}$ for the reaction in kJ.



$$\begin{aligned}
 \text{Solution : } \Delta H_{\text{Reaction}}^0 &= \Delta H_{\text{Product}}^0 - \Delta H_{\text{Reactants}}^0 \\
 &= \Delta H_{\text{CO}_2}^0 + 4 \times \Delta H_{\text{HCl}}^0 - \Delta H_{\text{CCl}_4}^0 - 2 \times \Delta H_{\text{H}_2\text{O}}^0 \\
 \text{or, } \Delta H_{\text{Reaction}}^0 &= -94.1 + 4 \times (-22.1) - (-25.5) - 2 \times (-57.8) \\
 \text{or, } \Delta H_{\text{Reaction}}^0 &= -41.4 \text{ kcals} = -41.4 \times 4.184 = -173.2 \text{ kJ}
 \end{aligned}$$

Example - 3

The molar heat of formation of $\text{NH}_4\text{NO}_3(\text{s})$ is -367.54 kJ and those of $\text{N}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{l})$ are 81.46 and -258.8 kJ respectively at 25°C and 1 atmospheric pressure. Calculate ΔH and ΔU of the reaction.



Solution :

$$\begin{aligned}
 \Delta H_{\text{Reaction}} &= H_{\text{product}} - H_{\text{reactant}} \\
 &= (\Delta H_{\text{N}_2\text{O}} + \Delta H_{\text{H}_2\text{O}} \times 2) - (\Delta H_{\text{NH}_4\text{NO}_3}) \\
 &= (81.46 + 2 \times -258.8) - (-367.54) \\
 &= -122.56 \text{ kJ}.
 \end{aligned}$$

$$\text{Again, } \Delta H = \Delta U + \Delta nRT$$

$$\text{Here } \Delta n = 1 - 0 = 1$$

$$R = 8.314 \text{ J}$$

$$T = 298 \text{ K}$$

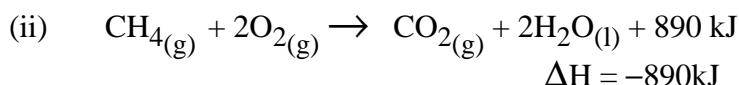
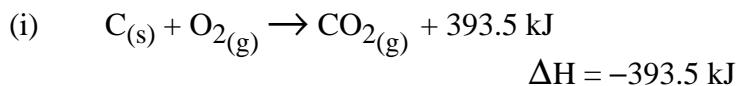
$$\therefore -122.56 \times 10^3 = E + 8.314 \times 298$$

$$\text{or } \Delta U = -125037 \text{ Joule}$$

$$= -125.037 \text{ k Joule.}$$

2. Enthalpy of combustion :

It is defined as the enthalpy change (ΔH) accompanying the complete combustion of one mole of the substance at a given temperature.



Since combustion is always accompanied with evolution of heat, enthalpy of combustion ΔH is always -ve.

Importance of Enthalpy of Combustion

The value of enthalpy of combustion helps us in comparing the efficiencies of fuels. A fuel having higher value of enthalpy of combustion is considered to be a better fuel.

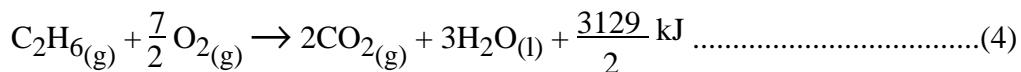
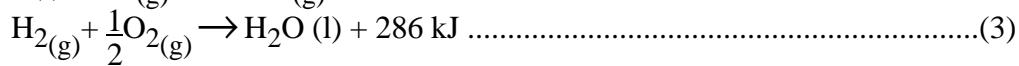
Example - 4

When 2 moles of $\text{C}_2\text{H}_6\text{(g)}$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $\text{C}_2\text{H}_6\text{(g)}$. ΔH_f for $\text{CO}_2\text{(g)}$ and $\text{H}_2\text{O(l)}$ are -395 and -286 kJ mole $^{-1}$ respectively. (Roorkee 1988)

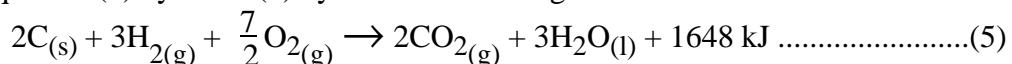
Solution - We have to find



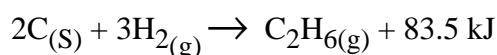
As per question.



Multiplying equation (2) by 2 and (3) by 3 and then adding.



Subtracting equ. (4) from (5)



$$\therefore \Delta H_f \text{ of } C_2H_6 = -83.5 \text{ kJ}$$

Example - 5

Calculate standard heat of formation of CS_2 . Given that standard heat of combustion of C, S and CS_2 are -393.3 , -293.72 and $-1108.76 \text{ kJ mole}^{-1}$ respectively (Roorkee 1989)

Solution :

The required equation is :



As given in the question





Multiplying equation (2) by 2 and adding equation (1)



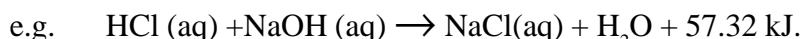
Subtracting equation (3) from equation (4)



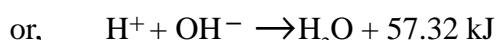
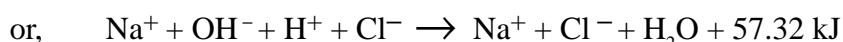
$$\therefore \Delta H = 128.02 \text{ kJ.}$$

3. Enthalpy of neutralisation :

It is defined as the enthalpy change when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice versa in a fairly dilute solution.



The process of neutralisation involves the reaction between H^+ ion of the acid with OH^- ion of the base leading to the formation of unionised water molecule. Consider the reaction between NaOH and HCl .

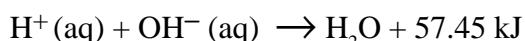


Thus, enthalpy of neutralisation of a strong acid with a strong base may be defined as the enthalpy of formation of water from H^+ and OH^- ions.

However, when acid or base is weak the enthalpy of neutralisation is lower than 57.32 kJ since a part of the heat evolved by the combination of H^+ and OH^- ions consumed in causing the ionisation of acid or base. The enthalpy of neutralisation is still lower when both acid and base are weak. For example enthalpy of neutralisation of NH_4OH (weak base) by HCl (strong acid) is -51.9 kJ whereas that of CH_3COOH by NH_4OH is -12.1 kJ (here both are weak)

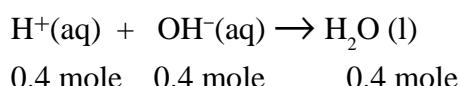
Example - 6

Given that :



Calculate the heat released when 0.4 moles of HCl is neutralised by 0.4 moles of KOH in aqueous solution.

Solution :



When 1 mole of water is formed heat released is 57.1 kJ

When 0.4 moles of water is formed heat released is $57.1 \times 0.4 = 22.84$ kJ.

Example - 7

Given $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + 57.1$ kJ. Calculate the heat released.

- (i) When 200 ml of 0.2 M HCl solution is mixed with 100 ml of 0.1 M KOH solution.
- (ii) An aqueous solution containing 0.5 moles of HNO_3 is mixed with an aqueous solution containing 0.2 moles of NaOH.

Solution :

- (i) 200 ml of 0.2 M HCl contains $\frac{200 \times 0.2}{1000} = 0.04$ moles of HCl
- (ii) 100 ml of 0.1 M KOH contains $\frac{100 \times 0.1}{1000} = 0.01$ moles of KOH

0.01 mole of KOH will neutralise 0.01 mole of HCl to form 0.01 mole of water and $(0.04 - 0.01)$ i.e. 0.03 mole of HCl remain unreacted.

So, amount of heat released in the formation of 0.01 mole of water = $57.45 \times 0.01 = 0.574$ kJ.

- (ii) 0.2 moles of NaOH neutralise 0.2 moles of NO_3^- to form 0.2 moles of H_2O and 0.3 moles of HNO_3 remain unreacted.

So, heat released as a result of formation of 0.2 mole of water is $57.45 \times 0.2 = 11.49$ kJ.

4. Enthalpy of solution :

When a solute is dissolved in a solvent heat is either evolved or absorbed. Consequently there is heat change accompanying the system and this heat change is known as **enthalpy of solution**.

It is defined as the amount of heat evolved or absorbed, when 1 mole of the solute is dissolved in a large excess of water so that any further dilution of the solution produces no heat change.

- e.g. (i) $\text{KCl} + \text{aq} \rightarrow \text{KCl(aq)} - 18.6$ kJ
 $\Delta H = 18.6$ kJ
- (ii) $\text{MgSO}_4 + \text{aq} \rightarrow \text{MgSO}_4(\text{aq}) + 84.9$ kJ
 $\Delta H = -84.9$ kJ

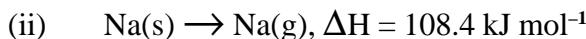
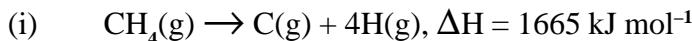
5. Enthalpy of atomisation

It is defined as the enthalpy change for the conversion of compounds and elements into free atoms. This is usually highly endothermic.

- e.g. $\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}, \Delta H = 435$ kJ mol⁻¹

In the above case the H atoms are formed by breaking H–H bond in hydrogen molecule. The enthalpy change is known as the enthalpy of atomisation of hydrogen. It is the enthalpy change in breaking 1 mole of bonds completely to get atoms in the gaseous phase. Here the enthalpy of atomisation is also the bond dissociation enthalpy.

Other Examples:



In this case the enthalpy of atomisation is same as enthalpy of sublimation.

6. Enthalpy of dilution

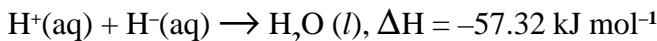
The enthalpy change when some moles of solvent is added to an aqueous solution is the enthalpy of dilution.



So the enthalpy of dilution of $\text{HCl}(\text{g})$ from 10aq to 40aq is $(72.8 - 69) = 3.8 \text{ kJ mol}^{-1}$

7. Enthalpy of ionisation

We know that enthalpy of neutralisation of strong acid with a strong base is same as the enthalpy of formation of water from H^+ and OH^- ions.



The standard enthalpies of neutralisation of strong acid by strong base are almost identical as evident from Table 8.1.

If however the acid or alkali is weak the enthalpy of neutralisation is less since the reaction involves ionisation of weak acid or weak alkali.

For example

1. The enthalpy of neutralisation of CH_3COOH by NaOH has been found to be $-55.23 \text{ kJ mol}^{-1}$. Since the average value for the combination of H^+ and OH^- ions is taken as $-57.32 \text{ kJ mol}^{-1}$, the standard enthalpy of ionisation or dissociation of acetic acid may be taken as $(57.32 - 55.23) = 2.09 \text{ kJ mol}^{-1}$
2. The enthalpy of neutralisation of HCl by NH_4OH is $-51.34 \text{ kJ mol}^{-1}$. So the enthalpy of ionisation/dissociation of NH_4OH is $(57.32 - 51.34) = 5.98 \text{ kJ mol}^{-1}$. The enthalpies of neutralisation of some weak acids with NaOH are given Table 8.2.

Table 8.1

Standard enthalpies of neutralisation of strong acids by strong bases (kJ mol^{-1})

Acid	Alkali	Enthalpy of neutralisation (kJ mol^{-1})
HCl	NaOH	-57.32
HNO_3	NaOH	-57.28
HCl	KOH	-57.45
HCl	LiOH	-57.38

Table 8.2
Standard enthalpies neutralisation of weak with NaOH

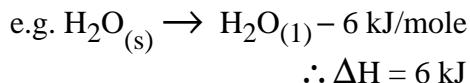
Acid	Enthalpy of neutralisation (kJ mol ⁻¹)	Enthalpy of ionisation of dissolution (kJ mol ⁻¹)
CH ₃ COOH	- 55.23	+ 2.09
HCOOH	- 56.06	+ 1.26
HCN	- 12.13	+ 45.19
H ₂ S	- 15.90	+ 41.42

8.9 ENTHALPY OF PHASE CHANGES

Matter exists in three different states namely solid, liquid and gas. When it changes its state there is heat change. This heat change is known as **Enthalpy of phase change**. For example solid changes over to liquid at its melting point whereas conversion of liquid to vapour takes place at boiling point of liquid. Each transformation is associated with change in heat content of the system.

(a) Enthalpy of fusion or Heat of fusion

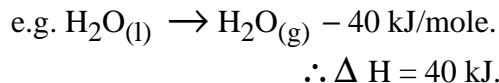
The enthalpy change accompanying the change of one mole of the substance from solid phase to the liquid phase at its melting point is known as **heat of fusion**. Heat of fusion is always positive.



The value of heat of fusion helps us in distinguishing ionic solids from molecular solids. The ionic solids have high value of heat of fusion whereas the molecular solids have low values. This is because of the presence of greater interparticle forces in case of ionic solids.

(b) Enthalpy of vaporisation or Heat of vaporisation

The enthalpy of vaporisation is defined as the change of enthalpy accompanying the change of one mole of the substance from liquid phase to vapour phase at its boiling point. Heat of vaporisation is also always positive.

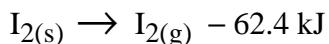


The more the value of enthalpy of vaporisation the stronger is the intermolecular forces existing between the molecules constituting the liquids. The enthalpy of vaporisation of water is + 40 kJ per mole whereas that of liquids O₂ is + 0.67. This is because in case of water the intermolecular forces are hydrogen bonds which are considered to be stronger than the van der Waals forces operating between the oxygen molecules.

(c) Enthalpy of sublimation or Heat of sublimation :

The enthalpy change associated with the change of 1 mole of the substance from the solid phase to the vapour phase at a given temperature below its melting point is known as **enthalpy of sublimation**.

Enthalpy of sublimation of a system is the sum of enthalpy of fusion at its melting point and enthalpy of vaporisation at its boiling point i.e. $\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$



$$\text{So, } \Delta H = 62.4 \text{ kJ}$$

8.10 HESS'S LAW OF CONSTANT HEAT SUMMATION

In 1840 **Hess**, a Russian chemist after performing a large number of experiments expressed his experimental findings in the form of a law known as **Hess's law**.

Statement : If a chemical change takes place in two or more different ways whether in one step or in several steps, the amount of heat evolved or absorbed in the total change is the same, no matter, by whichever method the change is brought about.

Example : Carbon can be oxidised to CO_2 in two different ways.

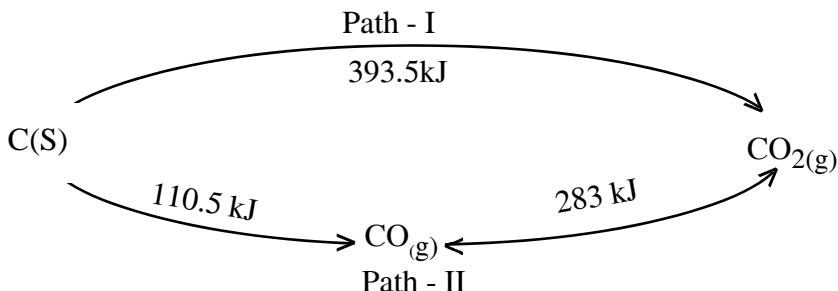
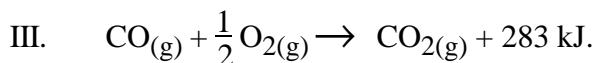
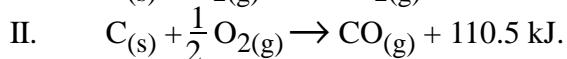
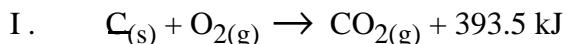


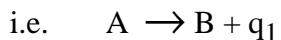
Fig 8.8 Demonstration of Hess's law

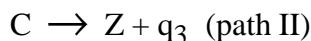
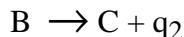
It is evident that 393.5 kJ heat is evolved when the change is brought about by path I. Again path II involves two steps in which the same quantity of heat ($110.5 + 283 = 393.5$ kJ) is evolved.

Proof : Let us start with a substance 'A' which is converted to 'Z' in one step via path -I. The conversion is associated with the evolution of Q_1 quantity of heat. (Fig 1.7)



Again let 'A' be converted to 'Z' through some intermediate steps via path-II with the evolution of Q_2 quantity of heat.





Total amount of heat evolved is $(q_1 + q_2 + q_3) = Q_2$

According to Hess's law $Q_1 = Q_2$

If Q_2 is not equal to Q_1 , let $Q_2 > Q_1$

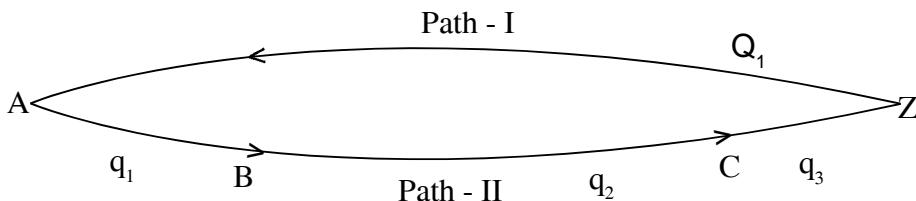


Fig 8.9 Proof of Hess's Law

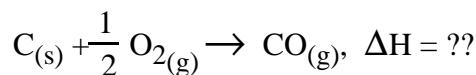
Consider the cyclic process AZA. If the system changes its state from A to Z via path II, Q_2 amount of heat will be evolved. Again when the system changes to state 'A' via path I, Q_1 amount of heat is to be absorbed. If we consider the whole cycle ($Q_2 - Q_1$) amount of heat will be gained by the system. So repeating the process a number of times, a huge amount of heat can be generated which is against the 1st law of Thermodynamics i.e. against law of conservation of energy. Hence, Q_2 can not be greater than Q_1 , it must be equal to Q_1 .

APPLICATION OF HESS'S LAW :

(1) Calculation of Enthalpies of reaction :

Enthalpies of many reactions can not be determined experimentally. However, these enthalpies can be calculated by the help of Hess's Law.

For example, it is difficult to measure the heat evolved during combustion of 'C' to CO.



But the combustion of 1 mole of 'C' to CO_2 involves the evolution of 393.5 kJ and that of CO to CO_2 involves evolution of 282 kJ of heat energy.

Since both these processes can be studied experimentally the heat evolved during the process of conversion of $C_{(s)}$ to $CO_{(g)}$ can be calculated by the use of Hess's Law. If heat evolved is Q then.

$$Q = [\text{Heat evolved during formation of } CO_2 \text{ from C}]$$

$$- [\text{Heat evolved during formation of } CO_2 \text{ from CO}]$$

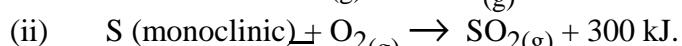
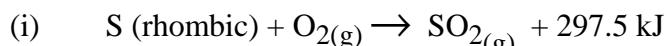
$$= -393.5 - (-282)$$

$$= -111.5 \text{ kJ.}$$

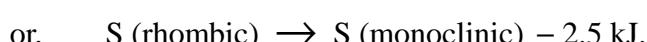
(2) Determination of enthalpy changes of slow reaction.

There are some reactions which take place so slowly that the enthalpy change accompanying such reactions can not be determined accurately. To determine the enthalpy change of such reactions accurately, Hess's law may be used.

For example, consider the transition of rhombic sulphur to monoclinic sulphur. Direct measurement of enthalpy change accompanying the transition is not possible since the process is very slow. But the enthalpies of combustion of rhombic and monoclinic sulphur are found to be – 297.5 and – 300 kJ respectively.



Subtracting (i) from (ii) and rearranging



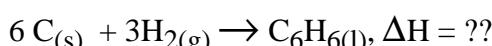
Thus transformation of 1 gm atom of rhombic to monoclinic sulphur involves absorption of 2.5 kJ of heat.

(3) Determination of Enthalpy of formation :

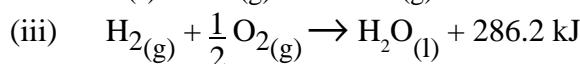
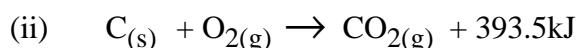
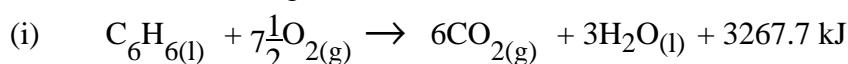
It is not possible to determine experimentally the heat of formation of some compounds. The same may be determined by the application of Hess's law.

For example, the enthalpy of formation of Benzene can be calculated from the enthalpy of combustion of benzene and enthalpies of formation of water and carbon dioxide.

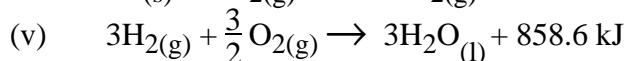
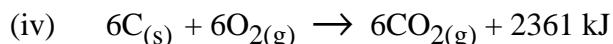
The desired thermochemical equation is



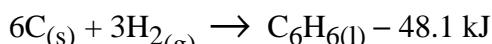
We have with us the following data.



Multiplying eqn (ii) by 6 (iii) by 3 we get



Adding (iv) and (v) and subtracting eqn. (i) we have



Thus, $\Delta H = 48.1 \text{ kJ.}$

8.11 BOND ENERGY

Bond energy is a measure of strength of a bond. The more the bond energy the stronger is the bond. Different types of bonds are associated with different bond energies.

When a chemical bond is formed between two free atoms in the gaseous state the energy of the system decreases i.e. some energy in the form of heat is given out. So, to break the same bond an equivalent amount of energy must be given to the system. This amount of energy required to break a type of bond in one mole of the compound is usually known as **bond energy**.

Definition : It may be defined in either of the ways given below.

- (i) It is defined as the average amount of energy required to break one type of bond present in one mole of the compound.
- (ii) It is referred to as the heat of formation of the bond. So, the enthalpy change associated with conversion of 1 mole of gaseous molecules to constituent gaseous atoms is known as **bond energy**.

In case of a diatomic molecule AB the bond energy is the energy required to break 1 mole of AB into its constituents A and B. But in case of polyatomic molecule, bond energy is the average value.

Calculation of Bond energy :

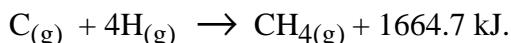
Steps involved

- (i) Determine the enthalpy of formation of compound and also the enthalpy of dissociation of molecules of common elements.
- (ii) Calculate the total heat of formation by Hess's law.
- (iii) Consider total no. of bonds and calculate average bond energy.

Bond energy of CH₄ can be calculated from the following data.

- (i) C_(s) + 2H_{2(g)} → CH_{4(g)} + 74.9 kJ.
- (ii) 2H_{2(g)} → 4H_(g) - 870.2 kJ
- (iii) C_(s) → C_(g) - 719.6 kJ.

Adding equations (ii) and (iii) and subtracting from equation (i).



So 1664.7 kJ of heat energy is required to break four moles of C – H bonds in methane. Thus the average bond energy per mole of C – H bond is = 1664.7/4 = 416.2 kJ

The value of enthalpies of formation of bonds i.e the bond energies at 25°C are given in the following Table 8.3.

Table 8.3 Value of Bond energy at 25°C

Bond	Enthalpy of formation (kJ mole ⁻¹)	Bond	Enthalpy of formation (kJ mole ⁻¹)
H – H	435.1	C – Cl	330.5
H – F	564.8	C – Br	276.1
H – Cl	430.9	C – S	259.4
H – Br	368.2	C = S	477.0
O – O	138.1	C – N	292.9
O = O	439.7	C = N	615.0
O – H	464.4	C ≡ N	878.6
C – H	416.2	N – N	159.0
C – O	351.4	N = N	418.4
C = O	711.3	N ≡ N	945.6
C – C	347.3	N – H	389.1
C = C	615.0	F – F	154.8
C ≡ C	811.7	Cl – Cl	242.7
C – F	439.3	Br – Br	192.5

Factors affecting the Bond energy :

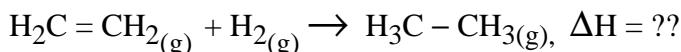
- Atomic size -** The strength of the bond depends on the size of the atoms. The smaller the size of the atom, greater is the force of attraction operating between the atoms and hence stronger is the bond and more is the bond energy.
e.g. Bond energy of H – H is 435.1 kJ mole⁻¹ whereas that of C – C is 347.3 kJ mole⁻¹
- Extent of overlapping of bonding orbitals :** It is a fact that more the extent of overlapping of bonding orbitals more is the energy released and more is the bond energy.
e.g. Bond energy of C – C bond is 347.3 kJ mole⁻¹ whereas that of C = C bond is 615.0 kJ mole⁻¹ and that of C ≡ C bond is 811.7 kJ mole⁻¹. This is because the overlapping of bonding orbitals is to a greater extent in case of a triple covalent bond (C ≡ C) than in case of a double covalent bond and single covalent bond (C = C and C – C bond)
- Electronegativity :** The difference in the values of electronegativities between the combining atoms also influence the bond energy. The greater the difference in electronegativities, the stronger is the bond and more is the bond energy. This is because of the greater polarisability of the bond.
e.g. bond energy, of HCl. is 430.9 kJ mole⁻¹ whereas that of HBr is 368.2 kJ mole⁻¹.
- Resonance energy :** Resonance energy greatly affects the stability of a molecule. The greater the resonance energy a molecule, the more is the stability and therefore stronger is the bond and more is the bond energy.

5. **Bond length :** Bond energy is also known as **bond dissociation energy**. Bond dissociation energy is less, if the bond length is more and vice versa.

e.g. Bond length of C–C is 1.54 \AA^0 whereas that of C=C bond is 1.36 \AA^0 . Thus bond energy of C–C bond is $347.3\text{ kJ mole}^{-1}$ whereas that of C=C bond is 615 kJ mole^{-1} .

Applications of Bond energy :

1. **Determination of Enthalpies of reactions :** Bond energy helps in the calculation of enthalpies of reactions. Suppose we want to determine the enthalpy of the reaction.



In the above reaction four C – H bonds in C_2H_4 remain unaffected. A double bond breaks in ethylene and the H – H bond breaks in H_2 . On the otherhand two new C – H bonds are formed in ethane.

$$\text{So, } \Delta H = \{\Delta H_{\text{C}=\text{C}} + \Delta H_{\text{H-H}}\} - \{\Delta H_{\text{C-C}} + \Delta 2H_{\text{C-H}}\}$$

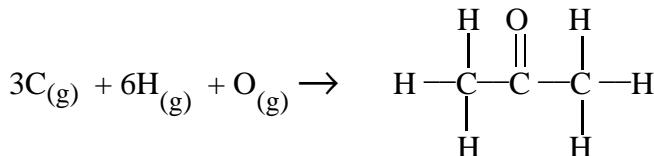
Substituting the value of bond energy from the above table. (1.1) we get

$$\begin{aligned}\Delta H &= (615 + 435.1) - (347.3 + 2 \times 416.2) \text{ kJ} \\ &= -129.6 \text{ kJ.}\end{aligned}$$

[$\Delta H = \text{B.E. of reactants} - \text{B.E. of products}$]

2. **Calculation of Enthalpy of formation :** Using the bond energy data as mentioned in the above table, the heat of formation of certain compounds can be calculated.

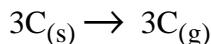
e.g. Consider the formation of acetone.



The bonds that break :

- (i) Three H – H bonds giving six H – atoms.
- (ii) Half O – O bond giving one 'O' atom.

Besides these two, sublimation of three atoms of $\text{C}_{(\text{s})}$ giving three atoms of $\text{C}_{(\text{g})}$ also takes place.



The bonds that are formed

- (i) Two C – C bonds.
- (ii) Six C – H bonds.
- (iii) One C = O bond

Enthalpy of formation of CH_3COCH_3 is :

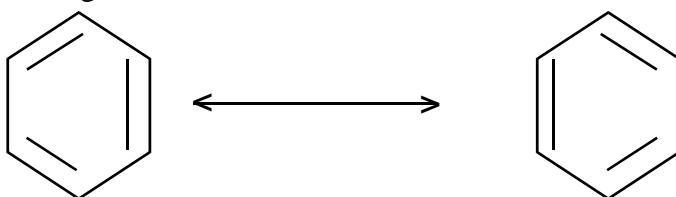
$$\begin{aligned}\Delta H_f &= [3(\Delta H_{\text{H-H}}) + \frac{1}{2}(\Delta H_{\text{O-O}}) + 3(\Delta H_{\text{C(s)}} \rightarrow \text{C(g)})] \\ &\quad - [2(\Delta H_{\text{C-C}}) + 6(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C=O}})]\end{aligned}$$

Substituting the values of B. E. from the above table (1.1) we have

$$\begin{aligned}\Delta H_f &= [(3 \times 435.1) + (\frac{1}{2} \times 138.1) + (3 \times 719.6)] \\ &\quad - [(2 \times 347.3) + (6 \times 416.2) + 711.3] \text{ kJ} \\ &= (1305.3 + 69.05 + 2157.9) - (694.6 + 2497.2 + 711.3) \text{ kJ} \\ &= 3532.25 - 3903.1 \text{ kJ} \\ &= -370.85 \text{ kJ mole}^{-1}\end{aligned}$$

3. Calculation of Resonance energy :

If a compound exhibits resonance it is considered to be a stable compound. It is a fact that more the number of resonating structures more is the stability. In case of Benzene there are two Kekulé resonating structures.



For this compound benzene, the enthalpy of formation as calculated from bond energy very much differs from the experimental value. The difference between the two values is a measure of resonance energy of benzene.

Let us consider dissociation of Benzene,



During dissociation of Benzene the following bonds break.

- (i) Three C – C single bonds
- (ii) Three C = C double bonds.
- (iii) Six C – H bonds

$$\begin{aligned}\text{The dissociation energy } \Delta H_d &= 3(\Delta E_{\text{C-C}}) + 3(\Delta E_{\text{C=C}}) + 6(\Delta E_{\text{C-H}}) \\ &= (3 \times 347.3) + (3 \times 615) + (6 \times 416.2) \\ &= 5384.1 \text{ kJ mol}^{-1}\end{aligned}$$

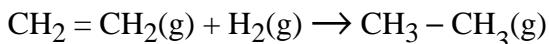
But the experimental value is known to be 5535.1 kJ mol⁻¹

So, the difference (5535.1 – 5384.1) = 151 kJ is attributed to the resonance energy of Benzene.

This is because the actual energy required to cause dissociation of Benzene is 151 kJ more than calculated value. Thus, Benzene molecule is more stable than any one of the two Kekulé structures.

Example 8

Calculate the enthalpy change of the following reaction.



The bond energy of C – H, C–C, C=C, H–H are 414, 347, 615 and 435 kJ mole⁻¹ respectively. (Roorkee 1985)

Solution :

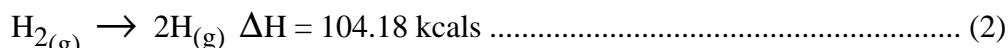
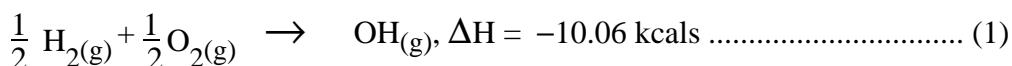
$$\begin{aligned}\Delta H_{\text{Reaction}} &= [\Delta H_{\text{C=C}} + 4(\Delta H_{\text{C-H}}) + \Delta H_{\text{H-H}}] \\ &\quad - [\Delta H_{\text{C-C}} + 6\Delta H_{\text{C-H}}]\end{aligned}$$

Substituting the bond energy data in the above expression.

$$\begin{aligned}\Delta H_{\text{Reaction}} &= [615 + (4 \times 414) + 435] - [347 + (6 \times 414)] \text{ kJ} \\ &= (615 + 1656 + 435) - (347 + 2484) \text{ kJ} \\ &= -125 \text{ kJ}\end{aligned}$$

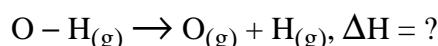
Example 9 :

The enthalpy change for the following reactions at 25° are given below.

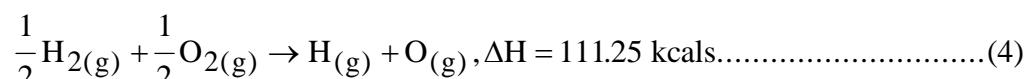


Calculate the OH bond energy in hydroxyl radical.

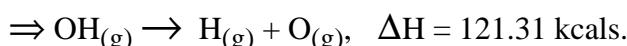
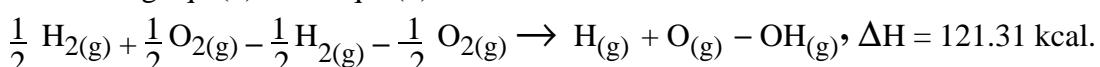
Solution : We have to arrive at



Dividing eqn (2) by 2 and eqn. (3) by 2 and adding



Subtracting eqn (1) from eqn. (4) we have



∴ Bond energy of OH radical is 121.31 kcals.

Example 10 :

The bond dissociation energies of methane and ethane are 360 and 620 kcals mol⁻¹ respectively. Calculate C – C bond energy.

Solution :

Given,



From (1) the B.E of 4 (C – H) bond = 360 kcals

$$\Rightarrow \text{B.E of 1 (C – H) bond} = \frac{360}{4} = 90 \text{ kcals}$$

$$\begin{aligned}
 \text{From (2) B.E of } \text{C}_2\text{H}_6 &= \Delta H_{\text{C}-\text{C}} + 6\Delta H_{\text{C}-\text{H}} \\
 &\Rightarrow 620 = \Delta H_{\text{C}-\text{C}} + 6 \times 90 = \Delta H_{\text{C}-\text{C}} + 540 \\
 &\Rightarrow \Delta H_{\text{C}-\text{C}} = 620 - 540 = 80 \text{ kcals} \\
 &\therefore \text{The bond energy of C-C} = 80 \text{ kcals (334.7 kJ)}
 \end{aligned}$$

SECOND LAW OF THERMODYNAMICS

8.12 LIMITATION OF FIRST LAW

According to 1st law of Thermodynamics “Various forms of energies are interconvertible”. When a given amount of one form of energy disappears, an equivalent amount other form of energy must appear. In otherwords, an exact equivalence between various forms of energies is indicated by 1st law. But sufficient informations are not provided by the law regarding:

- (i) The feasibility of the process i.e. whether a specified thermodynamic process is possible or not.
- (ii) The extent to which a given form of energy is consumed.
- (iii) The condition and direction of change that takes place.
- (iv) The maximum amount of work that can be obtained from a given quantity of heat.

To overcome the insufficiencies of 1st law, there is the need for another law i.e. the second law of thermodynamics.

8.13 SCOPE OF SECOND LAW

It helps us

- (i) To determine the direction in which the energy can be transferred.
- (ii) To know the equilibrium condition.
- (iii) To predict whether a thermodynamic process can occur spontaneously or not.
- (iv) To calculate the maximum fraction of heat that can be converted to work.

Thus, spontaneity forms the basis of second law of thermodynamics.

8.14 STATEMENT

The law was put forward by **Kelvin** and **Clausius**. Scintists like Planck, Carnot, Ostwald etc made significant contribution towards the development of the law. The law may be stated in a variety of ways.

- (1) It is impossible to convert heat completely to an equivalent amount of work without producing any change in the system or surrounding. (**Planck**)
- (2) It is impossible for a self acting machine unaided by an external agency to convey heat from a cold to a hot body. (**Clausius**)

- (3) All natural and spontaneous processes take place in one direction and are thermodynamically irreversible.
- (4) It is impossible to construct a machine operating in cycle, which will produce no effect other than absorption of heat from a reservoir and its conversion to an equivalent amount of work.
- (5) Heat can not of itself flow from a cold to a hot body.

8.15 SPONTANEOUS OR IRREVERSIBLE PROCESS

Consider the expansion of a gas.

Case-I : When the opposing pressure is infinitely smaller than pressure of the gas the expansion takes place infinitesimally slowly and the process is reversible one. The work obtained in this case is maximum.

Case-II : When the opposing pressure is much smaller than the gas pressure the expansion of the gas takes place rapidly and the process is irreversible. The work obtained in this case is less.

Case-III : When the gas expands in vacuum, there is no opposing force. The work obtained in this case is zero.

The natural processes are spontaneous and irreversible. The change proceeds with a net decrease in internal energy or enthalpy of the system.

Examples :

- (1) Water flows down the hill spontaneously. The flow can not be reversed without some external aid.
- (2) In case of a metal bar which is hot at one end and cold at the other, heat flows spontaneously from the hot end to the cold end until the temperature becomes uniform throughout.
- (3) Expansion of gas is spontaneous from a region of high pressure to a region of low pressure till the pressure is uniform throughout.
- (4) Flow of heat is spontaneous from a hot reservoir to a cold reservoir when both are connected.
- (5) Flow of electricity is spontaneous from a point at higher potential to a point at lower potential.
- (6) Diffusion of solute from a solution of high concentration to a solution of low concentration when these are brought in contact.

8.16 ENTROPY (S)

The concept of entropy was first introduced by **Clausius** in 1854. It is represented by the symbol 'S'. Like internal energy 'U', 'S' is also a state function since it depends upon the state of the system and independent of the path followed by the system. The actual entropy of the system can not be defined easily, it is rather best represented in terms of entropy change accompanying a particular process.

$$\text{Mathematically, } \Delta S = \frac{q}{T}$$

where, ΔS = Change in entropy ($S_{\text{final}} - S_{\text{initial}}$)

q = Amount of heat absorbed by the system.

T = Absolute temperature

Units of Entropy :

Since entropy term is the heat exchanged divided by absolute temperature, entropy is represented in terms of **calories per degree** i.e. **cal deg⁻¹**. This is also known as **entropy unit (eu)**. Again, since entropy is an extensive property i.e. it depends upon the amount of the substance present in the system, quantity of the substance is to be mentioned. This quantity is usually one mole. So the unit for entropy change may be written as **cal deg⁻¹ mole⁻¹**

In SI unit it is expressed as Joules per degree Kelvin (JK⁻¹)

Physical significance of Entropy :

We know that a process is said to be spontaneous when it has a natural tendency to occur of its own accord. The spontaneous processes are associated with net increase of entropy. If we examine such processes we will find that these are accompanied by increased randomness of distribution.

Consider a metal bar which is hot at one end and cold at the other end. There is perfect order in the bar so long as high energy molecules are assembled at one end and low energy molecules at the other end. But as soon as heat starts flowing from hot end to the cold end, there will be uniform distribution of energy throughout the bar. The state of order existing at both the ends is disturbed giving place to disorder. Similar type of change from ordered to disordered state is seen in the following phenomena.

- (i) Diffusion of solute from a concentrated to a dilute solution.
- (ii) Flow of electricity from a point at higher potential to a point at lower potential.
- (iii) Expansion of a gas in vacuum.

In case of fusion and vaporisation there is increase in entropy of the system, since both processes are accompanied with decrease in order. In solids the molecules, atoms or ions constituting the solid are arranged in a regular order in the crystal lattice. When solid melts, the molecular order is destroyed. Similarly, vaporisation is associated with conversion of liquid to vapour i.e. with more randomness of the molecules. Since these processes are associated with an increase in entropy

values it is justified to regard entropy as a measure of disorder, chaos or random arrangement of molecules of the system.

Important conclusions :

- (i) The greater the randomness of a system, greater is the entropy.
- (ii) The decreasing order of entropy in case of three states of matter is gas > liquid > solid.
- (iii) For all pure crystals, entropy is taken as zero.
- (iv) In an isolated system, for a process to be spontaneous its ΔS should be +ve i.e. $\Delta S > 0$
- (v) In case the system is not isolated,

$$\Delta S = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$
 So, $(\Delta S_{\text{syst}} + \Delta S_{\text{surr}}) > 0$ for a spontaneous process, when the system is not isolated.
- (vi) A thermodynamically irreversible process is always associated with an increase in the entropy of the system and its surrounding taken together whereas in a thermodynamically reversible process, the entropy of the system and the surrounding taken together remains unchanged.

8.17 FREE ENERGY (G)

The feasibility or spontaneity of a particular process can be decided by taking into account both enthalpy and entropy change. The important thermodynamic property which accounts for both enthalpy and entropy change of a system is **Gibb's Free Energy**. It is denoted by the symbol 'G'. It is defined as *the amount of energy available from a system that can be put into useful work*.

Mathematically, $G = H - TS$

where, $H \rightarrow$ Enthalpy of the system

$S \rightarrow$ Entropy of the system

$T \rightarrow$ Absolute temperature.

Since H and S both are state functions, G is also a state function. If G_1 , H_1 and S_1 represent the thermodynamic functions for the system in the initial state and G_2 , H_2 and S_2 in the final state, the temperature T remaining constant all through, we have

$$G_2 = H_2 - TS_2$$

$$G_1 = H_1 - TS_1$$

$$\therefore \Delta G (\text{change in F.E}) = G_2 - G_1$$

$$= (H_2 - TS_2) - (H_1 - TS_1)$$

$$= (H_2 - H_1) - T(S_2 - S_1)$$

$$= \Delta H - T \Delta S$$

$$\text{i.e. } \Delta G = \Delta H - T \Delta S$$

Standard Free Energy Change (ΔG^0)

The free energy change of a system at 25°C and one atmospheric pressure is known as **standard free energy change**.

$$\text{Mathematically, } \Delta G^0 = \Delta H^0 - T \Delta S^0$$

where, $\Delta H^0 \rightarrow$ Standard enthalpy change

$\Delta S^0 \rightarrow$ Standard entropy change

$\Delta G^0 \rightarrow$ Standard free energy change

T → 25°C i.e. 298 K.

Significance of ΔG :

- (i) For a system at **equilibrium** $\Delta G = 0$
- (ii) All **spontaneous** processes taking place at constant temperature and pressure are associated with net decrease in free energy i.e. for these processes ΔG is –ve or $\Delta G < 0$. Greater the –ve value, more is the spontaneity.
- (iii) A process is not thermodynamically feasible when ΔG is +ve or $\Delta G > 0$ i.e. the process is **not spontaneous** in the forward direction. It may take place in the opposite direction.

Effect of temperature on ΔG :

$$\text{We know, } \Delta G = \Delta H - T \Delta S$$

Enthalpy change ΔH is hardly affected by change of temperature. But the term $T\Delta S$ changes with temperature.

- (i) For exothermic reaction $\Delta H = -\text{ve}$. If temperature is low $T\Delta S$ will be less and ΔG becomes –ve. So, exothermic reactions are favoured by lowering the temperature.
- (ii) For endothermic reactions $\Delta H = +\text{ve}$. If temperature is high, $T\Delta S$ will be more and ΔG again becomes –ve. So, endothermic reactions are favoured at high temperature.

8.18 GIBB'S FREE ENERGY AND EQUILIBRIUM CONSTANT

Consider a general reaction



Gibbs free energy for the above reaction at equilibrium, $\Delta G = 0$

We know that $\Delta G = \Delta G^0 + RT \ln K \dots\dots\dots(1)$

Where $\Delta G^0 =$ Standard free energy change i.e. when all reactants and products are at their standard states of unit activity or concentration.

K = Thermodynamic equilibrium constant.

So at equilibrium,

We also know that

Case I

In case of endothermic reaction, ΔH is large and +ve. In such a case the value of K will be much smaller than 1 and reaction is unlikely to form more product.

Case II

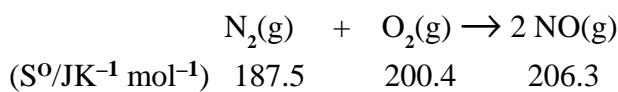
In case of exothermic reaction, ΔH is large and -ve. ΔG° is likely to be large and -ve. K will be much larger than 1, the reaction is likely to form more product.

Since ΔG also depends upon ΔS , the value of K also gets affected depending on whether ΔS is +ve or -ve.

Equation (5) may be used to estimate ΔG° from measurement of ΔH° and ΔS° . K can then be calculated.

Problem

1. Consider the following reaction



$$\Delta H^0 = 175.8 \text{ kJ mol}^{-1}$$

Assuming ΔH° and ΔS° to be independent of temperature, calculate the temperature at which the above reaction will be spontaneous.

Solution

$$\begin{aligned}\Delta S^{\circ} &= 2S_{\text{NO}}^{\circ} - S_{\text{N}_2}^{\circ} - S_{\text{O}_2}^{\circ} \\ &= (2 \times 206.3) - 187.5 - 200.4 \\ &\equiv 24.7 \text{ JK}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 175.8 - (T \times 24.7 \times 10^{-3}) \text{ kJ mol}^{-1}$$

For a reaction to be spontaneous $\Delta G^\circ < 0$ i.e. – ve & this occurs when $T\Delta S^\circ > \Delta H^\circ$

$$\Rightarrow T > \frac{\Delta H^o}{\Delta S^o}$$

$$\Rightarrow T > \frac{175.8 \times 10^3}{24.7}$$

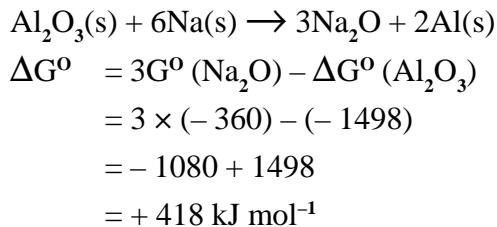
or $T > 7118\text{K}$

So the reaction becomes spontaneous above a temperature of 7118K

2. Can Aluminium oxide be reduced to Aluminium at 298K by metal Na ? Also calculate the value of equilibrium constant. Given $\Delta G^\circ(298\text{K}) / \text{kJ mol}^{-1}$
- | | |
|---|--|
| $\text{Al}_2\text{O}_3(\text{s}) = -1498$ | $\text{Na}_2\text{O}(\text{s}) = -360$ |
| | Element = 0 |

Solution

The reaction is

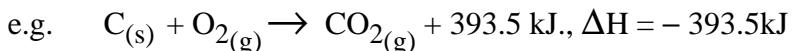


Since $\Delta G^\circ = +\text{ve}$, the reaction can not occur.

$$\begin{aligned}\text{Also } \Delta G^\circ &= -2.303 \text{ RT log K} \\ \Rightarrow 418 &= 2.303 \times 8.314 \times 10^{-3} \times 298 \log K \\ \Rightarrow \log K &= -73.33, \text{ so } K = 4.67 \times 10^{-74}\end{aligned}$$

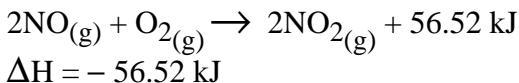
8.19 SPONTANEITY OF A PROCESS

We know that a spontaneous reaction is one which proceeds by itself with or without initiation. It is also a fact that all spontaneous chemical reactions proceed in direction in which there is decrease of energy. So all exothermic reactions should be spontaneous.



i.e. on ignition 'C' undergoes complete combustion giving CO_2 (case of initiation)

On the otherhand, in the reaction,



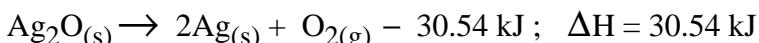
Here nitric oxide and oxygen combine readily forming nitrogen dioxide (no initiation is required),

However, there are several endothermic reactions which are also spontaneous.

e.g. (i) Evaporation of water,



(ii) Decomposition of Ag_2O to oxygen



This shows that reactions with -ve as well as +ve ΔH may be spontaneous. On the otherhand, the spontaneity of a reaction can not be judged only by the sign of ΔH . There must be some other factor which is involved for deciding the spontaneity of the process. This factor is **tendency for maximum randomness**.

In case of evaporation of water, when water is converted to vapour there is increase in randomness. In case of decomposition of Ag_2O , a gas appears in the product side. So, the randomness of the system increases. Thus, tendency to acquire maximum randomness is another factor that determines the spontaneity.

The overall tendency for a reaction to be spontaneous is to acquire a state of minimum energy and maximum randomness. This overall tendency is the **driving force**.

As discussed earlier, entropy is a measure of randomness of the system. As the entropy change and enthalpy change, both are contained in the expression for ΔG (change in free energy)i.e. $\Delta G = \Delta H - T\Delta S$, we can regard ΔG as the driving force for deciding the spontaneity of a reaction.

The following Table 8.4 summarises how signs of ΔH and ΔS for a given reaction determines its spontaneity.

Table 8.4 – Signs of ΔH , ΔS and ΔG for considering spontaneity.

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Remarks.
-	+	-	Reaction is spontaneous at all temperatures.
+	-	+	Reaction is nonspontaneous at all temperatures.
-	-	- (at low temp) + (at high temp)	Reaction is spontaneous at low temperature Reaction is nonspontaneous at high temperature
+	+	+ (at low temp) - (at high temp)	Reaction is nonspontaneous at low temperature Reaction is spontaneous at high temperature

This is to be noted that at high temperature the entropy factor predominates whereas at low temperature the energy factor predominates.

8.20 **THIRD LAW OF THERMODYNAMICS**

First law of Thermodynamics leads to concept of energy content of the system whereas second law leads to the concept of entropy of the system. Third law of thermodynamics, however, does not lead to a new concept, rather it places a limitation on the value of entropy of a crystalline solid. Third law is based on the generalisation made by scientist **Nernst**. According to Nernst heat theorem ΔG (change in Gibb's Free energy) and ΔH (change in enthalpy) of a system become equal to each other at absolute zero of temperature and approach each other asymptotically. This is illustrated in Figure 8.10.

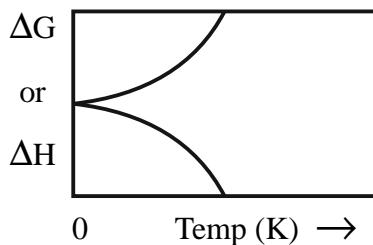


Fig. 8.10 : Plot of ΔG or ΔH against K

According to Gibbs - Helmholtz equation

$$\Delta G - \Delta H = T \left[\frac{\partial \Delta G}{\partial T} \right]_P \dots \dots \dots (1)$$

When $T = 0$ i.e. at absolute zero of temperature $\Delta G = \Delta H$.

Mathematically the Nernst Heat Theorem can be expressed as

$$\underset{T \rightarrow 0}{\text{Lt}} \left[\frac{\partial \Delta H}{\partial T} \right]_P = 0, \text{ and } \underset{T \rightarrow 0}{\text{Lt}} \left[\frac{\partial \Delta G}{\partial T} \right]_P = 0 \dots \dots \dots (2)$$

From the concept of entropy

$$\left[\frac{\partial \Delta G}{\partial T} \right]_P = -\Delta S \dots \dots \dots (3)$$

where ΔS = Entropy change of the reaction

From Kirchhoff equation

$$\left[\frac{\partial \Delta H}{\partial T} \right]_P = \Delta C_p \dots \dots \dots (4)$$

where ΔC_p = difference in heat capacities of the product and the reactant.

From equation 2, 3 and 4, it follows that

$$\underset{T \rightarrow 0}{\text{Lt}} \Delta S = 0 \dots \dots \dots (5) \text{ and } \underset{T \rightarrow 0}{\text{Lt}} \Delta C_p = 0 \dots \dots \dots (6)$$

The Nernst heat theorem holds good only in case of pure solids and is the forerunner of Third law of Thermodynamics.

From equation (6), it can be concluded that at absolute zero of temperature the products and reactants in solid state have same value of heat capacities. So ΔC_p tends to approach zero at 0K. From the concept of quantum theory, it is suggested that the heat capacities of solid tend to become zero at 0K.

$$\text{i.e. } \underset{T \rightarrow 0}{\text{Lt}} C_p = 0 \dots \dots \dots (7)$$

From equation (5) it can be concluded that at absolute zero of temperature the products and reaction in solid state have same value of entropies. So ΔS tends to approach zero at 0K. On analogy with zero value of heat capacity at absolute zero, the entropy value of all pure solids at 0K approach zero.

$$\text{i.e. } \underset{T \rightarrow 0}{\text{Lt}} S = 0 \dots \dots \dots (8)$$

This statement has led to following definition of Third law of thermodynamics.

At absolute zero of temperature the entropy of every substance may become zero and it does become zero in case of a perfectly crystalline solid.

In a crystalline solid the molecules, ions or atoms constituting the solid acquire definite positions in the crystal lattice. The arrangement has lowest energy. There is zero disorder and hence associated with zero value of entropy.

CHAPTER (8) AT A GLANCE

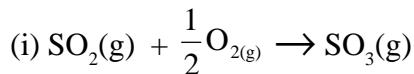
1. **Thermodynamics** deals with energy changes accompanying all physical and chemical processes.
2. **Internal energy** : The total energy stored in the substance by virtue of its chemical nature.
3. **First law of thermodynamics (Law of conservation of energy)**
Energy can neither be created nor destroyed.
4. **Heat capacity** : Amount of heat required to raise the temperature of the system from lower to higher temperature divided by the temperature difference.
Specific heat : When the mass of the system is one gram, heat capacity is called specific heat of the system.
Molar heat capacity : When the mass of the system is one mole, the heat capacity is called molar heat capacity.
5. $C_p - C_v = R$
6. **Relationship between Internal energy and Enthalpy**
 $\Delta H = \Delta U + P\Delta V$
7. **Enthalpy of reaction** : Quantity of heat evolved or absorbed when the number of gram molecules of the substances taking part in the chemical reaction have completely reacted.
Sign of ΔH : (a) –ve for Exothermic reaction.
(b) +ve for Endothermic reaction.
8. **Standard enthalpy of reaction (ΔH°)** : When the process is carried out at 298K and 1 atm. pressure, ΔH is referred to as standard enthalpy of reaction ΔH° .
9. ΔU and ΔH can be measured in water calorimeter and Bomb calorimeter.
10. **Thermochemistry** is a branch of physical chemistry which deals with heat changes accompanying chemical reactions.
11. $Q_p = Q_v + \Delta n RT$
12. **Standard enthalpy of reaction (ΔH°)** : When the process is carried out at 298K and 1 atm. pressure, ΔH is referred to as standard enthalpy of reaction ΔH° .
13. **Enthalpy of formation (ΔH_f)** : Quantity of heat evolved or absorbed when 1 mole of the substance is formed from its constituent elements under given conditions of temperature and pressure.
14. **Enthalpy of combustion** : Enthalpy change accompanying the complete combustion of 1 mole of the substance at a given temperature.
15. **Enthalpy of neutralisation** : Enthalpy change when one gram equivalent of an acid is neutralised by one gram equivalent of a base in a fairly dilute solution.

16. **Enthalpy of solution** : Quantity of heat evolved or absorbed when 1 mole of the solute is dissolved in a large excess of water so that any further dilution of the solution produces no heat change.
17. **Enthalpy of fusion** : The enthalpy change accompanying the change of one mole of substance from solid phase to liquid phase at its melting point.
18. **Enthalpy of vaporisation** : The enthalpy change accompanying the change of one mole of the substance from liquid phase to vapour phase at its boiling point.
19. **Enthalpy of sublimation** : The enthalpy change associated with the change of 1 mole of the substance from the solid phase to vapour phase at a given temperature below its melting point.
20. **Hess's law** : If a chemical change takes place in two or more different ways whether in one step or in several steps, the amount of heat evolved or absorbed in total change is the same, no matter, by whichever method the change is brought about.
21. **Bond Energy** : The average amount of energy required to break one type of bond present in one mole of the compound.
22. **Change in entropy** : $\Delta S = \frac{q}{T}$
23. **Entropy** is a measure of disorder or randomness of a system.
24. **Free Energy (G)** : The amount of energy available from a system that can be put to useful work.
25. $\Delta G = \Delta H - T \Delta S$
26. (a) $\Delta G = -ve$: Process is spontaneous.
 (b) $\Delta G = +ve$: Process is not thermodynamically feasible.
 (c) $\Delta G = 0$, The system is at equilibrium.
27. **Enthalpy of atomisation**
 Enthalpy change associated with conversion of compounds and elements into free atoms. This is usually highly endothermic.
28. **Enthalpy of dilution**
 The enthalpy change when some moles of solvent is added to an aqueous solution.
29. **Enthalpy of ionisation**
 The enthalpy change by which the enthalpy of neutralisation is less than that in case of neutralisation of strong acid with a strong base. This is the case where either the acid is weak or the base is weak.
30. **Second law of Thermodynamics**
 It is impossible to convert heat completely to an equivalent amount of work without producing any change in the system or surrounding.
31. **Third law of Thermodynamics**
 At absolute zero temperature the entropy of every substance may become zero and it does become zero in case of a perfectly crystalline solid.
32. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$.

QUESTIONS

Very short answer type (1 mark each)

1. In which of the following changes there is increase in entropy ?



(ii) Ice \rightarrow water

2. In which reaction the reactants have less energy than the products ?

3. What is the relationship between enthalpy (ΔH) and internal energy (E)?

4. In the endothermic reaction ΔH is _____.

5. Define enthalpy of combustion.

6. In an exothermic reaction, ΔH is _____.

7. The enthalpy of combustion is always _____

8. What is exothermic reaction ?

9. In an endothermic reaction, ΔH is always _____.

10. In the reaction $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_{2(\text{g})} = \text{CO}_2(\text{g})$ at constant T and P which one of the following is correct ?

- (i) $\Delta H = \Delta E$
- (ii) $\Delta H > \Delta E$
- (iii) $\Delta H < \Delta E$

11. Define Hess's law.

12. In which type of reaction heat is absorbed ?

13. What is heat of reaction ?

14. The dissociation energy of CH_4 is 360 kcals/mole. What is the energy associated with C-H bond ?

15. What is bond energy ?

16. Define heat of combustion.

17. Write the equation relating free energy, entropy and enthalpy.

18. When ice melts to water, its entropy _____.

Short Answer type (2 marks each)

1. What is understood by exothermic and endothermic reaction ? Give an example of each.
2. Explain the term Bond energy
3. Define Hess's law.
4. What is endothermic reaction. Give example.
5. When a reaction at constant temperature and pressure is at equilibrium the value of ΔG is _____.

6. Define enthalpy of combustion. Give an example.
7. Predict whether ΔS is +ve or -ve for the following reactions.
 - (i) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$
 - (ii) $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
8. If ΔH of the reaction $\text{CH}_4\text{(g)} + \text{C}_2\text{H}_4\text{(g)} \rightarrow \text{C}_3\text{H}_8\text{(g)}$ is -19.4 kcals, what will be the ΔH of the reaction $\text{C}_3\text{H}_8\text{(g)} \rightarrow \text{CH}_4\text{(g)} + \text{C}_2\text{H}_4\text{(g)}$?
9. How does the free energy change show the feasibility of a chemical reaction?
10. What is the free energy of a reaction at 27°C with an enthalpy change 5 Kcals mole $^{-1}$ and entropy change of 15 eu?
11. Calculate the entropy of vaporisation for a liquid boiling at 300K having enthalpy of vaporisation 27kJ mole^{-1} .
12. The dissociation energy of CH_2Cl_2 is $354.54\text{kcal mol}^{-1}$. What is the energy associated with C-H bond if bond energy of C-Cl is $77.99\text{Kcal mol}^{-1}$.
13. Define enthalpy. What is the SI Unit of enthalpy.

Short Answer type (3 marks each)

1. What is enthalpy of ionisation. Discuss with suitable examples.
2. Discuss enthalpy of atomisation with example.
3. What is enthalpy of dilution. Discuss with example.
4. Derive the expression $\Delta H^\circ = -RT \ln K$

Long Answer type (7 marks each)

1. Write a note on Hess's law.
2. Write a note on – Activation energy.
3. Write short notes on
 - (a) Heat of reaction
 - (b) Heat of fusion
4. Define enthalpy of vaporisation. State Hess's law. Mention two conditions under which enthalpy change (ΔH) may be equal to internal energy change (ΔE)
5. What are the limitations of 1st law of Thermodynamics? Discuss the scope of 2nd law and write the various forms of statement of 2nd law of thermodynamics.
6. Give a brief account of 3rd law of thermodynamics.

ADDITIONAL QUESTIONS

Very short Answer type (1 mark each)

1. Define heat of formation
2. The value of ΔH for combustion of 1 mole of ethanol when both reactants and products are at the same temperature is _____
3. What is the heat evolved or absorbed when a compound is formed from the elements called ?

4. At constant volume q equals to _____
5. Thermodynamically, adsorption is an _____ phenomenon.
6. Define internal energy.
7. Entropy of a gas is _____ than that of a solid.
8. How ΔH and ΔE are related ?
9. Entropy is a measure of _____ of the system.
10. Define heat of fusion.
11. What is bond energy?
12. Predict whether ΔS is +ve or -ve for the following reactions :
 - i) $N_2O(g) \rightarrow N_2O_3(g) + O_2(g)$
 - ii) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
13. Which of the following is an intensive property?
(mass, energy, temperature)
14. Write the equation relating free energy, entropy and enthalpy.

Short answer type (2 marks each)

1. What are the components of internal energy ?
2. Entropy of a pure substance is zero at zero degree Kelvin, Explain why ?
3. State two important conditions which account for the spontaneity of a reaction
4. Explain the term – bond energy.
5. What is heat of neutralisation.
6. Explain law of conservation of energy.
7. What are extensive and intensive properties. Give suitable example.
8. What are the factors on which internal energy 'E' depends ?
9. How ΔH and ΔE are related in case of reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
10. What is standard enthalpy of reaction ?
11. Discuss the importance of Heat of combustion.
12. Heat of neutralisation of a weak acid with a strong base is less than 57.1 kJ -Justify.
13. Explain how resonance energy affect bond energy.
14. What is meant by standard free energy change ?
15. Discuss the effect of temperature on ΔG .

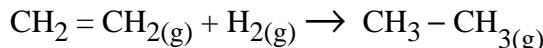
Long answer type (7 marks each)

1. Explain exothermic and endothermic reactions with suitable examples.
2. What do the symbols ΔH , ΔS and ΔG signify ? How are they interrelated ? What is the importance of the relation formed ?

3. Define Gibb's free energy change. How is the change in free energy related to spontaneity ?
 For the reaction, $M_2O_{(s)} \rightarrow 2M_{(s)} + \frac{1}{2}O_2(g)$
 $\Delta H = 30 \text{ kJ mole}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1}$ (at 1 atm)
 Calculate upto which temperature the reaction would not be spontaneous.
4. What is bond energy ? How it is calculated ? Discuss the various factors that effect bond energy.
5. (a) What is meant by heat of formation ?
 (b) State Hess's law of constant heat summation by taking suitable examples.
6. Give reasons for the following :
 (a) Entropy of a system increases with increase in temperature.
 (b) ΔG is always –ve for a spontaneous reaction.
 (c) A strong acid with strong base. Enthalpy of neutralisation of a weak acid with a strong base is less than that of a strong acid with strong base.
 (d) In exothermic reaction ΔH is –ve
 (e) ΔG is zero at equilibrium.
7. What do you understand by
 (i) Heat of solution (ii) Heat of neutralisation (iii) Heat of combustion (1984 Bihar Intermediate)
8. What is entropy ? What is its unit ? Discuss the physical significance of entropy. Explain why the entropy of ice is less than that of water.
9. Define entropy and free energy of a system. Predict the feasibility of a reaction when,
 (a) both ΔH and ΔS increase
 (b) both ΔH and ΔS decrease.
 (c) ΔH decreases but ΔS increases.
10. Write notes on (any three)
 (a) Enthalpy of formation
 (b) Enthalpy of combustion
 (c) Bond energy
 (d) Enthalpy of neutralisation.
11. State and explain Hess's law of constant heat summation. Discuss its application. Calculate the enthalpy of formation of methane. Given :
 a) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \Delta H_a = -393.5 \text{ kJ}$
 b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \Delta H_b = -571.8 \text{ kJ}$
 c) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \Delta H_c = -890.3 \text{ kJ}$

NUMERICAL PROBLEMS (UNSOLVED)

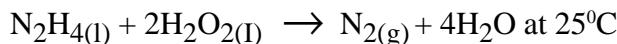
1. Calculate the enthalpy of following reaction :



The bond energies of C – H, C – C, C = C, and H – H are
416, 356, 598 and 436 kJ/mol respectively.

(Ans : 154 kJ/mole)

2. Find out the heat of reaction for the following :



Given at 25°C, heat of formation of

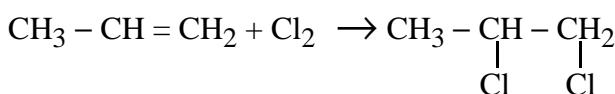
$$\text{N}_2\text{H}_{4(\text{l})} = 12 \text{ kcal / mole}$$

$$\text{H}_2\text{O}_{2(\text{l})} = -46 \text{ kcal/mole}$$

$$\text{H}_2\text{O}_{(\text{l})} = -57.5 \text{ kcal /mole}$$

(Ans : - 150 kcals)

3. Calculate ΔH for reaction



From the following bond energies :

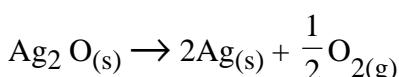
$$E_{\text{C}-\text{C}} = 347.3, E_{\text{C}=\text{C}} = 615$$

$$E_{\text{C}-\text{Cl}} = 330.5, E_{\text{Cl}-\text{C}} = 242.7 \text{ kJ /mole}$$

4. Standard heat of formation at 298 K for $\text{CCl}_{4(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$ and $\text{HCl}_{(\text{g})}$ are 25.5, -57.8, -94.1, 22.1 kcal/mole respectively. Calculate ΔH for the reaction



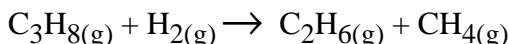
5. Free energy change ΔG for the reaction



is zero ΔS and ΔH for this reaction are $0.066 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and $31.218 \text{ kJ mol}^{-1}$ respectively. Find out the direction of the reaction below 200°C (Ans : $\Delta G < 0$, reaction is spontaneous)

6. The molar heats of combustion of $\text{C}_2\text{H}_{2(\text{g})}$, C(graphite) and $\text{H}_{2(\text{g})}$ are 310.62 kcals, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $\text{C}_2\text{H}_{2(\text{g})}$.
(Ans : 54.20kcals)

7. Determine the enthalpy of the reaction



at 25°C , using the give heat of combustion values under standard conditions.

Compound	$\text{H}_{2(\text{g})}$	$\text{CH}_{4(\text{g})}$	$\text{C}_2\text{H}_{6(\text{g})}$	C(graphite)
$\Delta H^0(\text{kJ/mol})$	-285.8	-890.0	-1560.0	-393.5

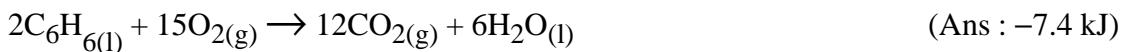
The standard heat of formation of $\text{C}_3\text{H}_{8(\text{g})}$ is -103.8 kJ/mol (Ans : -55.7 kJ/mol)

8. The standard molar heats of formation ethane, carbondioxide and liquid water are -21.1 , -94.1 , -8.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

(Ans = -372 kcal/mol)

9. Calculate the standard heat of formation of Carbon disulphide(l). Given that the standard heat of combustion of $C_{(s)}$, $S_{(s)}$ and $CS_2(l)$ are -393.3 , -293.72 and -1108.76 kJ mole^{-1} respectively. (Ans : $128.02 \text{ kJ mol}^{-1}$)

10. Calculate the difference between heat of reaction at constant pressure and constant volume for the reaction at 25^0C in kJ.



11. The standard heat of formation of $CH_4(g)$, $CO_{2(g)}$ and $H_2O_{(g)}$ are -76.2 , -394.8 and -241.6 kJ mole^{-1} respectively. Calculate the amount of heat evolved by burning 1m^3 of methane measured under normal conditions. (Ans = 35794.64 kJ)

12. Calculate the resonance energy of N_2O from the following data.

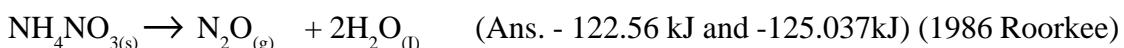
$$\Delta H^\circ f \text{ of } N_2O = 82 \text{ kJ mol}^{-1}$$

Bond energies of $N \equiv N$, $N=N$, $O=O$ and $N=O$ bonds are $946, 418, 498$ and 607 kJ mol^{-1} respectively. (Ans = 88 kJ mol^{-1})

13. When 2 moles of C_2H_6 are completely burnt 3129 kJ of heat is liberated. Calculate the heat of formation ΔH_f for C_2H_6 . Given ΔH_f for CO_2 and H_2O are -395 and -286 kJ respectively. (Ans = -83.5 kJ)

14. The molar heat of formation of NH_4NO_3 is 367.54 kJ and that of $N_2O_{(g)}$ and $H_2O(l)$ are 81.46 kJ and -285.75 kJ respectively at 25^0C and 1 atm . pressure.

Calculate ΔH and ΔE for the reaction



15. The bond dissociation energies of gases H_2 , Cl_2 and HCl are $104, 58$ and 103 kcal/mole respectively. Calculate the enthalpy of formation of HCl gas. (Ans.-22kcals) (1985 IIT)

MULTIPLE CHOICE QUESTIONS

1. A well stoppered thermosflask contains some ice Cubes. This is an example of a
 (a) Closed system (b) open system (c) isolated system (d) non-thermodynamic system

2. For the reaction



- (a) $\Delta E = 2RT$ (b) $\Delta E - 2RT$ (c) $\Delta E + RT$ (d) $\Delta E + 2RT$.

3. For an ideal gas, the relation between the enthalpy change and internal energy at constant temperature is given by

- (a) $\Delta H = \Delta E + PV$ (b) $\Delta H = \Delta E + \Delta nRT$ (c) $\Delta H = \Delta E + P\Delta V$ (d) $\Delta H = \Delta G + T\Delta S$

4. If $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta H = X$ and
 $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta H = Y$ then the heat of formation of CO is
 (a) $X + Y$ (b) $X - Y$ (c) $Y - X$ (d) XY
5. Enthalpies of elements in their standard states are taken as zero. Hence the enthalpy of formation of a compound
 (a) should always be negative.
 (b) should always be positive.
 (c) will be equal to twice the energy of combustion.
 (d) may be +ve or -ve
6. Which of the following values of heat of formation indicates that the product is least stable ?
 (a) -94 kcal, (b) -231.6 kcals (c) +21.4 kcal (d) +64.8 kcal.
7. For an adiabatic process, which of the following is correct
 (a) $P \Delta V = 0$, (b) $q = + w$, (c) $\Delta E = q$, (d) $q = 0$
8. Identify the intensive quantity from the following.
 (a) Enthalpy and temperature
 (b) Volume and temperature
 (c) Enthalpy and volume
 (d) Temperature and refractive index
9. An exothermic reaction is one which
 (a) takes place on heating
 (b) is accompanied by flame
 (c) is accompanied by absorption of heat
 (d) is accompanied by evolution of heat.
10. An endothermic reaction is one in which
 (a) Heat is converted into electricity
 (b) Heat is absorbed
 (c) Heat is evolved
 (d) Heat is converted to mechanical work
11. Which of the following reactions is exothermic ?
 (a) $CaCO_3 \rightarrow CaO + CO_2$
 (b) $Fe + S \rightarrow FeS$
 (c) $NaOH + HCl \rightarrow NaCl + H_2O$
 (d) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

- 12 Which of the following is an endothermic reaction.
- $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
 - $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$
 - $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
 - $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
13. In exothermic reactions
 (a) ΔE is zero (b) ΔH is -ve (c) ΔS is zero (d) ΔH is +ve.
14. For an endothermic reaction
 (a) ΔH is -ve (b) ΔH is +ve (c) ΔE is -ve (d) $\Delta H = 0$
15. Enthalpy for the reaction.
 $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ is
 (a) + ve (b) -ve (c) zero (d) none.
16. Enthalpy of a compound is equal to its.
 (a) Heat of combustion.
 (b) Heat of formation.
 (c) Heat of reaction.
 (d) Heat of solution.
17. During isothermal expansion of an ideal gas its.
 (a) Internal energy increases
 (b) Enthalpy increases,
 (c) Enthalpy remains unaffected
 (d) Enthalpy reduces to zero.
18. Heat of neutralisation of a strong acid and strong base is always.
 (a) 13.7 kcal/ mole.
 (b) 9.6 kcal/ mole
 (c) 6 kcal/ mole,
 (d) 11.4 kcal / mole.
19. The mutual heat of neutralisation of 40 grams NaOH and 60 grams CH_3COOH will be
 (a) 56.1 kJ (b) Less than 56.1 kJ (c) More than 56.1 kJ (d) 13.7 kJ.
20. In which of the following neutralisation reactions, the heat of neutralisation is the highest.
 (a) NH_4OH and H_2SO_4
 (b) HCl and NaOH
 (c) CH_3COOH and KOH
 (d) CH_3COOH and NH_4OH .
21. Hess's law deals with
 (a) Change in heat of reaction
 (b) Rate of reaction
 (c) Equilibrium constant
 (d) Influence of pressure on volume of a gas.

22. Hess's law of heat of summation includes
 (a) Initial reactants only,
 (b) Initial reactants and final products
 (c) Final products only
 (d) Intermediates only.
23. $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$, $\Delta H = -12.40$ kcals, Heat of formation of HI will be.
 (a) 12.4 kcals (b) -12.4 kcals (c) -6.20 kcals (d) 6.20 kcals
24. Combustion of methane
 (a) is an exothermic process. (b) is an endothermic process.
 (c) requires catalyst (d) gives H_2
25. For which reaction, S will be maximum ?
 (a) $\text{Ca(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CaO(s)}$
 (b) $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
 (c) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
 (d) $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$
26. The total entropy change for a system and its surroundings increases, if the process is
 (a) reversible (b) irreversible (c) exothermic (d) endothermic
27. When ice melts into water, entropy
 (a) becomes zero (b) decreases (c) increases (d) remains same.
28. Heat of combustion is always
 (a) +ve (b) -ve (c) neutral (d) all of the above
29. Energy required to dissociate 4 gms of gaseous hydrogen into free gaseous atoms is 208 kcals. at 25°C . The bond energy of H – H bond will be
 (a) 104 kcals (b) 10.4 kcals (c) 1040 kcal (d) 104 cals
30. If a refrigerator door is opened then we get
 (a) room heated (b) room cooled (c) more heat is passed out (d) no effect on room.

ANSWER TO MULTIPLE CHOICE QUESTIONS

1.c	6.d	11.b	16.b	21.a	26.b
2.b	7.d	12.b	17.c	22.b	27.c
3.b	8.d	13.b	18.a	23.c	28.b
4. b	9.d	14.b	19.b	24.a	29.a
5.d	10.b	15.b	20.b	25.b	30.a

(N.B : E has been replaced by U = Internal energy)



UNIT – VII

CHAPTER - 9

EQUILIBRIA

9.1 **IRREVERSIBLE AND REVERSIBLE REACTIONS**

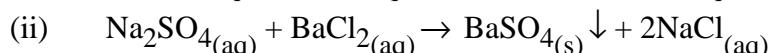
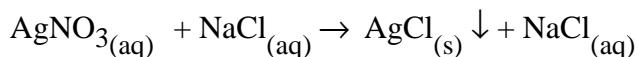
Irreversible reaction :

The chemical reactions in which the products formed do not react amongst themselves to produce the original reactants are known as **irreversible reactions**.

Irreversible reactions can otherwise be defined as the chemical reactions, where the reactants are completely changed to the products.

Examples :

- (i) When AgNO_3 solution is added to aqueous NaCl solution, a white precipitate is formed due to the formation of AgCl .



In these reactions, the reactants react completely and the reactions proceed only in forward direction. Backward reactions in these cases are not possible.

So, it can be said that,

- (a) All irreversible reactions can be carried to completion.
and (b) They proceed in one direction, i.e. they are unidirectional.

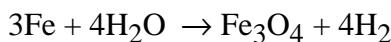
Reversible reaction :

The chemical reactions in which the products of the reactions can also react with one another under suitable conditions to produce back the original reactants are known as **reversible reactions**. So,

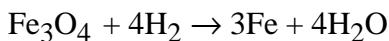
- (a) Reversible reactions can never be carried to completion.
and (b) They occur in both the directions i.e. forward and backward directions.

Examples :

- (i) If powdered hot iron is taken in a tube and steam is passed over it, magnetic oxide of iron, Fe_3O_4 is formed with the liberation of hydrogen gas.



Again, Fe_3O_4 can react with H_2 to give back iron and water.

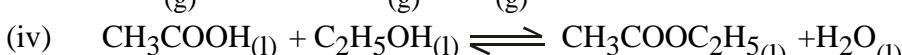
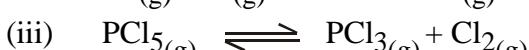
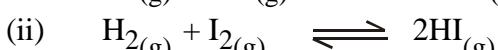
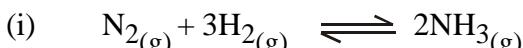


Such reactions, which can take place in both directions under the same conditions are known as reversible reactions.

These reactions are represented by the sign of reversibility between the reactants and the products. Thus,



Other examples of reversible reactions are,

**Characteristics of reversible reactions :**

The main characteristics of reversible reactions are,

(i) They never proceed to completion inside a closed vessel.

(ii) They can take place in both forward and backward directions.

and (iii) The rate of reaction in a particular direction depends upon the molar concentrations of the reacting species.

9.2 EQUILIBRIA IN PHYSICAL PROCESS

Phase transformation processes are the most familiar examples.

Solid \rightleftharpoons liquid

Liquid \rightleftharpoons gas

Solid \rightleftharpoons gas

Solid \rightleftharpoons liquid equilibrium :

Take a perfectly insulated thermos flask; place some ice and water in it at 273K and atm pressure. Both are solid to be in equilibrium with each other.

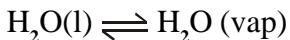


There is no change in mass of ice and since the rate of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atm. press. and 273K. For any pure substances at atm. pressure the temperature at which the solid and liquid phases are at equilibrium

is called the normal melting point or normal freezing point of the substance. The system is in dynamic equilibrium. Both the opposing process occur simultaneously at the same rate so that the amount of ice and water remains constant.

Liquid \rightleftharpoons vapour equilibrium

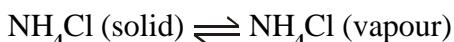
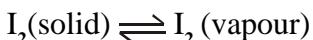
Consider the equilibrium



Here, rate of evaporation = rate of condensation. Liquid water and water vapour are in equilibrium with each other at atmospheric pressure and at 100°C in a vessel. For a pure liquid the temperature at which the liquid and its vapour are at equilibrium with each other is called boiling point of the liquid.

Solid \rightleftharpoons vapour equilibrium

Consider the equilibrium



In the first case solid iodine sublimes to give I_2 vapour and I_2 vapour condenses to give solid I_2 .

CHEMICAL EQUILIBRIA

9.3 STATE OF EQUILIBRIUM

It is defined as the state of a system in which its properties do not change with time.

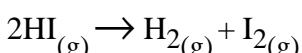
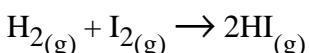
The equilibrium with reference to change in physical state is called **physical equilibrium**.

Example :

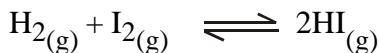
If a small quantity of water is introduced into an evacuated vessel, then evaporation will take place and inside pressure will increase. After some time constant pressure is indicated which proves that the system has attained equilibrium.

When equilibrium is attained in a chemical system, it is referred to as chemical equilibrium.

Example : When gaseous H_2 reacts with I_2 vapour, HI gas is produced and the reaction is reversible.



If the first reaction is carried out in a closed vessel, it seems to stop after some time. Similarly, the second reaction (decomposition of HI) also is not complete inside a closed vessel and stops after a while. So, it can be said that in reversible reaction, both reactions apparently seem to come to a state of equilibrium after some time. At this stage, the properties of the system remain unchanged with time. This is known as the state of chemical equilibrium or **equilibrium state** and hence the reaction is represented as,



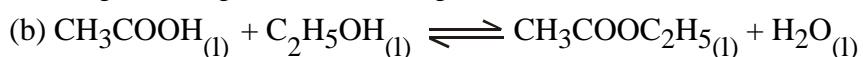
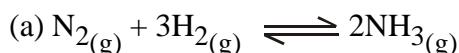
Types of chemical equilibrium :

Chemical equilibrium is of two types, **homogeneous** and **heterogeneous**.

(i) Homogeneous equilibrium :

If all the reactants and products are in the same phase, then the equilibrium is known as the homogeneous equilibrium. A mixture of gases or miscible liquids gives rise to this type of equilibrium.

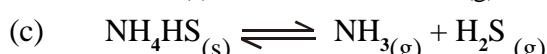
Examples :



(ii) Heterogeneous equilibrium

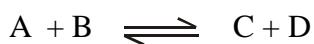
When the reactants and products are in different phases, then the equilibrium is known as the heterogeneous equilibrium.

Examples :

$$(a) \text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$$


Chemical equilibrium and Rate of reaction :

Consider a general reversible reaction,



Let the reactants A and B react in a closed vessel. At the beginning the concentrations of A and B are maximum and concentrations of C and D are zero. Since the rate of a reaction depends on the concentrations of the reactants, initially the rate of forward reaction will be high and the rate of backward reaction will be zero. With the progress of the reaction, the rate of forward reaction will decrease and that of backward reaction will increase. Finally, a stage will come, when the rates of both the reactions will be equal. The reaction comes to a stand still position. It appears as if the reaction has stopped, but the reaction has not actually stopped, it proceeds in both the directions with equal speed. This state is known as **equilibrium state**.

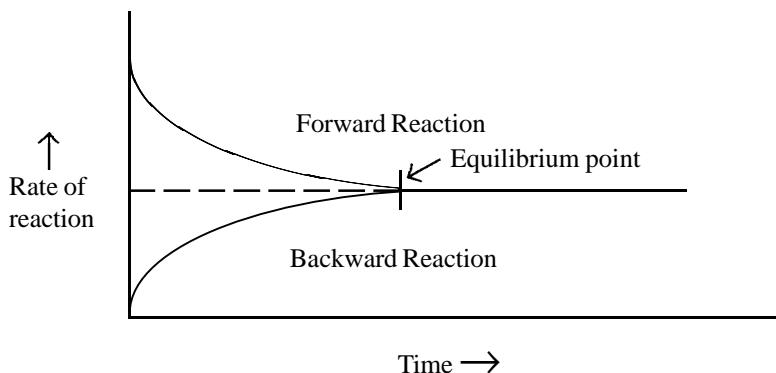


Fig 9.1 Attainment of equilibrium state in reversible reaction.

So, the state of chemical equilibrium can also be defined as that state at which the rates of the two opposing reactions are same and the concentrations of the reactants and the products do not change. Therefore, it can be called a **dynamic** chemical equilibrium.

Characteristics of Chemical equilibrium :

- (i) The state of equilibrium is possible only when the reaction is carried out in a closed vessel.
- (ii) At equilibrium, the properties of the system like concentration, temperature and pressure remain unchanged.
- (iii) Since equilibrium can shift either in the direction of the reactants or in the direction of products, it is dynamic in nature.
- (iv) The same state of equilibrium can be attained from either side of a reversible reaction.
- (v) At equilibrium, both the reactions operate simultaneously and the rate of the forward reaction is the same as that of the backward reaction.
- (vi) A catalyst added to the system does not affect the state of equilibrium.

9.4 LAW OF MASS ACTION

In the year 1864, two Norwegian chemists **Guldberg** and **Waage** suggested a qualitative relationship between rates of reaction and the concentrations of the reacting species. This relationship is known as **Law of mass action**.

Statement :

The law states that *the rate at which a substance reacts is proportional to its molar concentration (active mass) and the rate of a chemical reaction is proportional to the product of the molar concentrations of reacting substances.*

Let us apply law of mass action to a hypothetical reaction,



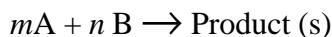
According to the law of mass action,

Rate of reaction, $r \propto [A][B]$

$$\text{or, } r = k[A][B]$$

where, $[A]$ and $[B]$ are the molar concentrations of the reactants A and B respectively, k is a proportionality constant, called **rate constant**.

For any general reaction,



where m and n are the no. of moles of A and B respectively,

Rate of reaction, $r \propto [A]^m [B]^n$

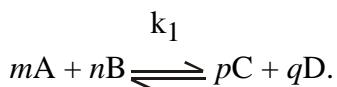
$$\text{or, } r = k[A]^m[B]^n$$

Here the number of moles becomes the power to which the concentration terms are to be raised.

Application of Law of mass action to reversible reactions :

With the limitations of its validity to only one step chemical reactions, the law of mass action can also be applied to reversible chemical reactions.

Consider a simple reversible reaction,



where p and q are the no. of moles of products C and D respectively.

Let r_1 and r_2 be the rates of forward and backward reactions respectively, k_1 and k_2 are respective rate constants.

Then, rate of forward reaction,

$$r_1 = k_1[A]^m[B]^n \dots \text{(i)}$$

and rate of backward reaction,

$$r_2 = k_2[C]^p[D]^q \dots \text{(ii)}$$

But, at the equilibrium point, the rate of forward reaction will be equal to the rate of backward reaction. This means, $r_1 = r_2$

Equating eqn (i) and (ii) we get,

$$k_1[A]^m[B]^n = k_2[C]^p[D]^q$$

$$\text{or, } \frac{k_1}{k_2} = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

$$\text{or, } K_C = \frac{[C]^p[D]^q}{[A]^m[B]^n} \dots \text{(iii)}$$

where, $K_C = k_1 / k_2$ is a constant, known as **equilibrium constant**.

Equation (iii) is known as **law of chemical equilibrium**.

Equilibrium constant in terms of partial pressure :

When all the reactants and products in a reaction are in gaseous form, their concentrations are proportional to their partial pressures.

Consider the reaction,



where the reactants and the products are in gaseous state.

So, the concentrations of A, B, C and D are proportional to their partial pressures,

p_A , p_B p_C and p_D respectively.

Applying law of mass action, we get, $K_p = \frac{(p_C)^r (p_D)^s}{(p_A)^m (p_B)^n}$ (iv)

where, K_p is the **equilibrium constant** in terms of partial pressure.

Equilibrium constant (K_x)

If the concentrations of the reactants and products at the state of equilibrium are expressed in terms of mole fractions, the equilibrium constant is represented as K_x . Considering the general reaction at equilibrium, $mA + nB \rightleftharpoons pC + qD$

$$K_p = \frac{X_C^p \cdot X_y^q}{X_A^m \cdot X_B^n} \dots \dots \dots \quad (v)$$

where, x_A , x_B , x_C and x_D are the molefractions of A, B, C and D respectively and m , n , p & q are the no. of moles of A, B, C and D respectively.

Relationship between K_p , K_c and K_x

(a) Relationship between K_p and K_x

Consider a general reversible reaction

$mA + nB \rightleftharpoons pC + qD$ where m, n, p, q be the number of moles of A, B, C and D respectively.

Assuming all reactants and the products to be ideal gases,

We can write

$$K_p = \frac{(p_C)^p \times (p_D)^q}{(p_A)^m \times (p_B)^n}$$

where p_C , p_D , p_A and p_B are the partial pressures of C, D, A and B respectively.

In an ideal mixture, each component obeys Dalton's law of partial pressure according to which partial pressure of individual gas is mole fraction times the total pressure (P) of equilibrium mixture.

i.e. $p_i = x_i P$ where p_i = partial pressure of the i^{th} component in the mixture.

x_i = Mole fraction of ith component

P = Total pressure

$$\text{So, } p_C = x_C P, \quad p_B = x_B P, \quad p_A = x_A P \text{ and } p_B = x_B P$$

$$\text{Hence } K_p = \frac{(P_C)^p \cdot (P_D)^q}{(P_A)^m \cdot (P_B)^n} = \frac{(X_C P)^p \cdot (X_D P)^q}{(X_A P)^m \cdot (X_B P)^n} = \frac{X_C^p \cdot X_D^q}{X_A^m \cdot X_B^n} P^{[(p+q) - (m+n)]}$$

where $\Delta n_{(g)} = [(p+q) - (m+n)]_g$ i.e. difference between the number of moles of gaseous products and reactants.

(b) Relationship between K_p and K_C

For an ideal gaseous mixture

$$p_i V = n_i RT \quad (\Theta \quad PV = nRT)$$

$$\text{or } p_i = \frac{n_i}{V} RT = C_i RT$$

where C_i is the molar concentration of the i^{th} component in the mixture of total volume V .

Thus, $p_A = C_A RT$, $p_B = C_B RT$, $p_C = C_C RT$ and $p_D = C_D RT$

$$K_p = \frac{p_C^p p_D^q}{p_A^m p_B^n} = \frac{(C_C RT)^p (C_D RT)^q}{(C_A RT)^m (C_B RT)^n} = \frac{C_C^p C_D^q}{C_A^m C_B^n} \cdot RT^{[(p+q) - (m+n)]}$$

$$\text{or, } K_p = K_C RT^{\Delta n(g)} \dots \dots \dots \quad (2)$$

From equation (1) and (2)

$$K_p = K_x P^{\Delta n(g)} = K_C (RT)^{\Delta n(g)}$$

When $\Delta n(g) = 0$, i.e. for the reactions which proceed with no change in the number of moles,

$$K_P = K_X = K_C$$

Table : 9.1 Relationship between K_p , K_x & K_c in different equilibria

Equilibrium	$\Delta n(g)$	$K_p = K_c (RT)^{\Delta n(g)}$	$K_p = K_x (P)^{\Delta n(g)}$
1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	0	$K_c = K_c$	$K_p = K_x$
2. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	-1	$K_c = K_p RT$	$K_x = PK_p$
3. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	-2	$K_p = K_p(RT)^2$	$K_x = P^2 K_p$
4. $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$	2	$K_c = K_p(RT)^2$	$K_p = K_x P^2$
5. $NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(l)}$	-1	$K_c = K_p RT$	$K_x = PK_p$

Reaction Quotient and its relationship with equilibrium

Consider a general reversible reaction



At each point in a reaction a ratio of concentration terms can be formulated. It is having the same form as the equilibrium constant expression. This ratio is called **reaction quotient** and is represented by 'Q'

$$\text{So, } Q = \frac{[C]^p [D]^q}{[A]^m [B]^n}$$

The following cases may arise.

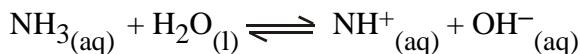
- (i) If the reaction is in equilibrium, $Q = K_c$
- (ii) The net reaction to proceed from left to right i.e.
for the forward reaction to take place, $Q < K_c$
- (iii) The net reaction to proceed from right to left i.e.
for the backward reaction to take place, $Q > K_c$

Equilibrium constant expression for some reactions :

While writing the expressions for equilibrium constant, the following points should be kept in mind.

- (i) Concentration of a **pure** solid or a liquid is taken as **unity**.
- (ii) Concentration of **solvent** is considered as **constant**, because it is present in large excess and its concentration does not change appreciably during the reaction.

(a) For the reaction,



Rate of forward reaction,

$$r_1 = k_1 [\text{NH}_3\text{(aq)}] [\text{H}_2\text{O(l)}]$$

and, rate of backward reaction,

$$r_2 = k_2 [\text{NH}^+\text{(aq)}] [\text{OH}^-\text{(aq)}]$$

We, know at equilibrium, $r_1 = r_2$

$$\text{Hence, } k_1 [\text{NH}_3\text{(aq)}] [\text{H}_2\text{O}] = k_2 [\text{NH}^+\text{(aq)}] [\text{OH}^-\text{(aq)}]$$

$$\text{or, } K_c = \frac{k_1}{k_2} = \frac{[\text{NH}^+\text{(aq)}] [\text{OH}^-\text{(aq)}]}{[\text{NH}_3\text{(aq)}] [\text{H}_2\text{O}]}$$

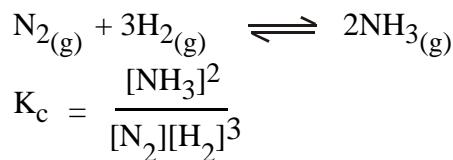
$$\text{or, } K_c = \frac{[\text{NH}^+\text{(aq)}] [\text{OH}^-\text{(aq)}]}{[\text{NH}_3\text{(aq)}]} \quad (\Theta [\text{H}_2\text{O}] = 1)$$

(b) Reaction between gaseous hydrogen and iodine to form hydrogen iodide :

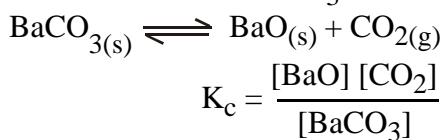


$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

(c) Formation of ammonia :



(d) Decomposition of BaCO_3 :



Since, $[\text{BaCO}_3\text{(s)}] = 1$ and $[\text{BaO}\text{(s)}] = 1$,
 $K_c = [\text{CO}_2\text{(g)}] = p_{\text{CO}_2}$

Characteristics of equilibrium constant (K) :

The main characteristics of the equilibrium constant are as follows.

- (i) The equilibrium constant has a definite value for every reaction at a given temperature.
However, it varies with change in temperature.
- (ii) K_c does not depend upon the individual concentrations of the reacting substances.
- (iii) The value of equilibrium constant is not affected by adding a catalyst.
- (iv) The value of equilibrium constant for the forward reaction is reciprocal of that for the backward reaction.

Example : $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

$$k_1 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad \text{For forward reaction.}$$

$$\text{and } k_2 = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \quad \text{For backward reaction}$$

$$\text{Hence, } k_1 = \frac{1}{k_2}$$

- (v) The value of K tells us the extent to which the forward or backward reaction has taken place. Greater value of K_c and K_p means that the reaction has proceeded to a greater extent in the forward direction.

9.5 LE - CHATELIER'S PRINCIPLE

The principle was generalised by **Le-Chatelier** and **Braun** in 1884. It helps us to predict the effect of change in temperature, pressure and concentration on a system at equilibrium.

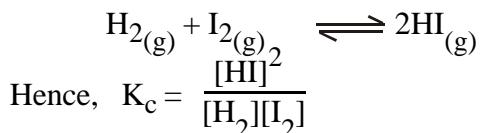
Statement :

If a system at equilibrium is subjected to a change in concentration, pressure or temperature, then the equilibrium shifts in that direction of reaction which tends to undo or reduce the effect of change.

1. Effect of change of concentration :

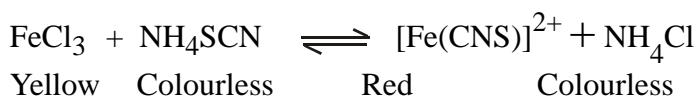
If the concentration of any one of the substances (reactants and products) is increased at equilibrium, then the equilibrium shifts in the direction in which the added substance will be consumed.

Example : Consider a reaction between gaseous H_2 and I_2 in a closed vessel at equilibrium.



In the above reaction, if the concentration of H_2 or I_2 increases, then the equilibrium will shift in that direction in which the added H_2 and I_2 will be consumed forming HI . That means, the equilibrium will shift in the forward direction. Similarly, if the concentrations of HI increases, the reaction will proceed in the backward direction as in that direction the added HI can be consumed by forming H_2 and I_2 . In both the cases the value of K_c remains constant.

The effect of concentration can be illustrated by studying the reaction between $FeCl_3$ and NH_4SCN .



At equilibrium, if $FeCl_3$ is added to the system, the equilibrium shifts in the forward direction and more $[Fe(CNS)]^{2+}$ is formed. So the red colour deepens. But if NH_4Cl is added, the equilibrium shifts in the backward direction and more $FeCl_3$ is formed. So the red colour will gradually fade.

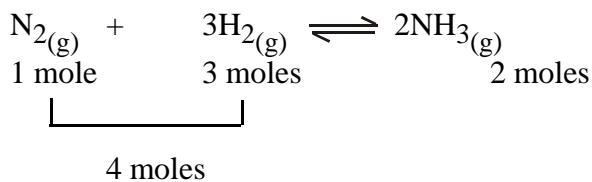
Conclusions :

- i. Increase in concentration of any of the reactants $\xrightarrow{\text{shifts the equilibrium to}}$ Forward direction.
- ii. Increase in concentration of any of the products $\xrightarrow{\text{shifts the equilibrium to}}$ Backward direction.

2. Effect of change of pressure :

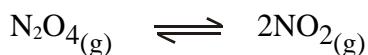
If the system in equilibrium consists of gases, then the state of equilibrium is disturbed by the change of pressure. Three types of situations may arise.

- (a) When the number of moles in the reactant side in the gaseous state is more than that in the product side in an equilibrium reaction, the increase in pressure favours the formation of products. Consider the formation of ammonia molecules,



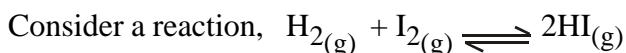
By increasing pressure, the volume of the system will decrease considerably. The total number of moles per unit volume will now be more than before. The change can be counteracted if equilibrium shifts in that direction in which the total number of moles is decreased. This can take place by the combination of H₂ and N₂ molecules to produce NH₃ molecule. Thus, higher the pressure, the greater would be the yield of ammonia.

- (b) When the number of moles in the reactant side is less than the number of moles on the product side in an equilibrium reaction, then the increase in pressure favours the backward reaction,



For such reactions in equilibrium high pressure favours the backward reaction and the equilibrium shifts to left. So, the above reaction is favoured by the decrease in pressure.

- (c) In an equilibrium reaction in which the number of moles on the reactant side is equal to those on the product side, then the effect in pressure does not change the state of equilibrium.



The above reaction proceeds in either direction without any change in the number of moles. According to Le-Chatelier's principles, therefore, the pressure would have no effect on this equilibrium.

Conclusions :

- i. Increase in pressure $\xrightarrow{\text{shifts the equilibrium to Less number of gaseous moles.}}$
in a direction of
- ii. Decrease in pressure $\xrightarrow{\text{shifts the equilibrium to large number of gaseous moles}}$
in a direction of

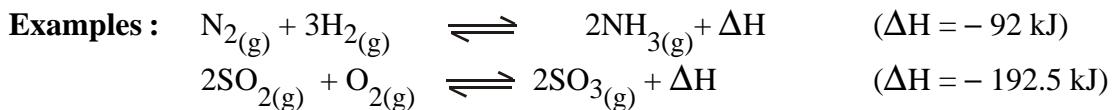
3. Effect of change of temperature :

To find the effect of temperature, reactions are divided into two categories.

- (a) Exothermic reversible reaction.
and (b) Endothermic reversible reaction.

(a) Exothermic reversible reaction :

In this type of reactions the heat is liberated in the forward direction, so it can also be said that, the heat is absorbed in the backward direction.



In these reactions, ΔH amount of heat, is liberated in the forward direction. So, when the temperature is increased, the equilibrium shifts in that direction in which this extra heat will be absorbed, that is in the backward direction. Such reactions are, therefore, favoured by decrease in temperature. Thus, the formation of NH_3 and SO_3 are favoured by a decrease in temperature.

(b) Endothermic reversible reactions :

In this types of reactions, the heat is absorbed in the forward direction. So, it can be said that, the heat is liberated in the backward direction.



In this reaction ΔH amount of heat, is absorbed in the forward direction. So, when the temperature is increases, the equilibrium shifts in the forward direction, so that extra amount of heat is used up. These reactions are, therefore, favoured by increase in temperature.

It must be remembered that when a reaction is exothermic in the forward direction, it is endothermic in the backward direction.

Conclusion :

- | | |
|------------------------------|---|
| (i) Increase in temperature | $\xrightarrow{\text{shifts the equilibrium in the direction}}$
Endothermic reaction. |
| (ii) Decrease in temperature | $\xrightarrow{\text{shifts the equilibrium in the direction}}$
Exothermic reaction |

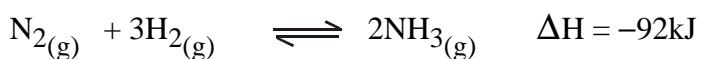
4. Effect of catalyst :

The addition of a catalyst increases the rates of the opposing reactions to the same extent. This hastens the approach of equilibrium. Thus, a catalyst has no effect on the state of equilibrium.

Applications of Le-Chatelier's principle :

1. Manufacture of ammonia (Haber's Process) :

Ammonia is manufactured by mixing one volume of nitrogen with three volumes of hydrogen at 500°C under 200-900 atmospheric pressure in presence of catalyst,. The best catalyst known is highly porous finely divided iron containing small amounts of promoters usually molybdenum or oxide of aluminium.



For this reaction, $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$

(a) Effect of change of concentration :

By increasing the concentration of N₂ or H₂ or both, the equilibrium shifts towards right, so as to keep the value of K_c constant. Hence, concentration of NH₃ increases by increasing the molar concentration of H₂ or N₂ or both.

(b) Effect of change of pressure :

Four volumes of reactants give two volumes of product. Thus formation of ammonia is facilitated by decrease in volume. Hence increase of pressure shifts the equilibrium towards right and favours the formation of ammonia.

(c) Effect of change of temperature :

This reaction is an exothermic reaction. The increase in temperature will not favour the forward reaction. So, production of NH₃ will decrease by increasing temperature. In this case, low temperature favours the formation of ammonia as the equilibrium shifts towards right. But in order to start the reaction, some amount of heat is necessary. Therefore, the reaction mixture is kept at 500°C and is never increased beyond it. This is called **optimum temperature**.

Conclusion : The ammonia can be manufactured industrially by Haber's process at.

- (i) high pressure, (ii) low temperature and (iii) by increasing the concentration of reactants.

2. Manufacture of sulphuric acid by Contact process :

For the manufacture of H₂SO₄, SO₂ is first oxidised to SO₃ in presence of platinised asbestos. The reaction is exothermic.



Here, 2 volumes of SO₂ combine with one volume of oxygen to give two volumes of sulphur trioxide. In this, volume is decreased in the forward reaction. So, high pressure favours the forward reaction. As this is exothermic reaction, low temperature favours the forward reaction. High concentrations of SO₂ and O₂ also favour the forward reaction and give more yield of SO₃.

3. Manufacture of nitric oxide :

Nitrogen and oxygen are made to combine at 3000°C. This high temperature is achieved by means of an electric spark.



This reaction is endothermic and takes place by absorption of heat. So, high temperature favours the forward reaction. One volume of nitrogen combines with one volume of oxygen to give two volumes of nitric oxide. Since there is no volume change, pressure has no effect on the equilibrium.

4. Dissociation of nitrogen tetroxide :

Nitrogen tetroxide is a colourless gas. This on heating dissociates to nitrogen peroxide, which is a reddish brown gas.



This is an endothermic reaction. Hence increase in temperature favours the forward reaction giving more yield of NO_2 . One molecule of nitrogen tetroxide gives two molecules of nitrogen peroxide. So in this case volume increases in the forward reaction. So, low pressure will facilitate the forward reaction giving more yield of NO_2 . If the concentration of N_2O_4 is increased, the yield of NO_2 will increase.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Thus, according to Le Chatelier's principle, the equilibrium shifts toward the right, in order to keep K_c constant.

Thermal dissociation :

It is a process in which the molecule of a substance breaks up into simpler molecules or atoms on heating. It is a reversible process.

Example : NH_4Cl dissociates on heating to give NH_3 and HCl



It is a reversible reaction. On cooling NH_3 and HCl combine to give NH_4Cl .

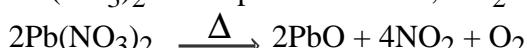
Other examples are :



Thermal decomposition :

It is a process in which the molecule of a substance on heating breaks up into simpler molecules or atoms. It is **not** a reversible process.

Example : $\text{Pb}(\text{NO}_3)_2$ decomposes into PbO , NO_2 and O_2



Distinction between dissociation and decomposition :

Dissociation	Decomposition
i. It is a reversible process	i. It is an irreversible process.
ii. Reaction never goes to completion.	ii. Reaction always goes to completion.
iii. Le-Chatelier's principle is applicable	iii. Le-Chatelier's principle is not applicable.

Application of Law of mass action to different equilibria :

1. **Homogenous equilibria :** The equilibria in which both the reactants and the products are in the same phase are called homogenous equilibria.

(a) **Gaseous phase equilibria :** This type of equilibria involves the following cases:

case (1) When $\Delta n = 0$.

For example, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

a	b	0 (Initially)
(a-x)	(b-x)	2x (at equilibrium)

Let 'a' moles of $\text{H}_2(\text{g})$ react with 'b' moles of I_2 to give $\text{HI}(\text{g})$ and let 'x' moles of $\text{HI}(\text{g})$ is produced at equilibrium.

Let the volume of the container be 'v' litre,

$$\text{Hence, } [\text{H}_2] = \frac{a-x}{V} \quad [\text{I}_2] = \frac{b-x}{V}$$

and $[HI] = \frac{2x}{V}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{4x^2}{(a-x)(b-x)} \dots \dots \dots \quad (1)$$

Again, let 'P' be the pressure of the gas at equilibrium.

$$\text{Total moles at equilibrium} = (a - x) + (b - x) + 2x = a + b.$$

$$\text{Mole fraction of } [\text{H}_2] = \frac{a - x}{a + b}$$

$$\text{Mole fraction of } [I_2] = \frac{b-x}{a+b}$$

$$\text{and Mole fraction of [HI]} = \frac{2x}{a+b}$$

We know, partial pressure of a component = Total pressure \times its mole fraction.

From eqn (1) and (2), we get, K_p and K_c are same for the formation of HI. Hence, when number of moles of the reactants and products are same, that is, when $\Delta n = 0$, $K_p = K_c$.

Case (ii) when $\Delta n \neq 0$,

For example, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

a	b	o	(Initially)
$(a - x)$	$(b - 3x)$	2x	(at equilibrium)

Initially let 'a' moles of $\text{N}_2^{(g)}$ react with 'b' moles of $\text{H}_2^{(g)}$ to produce $\text{NH}_3^{(g)}$.

Let. x moles of NH_3 is produced at equilibrium and the volume of the container be 'v' litre.

$$\therefore [N_2] = \frac{a-x}{v}, [H_2] = \frac{b-3x}{v} \text{ and } [NH_3] = \frac{2x}{v}$$

$$\therefore K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x/v)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3}$$

$$\text{or, } K_c = \frac{4x^2 \cdot v^2}{(a-x)(b-3x)^3} \quad \dots \dots \dots \quad (3)$$

Let pressure at equilibrium is P .

Total moles at equilibrium = $a - x + b - 3x + 2x = a + b - 2x$.

$$P_{N_2} = P \times \frac{a - x}{a + b - 2x}$$

$$p_{H_2} = P \times \frac{b - 3x}{a + b - 2x}$$

$$\text{and } p_{\text{NH}_3} = P \times \frac{2x}{a + b - 2x}$$

$$\therefore K_p = \frac{(pNH_3)^2}{(pN_2)(pH_2)^3} = \frac{\left(P \times \frac{2x}{a+b-2x}\right)^2}{\frac{P(a-x)}{a+b-2x} \times \left(\frac{P(b-3x)}{a+b-2x}\right)^3}$$

$$\text{or, } K_p = \frac{4x^2(a+b-2x)^2}{P^2(a-x)(b-3x)^3} \quad \dots \dots \dots (4)$$

From eqn. (3) and (4) we get,

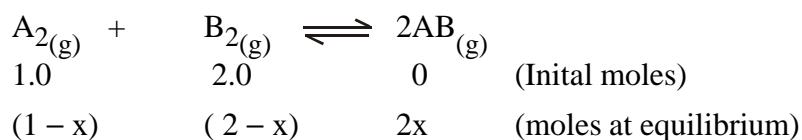
$K_p \neq K_c$ for the formation of NH_3 :

Hence, when the $\Delta n \neq 0$, $K_p \neq K_c$

Solved numerical problems :

1. The K_c for $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$ at 100°C is 50. If one litre flask containing one mole of A_2 is connected with a two liter flask containing 2 moles of B_2 , how many moles of AB will be formed at 100°C (IIT., 1985).

Solution :



The volume (v) becomes 3 liter on joining two containers.

At equilibrium, $[A_2] = \frac{1-x}{3}$, $[B_2] = \frac{2-x}{3}$ and $[AB] = \frac{2x}{3}$

Hence, according to law of mass action,

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\frac{(1-x)}{3} \frac{(2-x)}{3}} = \frac{4x^2}{2-3x+x^2}$$

or, $50 = \frac{4x^2}{2-3x+x^2}$ (1)

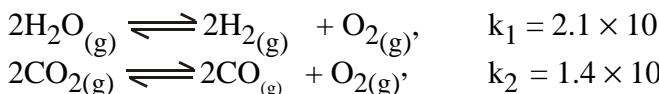
Solving eqn (i) we get, $x = 0.93$ and 2.326 . Since the value of x should not be equal to or more than 2, the value of x will be 0.93 .

$$\therefore \text{Number of moles of AB} = 2x = 2 \times 0.93 = 1.86$$

2. Calculate the equilibrium constant for the reaction,



if the equilibrium constant at 1395 K for the following are,

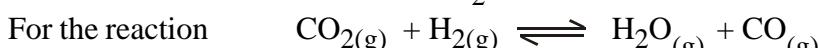


Solution For the reaction, $2H_{2O(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$

$$k_1 = \frac{[H_2]^2 [O_2]}{[H_2O]^2} \quad \dots \quad (\text{i})$$



$$k_2 = \frac{[CO]^2 [O_2]}{[CO_2]^2} \quad \dots \quad (\text{ii})$$



$$K = \frac{[H_2O][CO]}{[CO_2][H_2]} \quad \dots \quad (\text{iii})$$

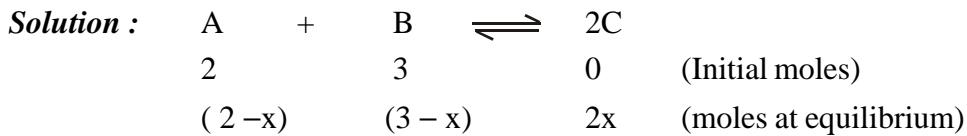
Dividing eqn (ii) by (i) we get,

$$\frac{k_2}{k_1} = \frac{[CO]^2 [O_2]}{[CO_2]^2} \times \frac{[H_2O]^2}{[H_2]^2 [O_2]}$$

$$\text{or, } \frac{k_2}{k_1} = \frac{[CO]^2 [H_2O]^2}{[CO_2]^2 [H_2]^2} = K^2 \quad \dots \quad (\text{iv})$$

$$\therefore K = \sqrt{\frac{k_2}{k_1}} = \sqrt{\frac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}}} = 2.58$$

3. For the reaction, $A + B \rightleftharpoons 2C$, 2 moles of A and 3 moles of B are allowed to react. If the equilibrium constant is 4.0 at 400° C , what will be the moles of C at equilibrium.



Let volume of the container be V litre.

$$\therefore K_c = \frac{[C]^2}{[A][B]} = \frac{(2x/v)^2}{\frac{2-x}{v} \times \frac{3-x}{v}}$$

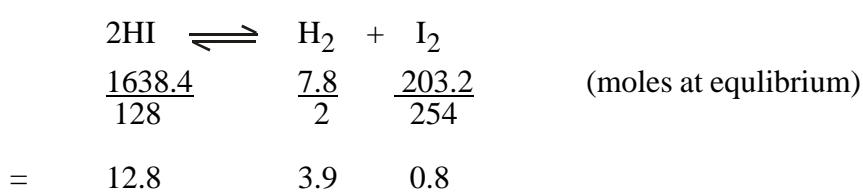
$$\therefore 4.0 = \frac{4x^2}{(2-x)(3-x)}$$

$$\therefore x = 1.2$$

or, Moles of C at equilibrium = $2x = 2 \times 1.2 = 2.4$

4. For a reaction $2HI \rightleftharpoons H_2 + I_2$ at equilibrium 7.8g, 203.2g and 1638.4g of H_2 , I_2 and HI respectively were found. Calculate K_c .

Solution :



Let volume of the container be v litres

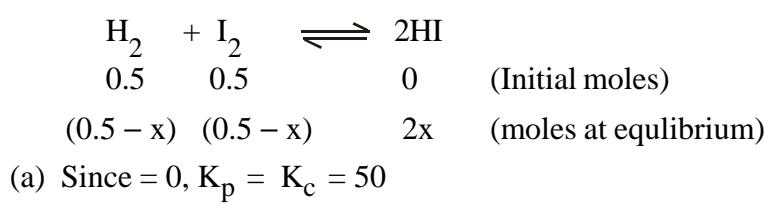
$$\therefore [H_2] = \frac{3.9}{v}, [I_2] = \frac{0.8}{v} \text{ and}$$

$$[HI] = \frac{12.8}{v}$$

$$\therefore K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{3.9}{v} \times \frac{0.8}{v}\right)}{\left(\frac{12.8}{v}\right)^2} = 0.019$$

5. 0.5 moles of H_2 , 0.5 moles of I_2 reacts in 10 litre flask at $448^\circ C$. The equilibrium constant (K_c) is 50 for $H_2 + I_2 \rightleftharpoons 2HI$
- What is the value of K_p ?
 - Calculate moles of I_2 at equilibrium.

Solution :



$$(b) K_c = \frac{[HI]^2}{[H_2][I_2]}$$

The volume of the flask is 10 litre.

$$[H_2] = \frac{0.5 - x}{10}, [I_2] = \frac{0.5 - x}{10}$$

$$\text{or, } [HI] = \frac{2x}{10}$$

$$\therefore K_c = \frac{\left(\frac{2x}{10}\right)^2}{\frac{0.5-x}{10} \times \frac{0.5-x}{10}} = \frac{4x^2}{(0.5-x)^2}$$

$$\text{or, } \frac{4x^2}{(0.5-x)^2} = 50$$

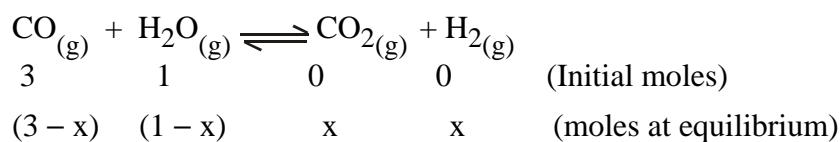
$$\text{or, } \frac{2x}{0.5-x} = \sqrt{50} \quad \text{or, } x = 0.39$$

Hence, moles of I_2 at equilibrium.

$$= 0.50 - 0.39 = 0.11 \text{ moles.}$$

6. K_c for $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_{2(g)}$ at 986°C is 0.63. A mixture of 1 mole $\text{H}_2\text{O}_{(g)}$ and 3 moles $\text{CO}_{(g)}$ is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm. (a) How many moles of H_2 are present at equilibrium? (b) Calculate partial pressure of each gas at equilibrium.

Solution :



$$\text{Total moles at equilibrium} = 3 - x + 1 - x + x + x = 4$$

$$(a) K_c = \frac{x^2}{(3-x)(1-x)} = 0.63$$

$$\text{or, } x = 0.681$$

Thus, moles of H_2 formed at equilibrium = 0.681.

(b) Partial pressure of each gas

= Pressure at equilibrium \times mole fraction of gas.

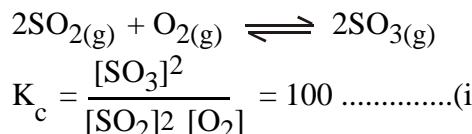
$$\therefore p_{H_2} = p_{CO_2} = 2.0 \times \frac{0.681}{4} \quad (\Theta \text{ mole fraction} = \frac{\text{no of moles}}{\text{total moles at equilibrium}}) \\ \equiv 0.34 \text{ atm}$$

$$p_{CO} = \frac{2.0 \times (3-x)}{4} = \frac{2(3 - 0.681)}{4} = 1.16 \text{ atm}$$

$$p_{H_2O} = \frac{2(1-x)}{4} = \frac{2(1-0.681)}{4} = 0.16 \text{ atm}$$

7. A mixture of SO_3 , SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a temperature at which K_c for the reaction $2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{SO}_{3(\text{g})}$ is 100. At equilibrium (a) if number of moles of SO_3 and SO_2 in flask are same, how many moles of O_2 are present. (b) if number of moles of SO_3 in flask is twice the number of moles of SO_2 , how many moles of O_2 are present ?

Solution :



$$(a) \quad [SO_3] = [SO_2]$$

Putting these values in eqn (i), we get

$$K_c = \frac{1}{[O_2]} = 100$$

or, $[O_2] = \frac{1}{100} = 0.01$

$$\text{Hence, } \frac{\text{moles of O}_2}{\text{volume}} = 0.01$$

$$\text{or, Moles of O}_2 = 0.01 \times 10 (\therefore v = 10 \text{ litre}) \\ \equiv 0.1$$

(b) If, $[SO_3] = 2[SO_2]$

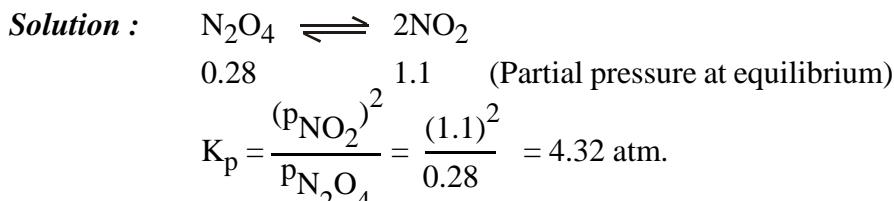
Putting these values in eqn(i) we get,

$$K = \frac{4}{[O_2]} = 100$$

$$\text{or, } [\text{O}_2] = \frac{4}{100} = 0.04$$

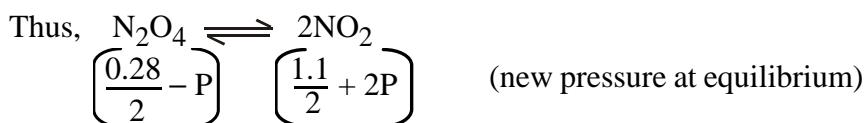
$$\text{Hence, } \frac{\text{moles of O}_2}{\text{volume}} = 0.04 \text{ or, Moles of O}_2 = 0.04 \times 10 = 0.4$$

8. An equilibrium mixture at 300K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases.



If volume of the container is doubled, its pressure will be reduced to half. According to Le-chateliers principle, by decreasing the pressure, the equilibrium will shift towards the side consisting of large number of moles. That means the decomposition of N_2O_4 will be favoured by decreasing pressure.

Let P = Pressure used up for decomposition of N_2O_4 .



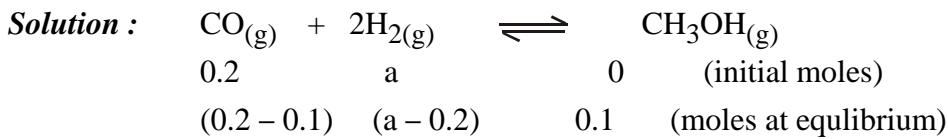
$$\therefore K_p = \frac{\left(\frac{1.1}{2} + 2P \right)^2}{\left(\frac{0.28 - P}{2} \right)} = 4.32 \text{ atm.}$$

or, $P = 0.045 \text{ atm.}$

$\therefore p_{\text{N}_2\text{O}_4}$ at new equilibrium
 $= 0.14 - 0.045 = 0.095 \text{ atm.}$

p_{NO_2} at new equilibrium
 $= 0.55 + 2 \times 0.045 = 0.64 \text{ atm.}$

9. For the reaction $\text{CO}_{(\text{g})} + \text{H}_{2(\text{g})} \rightleftharpoons \text{CH}_3\text{OH}_{(\text{g})}$, H_2 gas is introduced into a five litre flask at 327°C , containing 0.2 mole of $\text{CO}_{(\text{g})}$ and a catalyst till pressure is 4.92 atomsphere. At this point 0.1 mole of $\text{CH}_3\text{OH}_{(\text{g})}$ is formed. Calculate K_c and K_p .



Total moles at equilibrium = $0.1 + a - 0.2 + 0.1 = a$

We know, the ideal gas eqn, $PV = nRT$

$$\text{or, } n = PV/RT = \frac{4.92 \times 5}{0.0821 \times 600} = 0.499$$

\therefore The moles at equilibrium, $a = 0.499$

$$[\text{CH}_3\text{OH}] = \frac{0.1}{5} [\text{H}_2] = \frac{0.499 - 0.2}{5} = 0.299/5$$

and $[CO] = 0.1/5$.

$$\therefore K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.1/5}{0.1/5 \times (0.299/5)^2} = 279.64 \text{ litre}^2 \text{ mole}^{-2}$$

We know, $K_p = K_c \cdot (RT)^{\Delta n}$

In the above reaction, $\Delta n = -2$

$$\begin{aligned}\therefore K_p &= 279.64 \times (0.0821 \times 6000) \\ &= 0.115 \text{ atm}^{-2}\end{aligned}$$

10. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction.



If we take one mole each of all the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2 gases ? (IIT, 1987)

Solution :	$SO_{2(g)}$	$+ NO_{2(g)}$	\rightleftharpoons	$SO_{3(g)}$	$+ NO_{(g)}$	
	1	1		1	1	(Initial moles)
	$(1-x)$	$(1-x)$		$1+x$	$1+x$	(moles at equilibrium)

Let 'v' be the volume of the container at equilibrium.

$$\begin{aligned}\therefore K_c &= \frac{[SO_3][NO]}{[SO_2][NO_2]} ; \quad \text{Since } v = 1 \text{ litre, } K_c = \frac{(1-x)(1+x)}{(1-x)(1-x)} \\ \text{or, } 16 &= \frac{(1+x)^2}{(1-x)^2} \quad \text{or} \quad \frac{1+x}{1-x} = 4 \quad \text{or, } x = 0.6\end{aligned}$$

Thus, the equilibrium concentration of $NO = \frac{1+x}{v} = \frac{1+0.6}{1} = 1.6$ moles/litre

The equilibrium concentration of $NO_2 = \frac{1-x}{v} = \frac{1-0.6}{1} = 0.4$ mole/litre.

2. Heterogeneous Equilibria

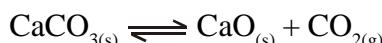
If the reactants and the products are in different phases, the equilibrium is said to be heterogeneous.

For example (i) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

(ii) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

(i) Study of equilibria $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

Consider the equilibrium reaction



Initial no. of moles	1	0	0
----------------------	---	---	---

Equilibrium no. of moles	$1-x$	x	x
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Total no. of moles at equilibrium = x (since no. of moles of solids are not considered)

$$\text{Molefraction of CO}_2 = \frac{x}{x} = 1$$

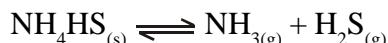
Partial pressure = molefraction \times total pressure

$$= 1 \times P = P$$

$$K_p = p_{CO_2} = P$$

(ii) **Study of equilibria** $\text{NH}_4\text{HS}_{(s)} \rightleftharpoons \text{NH}_{3(g)} + \text{H}_2\text{S}_{(g)}$

Consider the equilibrium reaction



Initial no. of moles	1	0	0
Equilibrium no. of moles	1-x	x	x

Total no. of moles at equilibrium = $x + x = 2x$

$$\text{Molefraction of NH}_3 = \frac{x}{2x} = \frac{1}{2}$$

$$\text{Partial pressure of NH}_3 = \text{mole fraction} \times \text{total pressure} = \frac{P}{2}$$

$$\text{Mole fraction of H}_2\text{S} = \frac{x}{2x} = \frac{1}{2}$$

$$\text{Partial pressure of H}_2\text{S} = \frac{P}{2}$$

$$K_p = p_{NH_3} \times p_{H_2S} = \frac{P}{2} \times \frac{P}{2} = \frac{P^2}{4}$$

IONIC EQUILIBRIA

9.6

THEORIES OF ACIDS AND BASES

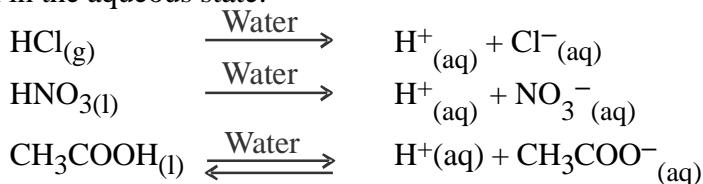
Introduction :

Various theories have been put forward by different workers in order to explain the nature of acids and bases. These theories are based on the configuration or inner structure of acids and bases.

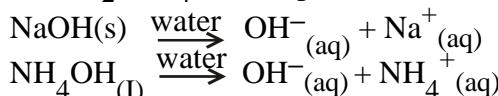
These theories are,

- (i) Arrhenius theory
- (ii) Bronsted – Lowry theory
- (iii) Lewis theory.

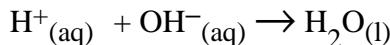
- (i) Arrhenius theory :** The important postulates of Arrhenius theory are,
- (a) Acids are those substances which yield H^+ ions in the aqueous solution. Thus, HCl , H_2SO_4 , HNO_3 , H_3PO_4 , CH_3COOH , HCN and $HOCl$ are acids, because they contain replaceable H^+ ion in the aqueous state.



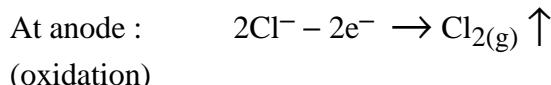
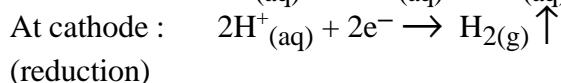
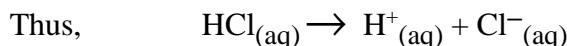
- (b) Bases are those substances which provide OH^- ions in the aqueous state. Thus, $NaOH$, KOH , $Ba(OH)_2$, NH_4OH etc. provide OH^- ions in the aqueous state and are bases.



- (c) Neutralisation of an acid and a base is based on the key reaction between H^+ ions and OH^- ions to form undissociated water molecules.



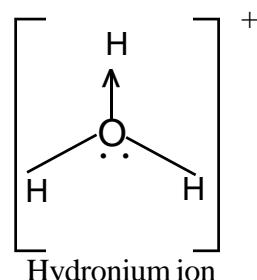
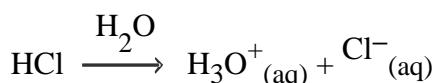
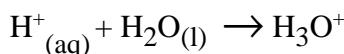
- (d) During electrolysis of an aqueous solution of an acid, H^+ ions proceed to the cathode and negative ions, to the anode.

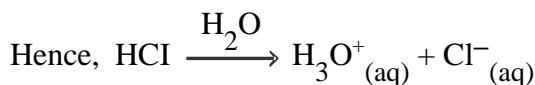


Limitations of Arrhenius theory :

The limitations of Arrhenius theory are as follows,

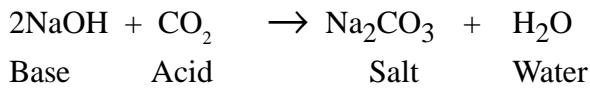
- (a) This theory explains the acidic and the basic characters of the substances in aqueous solution. It has been found that $NaOH$ exists as Na^+ ions OH^- ions even in the solid state. This theory fails to explain such facts.
- (b) According to Arrhenius, an acid releases H^+ ions in aqueous medium. H^+ ion is proton, which can not exist independently in the aqueous state. It accepts a pair of electrons from water molecule to form hydrated proton or hydronium ion.
- Hence, H^+ ions in acidic solution can not exist independently, but exist in combination with water molecules, hydronium ions.



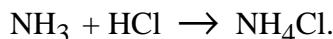


- (c) There are number of substances which do not provide H^+ ions and OH^- ions, but still behave as acids and bases.

For example, CO_2 does not contain any hydrogen atom, but it acts as an acid. It reacts with NaOH to form salt.



Similarly, NH_3 , although does not contain OH^- ions, behaves as a base, because, it reacts with HCl to form a salt.



(ii) Bronsted – Lowry theory (Proton transfer theory) :

According to this theory,

- (a) Acid is a substance (molecule or ion) which has tendency to donate a proton to any other substance.
- (b) Base is a substance (molecule or ion) which has a tendency to accept a proton from any other substance.

In other words, an acid is a proton donor and base is a proton acceptor. So, this theory is also known as **proton transfer theory**. since it involves the transfer of proton. Hence, acids are protogenic and bases are protophilic.

Examples :

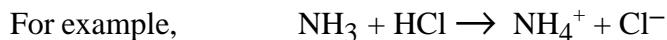
Molecular acids : $\text{HF}, \text{HCl}, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$ etc.

Ionic acids : $\text{H}_3\text{O}^+, \text{NH}_4^+, \text{HSO}_4^-, \text{HCO}_3^-$ etc.

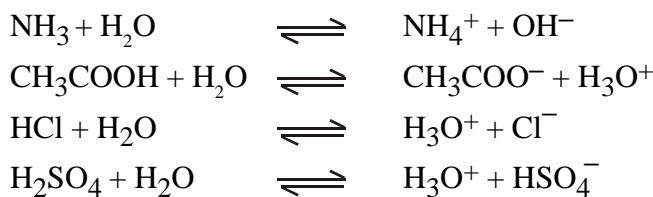
Molecular bases : $\text{R-NH}_2, \text{R}_2\text{NH}, \text{R}_3\text{N}, \text{NH}_3, \text{H}_2\text{O}$ etc.

Ionic bases : $\text{OH}^-, \text{S}^{2-}, \text{CO}_3^{2-}, \text{Cl}^-, \text{NO}_3^-$, etc.

It is important to note that, no single substance is an acid or a base. A single substance can not donate a proton unless and until some other substance which accepts the proton is also present.



Here, HCl donate a proton to NH_3 Thus, HCl is an acid and NH_3 is a base. Other examples of acid-base reactions are given below.

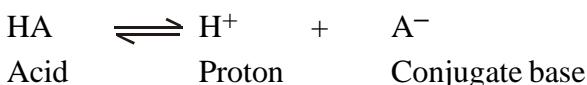


From the above examples, we know that water is an acid with respect to NH_3 . But, it is a base with respect to CH_3COOH or HCl or H_2SO_4 . Such substances (like H_2O , HCO_3^- , HSO_4^- etc.) which can act both as acids as well as bases are called amphoteric or amphiprotic substances.

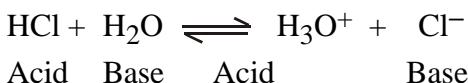
Conjugate acid-base pairs :

When an acid loses a proton, the residual part of it will have a tendency to accept a proton. Thus, the residual part will behave as a base. Such pairs of substances which differ from one another by a proton are known as **conjugate** acid-base pairs.

Consider a general example of an acid, HA .

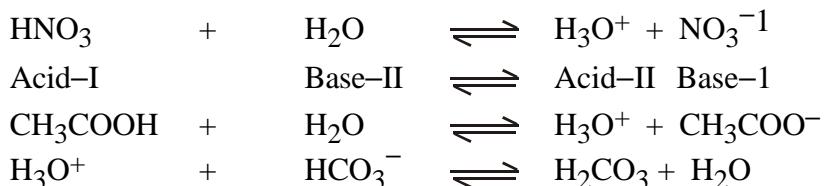


Consider the reaction between HCl and H_2O



Here, HCl donates a proton to water in the forward reaction. Thus, HCl is an acid and H_2O is a base. In the backward reaction, H_3O^+ ion donates its proton to Cl^- ion. Thus, H_3O^+ ion is an acid and Cl^- is a base. It is clear that, HCl loses a proton and forms Cl^- ion, which is a base. HCl and Cl^- ion are called conjugate acid – base pair.

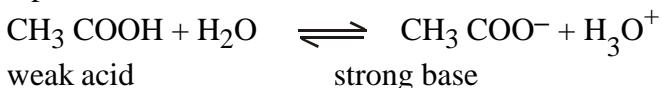
Other examples of conjugate acid - base pairs are,



Relative strength of acids and bases :

According to proton transfer theory, (a) the strength of the acid depends upon the tendency to donate proton, and (b) strength of the base depends upon its tendency to accept a proton.

For example, consider the reaction between acetic acid and water.



Acetic acid has a poor tendency to donate a proton. Therefore, it is a weak acid. The above equilibrium lies mostly towards the left. It follows, therefore, that CH_3COO^- ion must have a strong tendency to accept a proton. Hence, CH_3COO^- , a conjugate base of acetic acid is a strong base.

Hence, **weak acid** \rightleftharpoons $\text{H}^+ + \text{strong conjugate base}$.

Similarly, HCl is a strong acid in water.



The above equilibrium lies mostly towards the right. It follows, therefore, that Cl^- ion must have a little tendency to accept a proton. Hence, Cl^- ion is a weak conjugate base.

Strong acid \rightleftharpoons $\text{H}^+ + \text{weak conjugate base}$

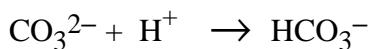
Thus, we conclude that, every strong acid has a weak conjugate base and vice-versa.

Important note :

All Arrhenius acids are also Bronsted acids, but all Bronsted bases are not Arrhenius bases.

Reason :

According to Arrhenius theory, base must furnish OH^- ion in aqueous state. But, according to Bronsted, a base must accept a proton. So, CO_3^{2-} ion is a base, as it accepts a proton, according to Bronsted theory. But CO_3^{2-} is not a base according to Arrhenius theory, as it does not furnish OH^- ion in aqueous solution.



Limitations of Bronsted -Lowry theory :

- (a) This concept has a greater field of application to aqueous as well as non-aqueous solutions.
- (b) It fails to explain the acidic nature of oxides like, CO_2 , SO_2 etc. and basic nature of ZnO , CaO etc.
- (c) It also fails to explain the acidic character of AlCl_3 , FeCl_3 , BF_3 etc.

(iii) Lewis Theory :

G. N. Lewis (1923) gave new definitions of acids and bases, taking into account their electronic configurations. According to this theory, an acid is a substance (molecule or ion) which can accept a pair of electrons, while a base is any substance (molecule or ion) which can donate a pair of electrons.

In short, acid is an electron pair acceptor and base is an electron pair donor.

Classification of Lewis bases :

- (a) All simple anions are Lewis bases.
For example, Cl^- , CN^- , CH_3COO^- , Cl^- , Br^- , NO_3^- , HSO_4^-
- (b) Neutral molecules having one or more lone pairs of electrons.
For example, NH_3 , $\text{R}-\text{NH}_2$, R_2NH , R_3N , H_2O , $\text{R}-\text{OH}$, $\text{R}-\text{O}-\text{R}$ etc. (R = any alkyl group)



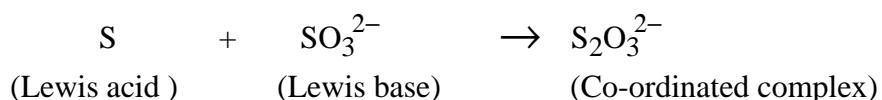
Lewis base Co-ordinated complex

Classification of Lewis acids :

- (a) All simple cations are lewis acids. For example, Cu^{++} , Ag^+ , Ca^{++} , Fe^{+++} etc.
- (b) Molecules, whose central atoms have incomplete octet, also act as lewis acids.
For example, BF_3 , AlCl_3 , ZnCl_2 , SO_3 , FeCl_2 etc.
- (c) Molecules having multiple bonds between atoms of different electronegativities act as Lewis acids. For example CO_2 , SO_2 , SO_3 , etc.
- (d) Molecules having atoms which can accomodate more electrons in the vacant d-orbitals in the valency shell. For example SiCl_4 , SiF_4 , etc.

(e) Element with six electrons in its valence shell also acts as Lewis acid.

For example, SO_3^{2-} ion is oxidised to thiosulphate ion by the acidic nature of sulphur.



Acid-base reactions :

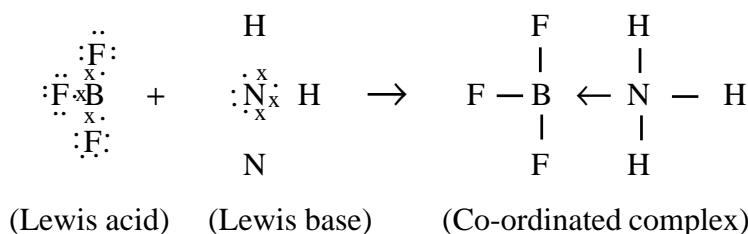
According to the orbital concept,

- (a) any substance having vacant orbital in valence shell can act as an acid.
and (b) an atom with a lone-pair of electrons in its valence shell can act as a base.

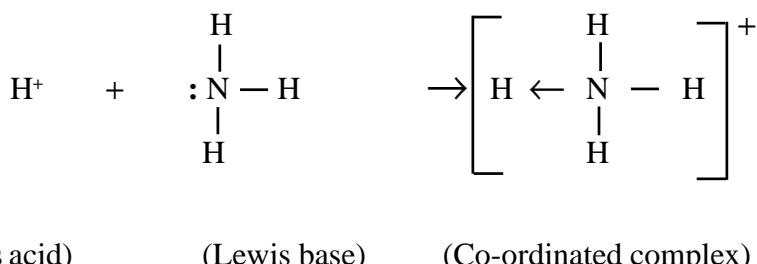
The examples of acid-base reactions are given below.

(a) Action of BF_3 (acid) with NH_3 (base) to form co-ordinated complex, $[\text{F}_3\text{B} \leftarrow \text{NH}_3]$

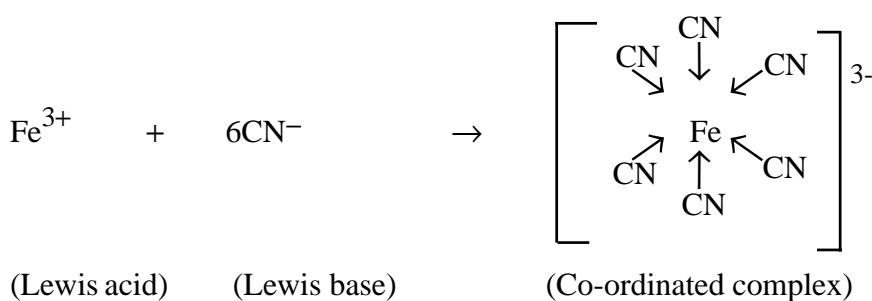
Here, BF_3 behaves as an acid as boron atom is electron deficient and NH_3 acts as a base, as there is a lone pair of electrons on nitrogen atom



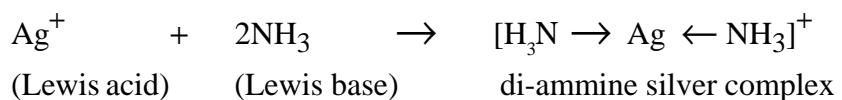
(b) Action of NH_3 (base) on H^+ (acid) to from NH_4^+ ion



(c) Fe^{3+} ion (Lewis acid) reacts with CN^- ion (Lewis base)



- (d) Action of Ag^+ (acid) with NH_3 (base)



Limitations of Lewis concept :

Lewis theory has the following limitations.

- (a) The relative strength of acids and bases can not be explained as it does not consider ionisation.
 - (b) According to this theory an acid - base reaction is associated with the formation of a dative bond, but no such bond is formed when HCl reacts with NaOH.
 - (c) Acid - base reactions are instantaneous, but dative bond formation is a slow process.
 - (d) The catalytic properties of acids are not explained by Lewis theory.
 - (e) It fails to explain the amphoteric nature of H_2O , HCO_3^- ion etc.

9.7 IONISATION OF WEAK ACIDS AND BASES

Ionisation of weak acid

Consider the ionisation of weak monobasic acid HA in water.



Applying law of chemical equilibrium

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \dots \quad (1)$$

where K_c = Equilibrium constant in terms of molar concentration. In dilute solution since water is present in large excess, its concentration is taken as constant. i.e. $[H_2O] = k$ (say),

Further, H_3O^+ indicates that H^+ ion is hydrated and it may be replaced by H^+ , Thus equation (1) can be written as

$$K_c = \frac{[H^+][A^-]}{[HA]_k} \dots \dots \dots (2)$$

$$\text{or, } K_c \cdot k = \frac{[H^+][A^-]}{[HA]}$$

where $K_{C,k}$ = a new constant K_a (say)

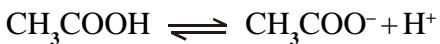
K_a is known as **dissociation constant** or **ionisation constant** of weak acid HA. K_a is constant at a constant temperature. It varies only with temperature. The K_a values of a few weak acids are given below (Table 9.2.)

Table 9.2 K_a of some carboxylic acids at 25°C

Acid	Value of K_a at 25°C
HCOOH	17.7×10^{-5}
CH_3COOH	1.75×10^{-5}
ClCH_2COOH	136×10^{-5}
Cl_2CHCOOH	5530×10^{-5}
$\text{Cl}_3\text{C.COOH}$	23200×10^{-5}
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	1.52×10^{-5}
$\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}
(p-NO ₂)C ₆ H ₄ COOH	36×10^{-5}
(p-Cl)C ₆ H ₄ COOH	10.3×10^{-5}
(p-OH)C ₆ H ₄ COOH	2.6×10^{-5}

Relative strengths of weak acids

The ionisation constant of the weak acid may also be represented in terms of degree of ionisation and molar concentration. Consider the ionisation of acetic acid.



Original conc. c	0	0
Equil. conc. c - cα	cα	cα

where c = molar concentration and α = degree of ionisation.

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \cdot c\alpha}{c - c\alpha} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \dots \quad (4)$$

For a weak acid ' α ' is very small and may be neglected in comparison to 1.

$$\text{So, } K_a = c\alpha^2$$

If two weak acids 1 and 2 have the ionisation constants K_{a_1} and K_{a_2} respectively and have same molar concentration ‘c’ from equation (5).

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

where α_1 = degree of ionisation of acid 1

and α_2 = degree of ionisation of acid 2.

Further, degree of ionisation is a measure of strength of acid.

$$\text{Here, } \frac{\text{Strength of Acid 1}}{\text{Strength of Acid 2}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Problem 1 : Formic acid and acetic acid have ionisation constant 17.7×10^{-5} and 1.75×10^{-5} respectively at 298K. Calculate the relative strength of two acids.

$$\text{Solution : } \frac{\text{Strength of Formic Acid}}{\text{Strength of Acetic Acid}} = \sqrt{\frac{17.7 \times 10^{-5}}{1.75 \times 10^{-5}}} = 3.18$$

Hence formic acid is 3.18 times stronger than acetic acid.

Equation (5) may be used to calculate the hydrogen ion concentration ($[H^+]$) of the weak acid.

$$[H^+] = c\alpha = c \sqrt{\frac{K_a}{c}} = \sqrt{K_a c} \quad \dots \dots \dots \quad (6)$$

Problem-2 : A weak monobasic acid has a dissociation constant equal to 1.6×10^{-5} at $25^\circ C$. Calculate its degree of dissociation at a concentration of 0.1M at the same temperature. What will be the concentration of H^+ ions furnished by it ?

$$\text{Solution : } \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.6 \times 10^{-5}}{0.1}} = 16 \times 10^{-5}$$

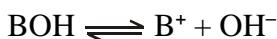
So, the degree of dissociation of 0.1M acid = 0.00016

$$\text{Again, } [H^+] = \sqrt{K_a c} = \sqrt{1.6 \times 10^{-5} \times 0.1} = 0.0531 \text{ mol dm}^{-3}$$

Ionisation of Weak base

The weak monoacidic base is represented by BOH.

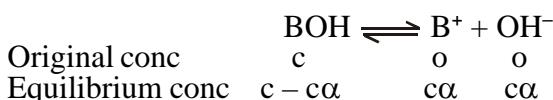
According to Arrhenius concept,



$$\text{The ionisation constant } K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

If c = Initial concentration of the base in moles per litre and

α = degree of ionisation



$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \quad \dots\dots\dots (7)$$

For a weak base ' α ' is very small compared to 1.

$$\text{So, } K_b = c\alpha^2 \text{ or, } \alpha = \sqrt{\frac{K_b}{c}}$$

$$\text{Also, } [OH^-] = c\alpha = c \sqrt{\frac{K_b}{c}} = \sqrt{c \cdot K_b} \quad \dots\dots\dots (8)$$

Ionisation constants of some common weak bases are given in Table 9.3 below.

Table 9.3 Ionisation constants of some common weak bases at 25°C

Bases	K _b values at 25°C
NH ₄ OH	1.81 × 10 ⁻⁵
C ₆ H ₅ NH ₂	3.83 × 10 ⁻¹⁰
(CH ₃) ₂ NH	5.12 × 10 ⁻⁴
CH ₃ NH ₂	4.38 × 10 ⁻⁴
C ₂ H ₅ NH ₂	5.60 × 10 ⁻⁴
(CH ₃) ₃ N	5.21 × 10 ⁻⁵
C ₅ H ₅ N	1.30 × 10 ⁻⁹

9.8 IONISATION OF POLYBASIC ACIDS

Acids having more than one ionisable proton per molecule are known as polybasic acids.

e.g. H₂C₂O₄ (oxalic acid), H₂SO₄ (Sulphuric acid)

H₃PO₄ (phosphoric acid)

For a dibasic acid H₂X the ionisation reactions are represented as



Equilibrium constant for (i) is

$$K_1 = \frac{[H^+][HX^-]}{[H_2X]}$$

Equilibrium constant for (ii) is

$$K_2 = \frac{[H^+][X^{2-}]}{[HX^-]}$$

where K_1 and K_2 are called 1st and 2nd ionisation constant of the acid H_2X . The values of ionisation constants for some polybasic acids are given in the following table 9.4.

Table 9.4 - Ionisation constant of some polybasic acid (298K)

Acid	K_1	K_2	K_3
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphuric acid	Very large	1.2×10^{-2}	
Carbonic acid	4.3×10^{-7}	5.6×10^{-11}	4.0×10^{-7}
Phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

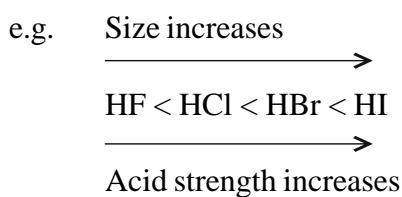
The value of K_2 , K_3 are smaller than K_1 in case of polybasic acids. This is because it is increasingly difficult to remove positively charged proton from a negative ion due to electrostatic forces.

9.9 FACTORS AFFECTING ACID STRENGTH

We know that the extent of dissociation or ionisation of an acid HA depends upon the strength and polarity of HA bond.

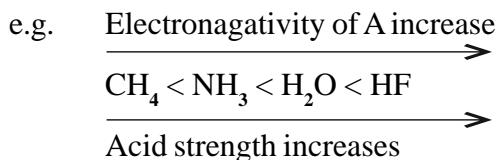
When strength of H–A bond decreases the energy required to break the bond decreases. So HA becomes a stronger acid. Also more the polarity of bond between H and A, more prominent will be the charge separation, easier will be the bond cleavage, thereby increasing acid strength.

If we consider the elements in the same group of periodic table, the H–A bond strength is the important factor in deciding acidity as compared to bond polarity. On going down a group the size of A increases gradually thereby decreasing the H–A bond strength. So the acid strength increases.



In case of Gr 16 elements H_2S is a stronger acid as compared to H_2O .

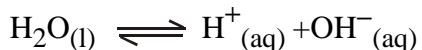
If we consider elements in the same period of the periodic table, polarity of H–A bond becomes the deciding factor in determining the acid strength. As the electronegativity of A increases, the polarity of HA bond increases and acid strength increases.



9.10 IONISATION OF WATER

Pure water is a weak electrolyte, since it ionises to a very small extent. It has a low electrical conductivity.

Pure water ionises as,



Applying the law of mass action, we have the equilibrium constant,

$$K = \frac{[H^+][OH^-]}{[H_2O]} \dots\dots\dots(1)$$

Since water dissociates or ionises to a very small extent, its concentration remains almost unchanged and can be taken as constant.

Thus, equation (1) can be written as,

$$K \times [H_2O] = [H^+] [OH^-]$$

$$\text{or, } K_w = [H^+] [OH^-] \dots \dots \dots (2)$$

where, K_w is called the **ionic product of water**. The value of ionic product (K_w) of water at 25°C found to be 1.0×10^{-14}

In pure water, the concentration of H^+ ions and OH^- ions are same.

Hence, In pure water $[\text{H}^+] = [\text{OH}^-]$

$$\text{So, } K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Hence, in pure water, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ moles/litre

Although K_w is a constant, it is temperature dependent. The numerical value of K_w increases with increase in temperature.

Table 9.5- Numerical value of K_w at various temperatures.

Temperature	K_w (in $\text{mol}^2 \text{ lit}^{-2}$)
0°C	0.11×10^{-14}
10°C	0.30×10^{-14}
25°C	1.00×10^{-14}
40°C	3.00×10^{-14}
100°C	7.5×10^{-14}

The solution in which the concentration of H^+ ions and OH^- ions are same is called a neutral solution. But, the solution in which H^+ ion concentration is more than 1.0×10^{-7} is called acidic solution and where it is less than 1.0×10^{-7} is called basic or alkaline solution. Since K_w is a constant at constant temperature, by increasing H^+ ion concentration in a solution, the concentration of OH^- ion will decrease.

Knowing H^+ ion concentration of a solution, its OH^- ion concentration can be calculated as follows.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

Example : 1

Calculate the H⁺ion concentration in NaOH solution, 2 gms of which are dissolved in 2 litres solution.

solution : Amount of NaOH in 2 litres solution = 2 gms.

Amount of NaOH in 1 litres solution = 1 gm.

As NaOH is a strong base, $[NaOH] = [OH^-]$

$$\therefore [\text{OH}^-] = \frac{1.0 \text{ gm/litre}}{40} = 1/40$$

$$\therefore H^+ = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1/40} = 40 \times 10^{-14} = 4.0 \times 10^{-13} M$$

9.11 HYDROGEN ION EXPONENT : pH

Sorenson introduced a new term to express the hydrogen ion concentration. The term *pH* has been derived from the French word **Puissance hydrogen**, meaning *power of hydrogen*.

According to him, pH of a solution is defined as the negative logarithm of hydrogen ion concentration in moles per litre.

We know,

$$K_w = [H^+] [OH^-]$$

$$\text{or, } [\text{H}^+] [\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

Taking logarithm, we get,

$$\log [H^+] + \log [OH^-] = -14$$

$$\text{or, } -\log [\text{H}^+] - \log [\text{OH}^-] = 14$$

In neutral solution

$$[\text{H}^+] = 1.0 \times 10^{-7}$$

Hence, the pH value of neutral solution (pure water)

$$= -\log (10^{-7}) = 7.0$$

In acidic solution :

In all acidic solutions H^+ ion concentration is more than $1.0 \times 10^{-7} M$. H^+ ion concentration in an acidic solution may be $10^{-6} M$, $10^{-5} M$, $10^{-4} M$ etc.

Consider an acidic solution whose H^+ ion concentration = 10^{-6}M .

$$\text{Its pH} = -\log [\text{H}^+] = -\log [10^{-6}] = 6.0.$$

Hence, pH value of all acidic solutions will be less than 7.0.

In basic solution :

In all basic solutions, the H⁺ ion concentration is less than 1.0×10^{-7} M

Hence their OH^- ion concentration will be more than $1.0 \times 10^{-7}\text{M}$. In order to keep K_w value constant at a particular temperature, the increase in H^+ ion concentration decreases the OH^- ion concentration in a solution.

Consider a solution whose OH^- ion concentration is more than $1.0 \times 10^{-7}\text{M}$, say 10^{-5}M

Hence, its H^+ ion concentration will be 10^{-9}M

∴ pH of the solution will be, $-\log [H^+] = -\log [10^{-9}] = 9.0$

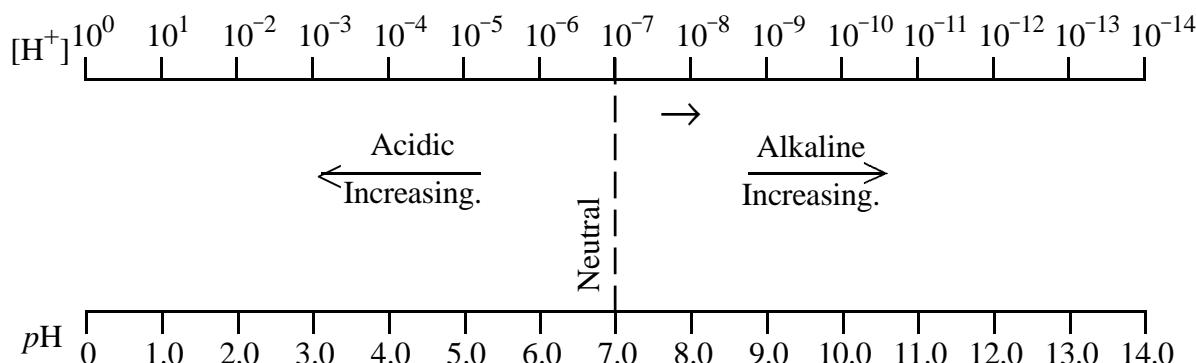
Thus, if $[H^+] > 10^{-7} M$ solution is acidic, $pH < 7.0$

$[H^+] < 10^{-7} M$ solution is basic, $pH > 7.0$

$[\text{H}^+] = 10^{-7}\text{M}$ solution is neutral, $p\text{H} = 7$.

as H⁺ ion concentration varies from 1.0M to 10⁻¹⁴M at 25°C in aqueous solution, the pH value vary from 0 to 14.0.

The pH scale for neutral, acidic and basic solutions are given below.



We know that, the ionic product of water increases with increase in temperature. Therefore, H^+ ion concentration will increase with increase in temperature. Hence, $p\text{H}$ value will decrease with increase in temperature. Thus, $p\text{H}$ value of boiling water is 6.56, although it is neutral.

Table 9.6 $p\text{H}$ and $p\text{OH}$ value of aqueous solutions

[H ⁺]	pH	pOH	[OH ⁻]
10 ⁰	0	14	10 ⁻¹⁴
10 ⁻¹	1	13	10 ⁻¹³
10 ⁻²	2	12	10 ⁻¹²
10 ⁻³	3	11	10 ⁻¹¹
10 ⁻⁴	4	10	10 ⁻¹⁰
10 ⁻⁵	5	9	10 ⁻⁹
10 ⁻⁶	6	8	10 ⁻⁸
10 ⁻⁷	7	7	10 ⁻⁷
10 ⁻⁸	8	6	10 ⁻⁶
10 ⁻⁹	9	5	10 ⁻⁵
10 ⁻¹⁰	10	4	10 ⁻⁴
10 ⁻¹¹	11	3	10 ⁻³
10 ⁻¹²	12	2	10 ⁻²
10 ⁻¹³	13	1	10 ⁻¹
10 ⁻¹⁴	14	0	10 ⁻⁰

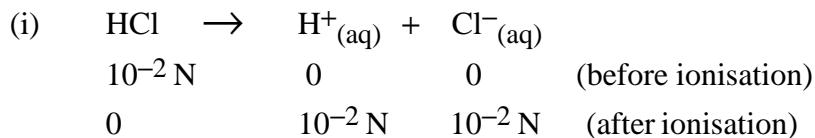
Importance of pH value :

- Soil testing :** In agriculture $p\text{H}$ of soil is often tested for the application of acidic or basic fertiliser for a particular crop.

- ii. **Food preservation :** A definite value of pH is to be maintained for food preservation.
- iii. **Qualitative and quantitative analysis :** pH finds its use in various qualitative and quantitative analysis.
- iv. **Biochemical reactions :** In human metabolic system, pH value plays an important role. Blood is slightly alkaline, its pH value is 7.4. People suffering from gastritis have lower value of pH , that is $pH < 7.0$

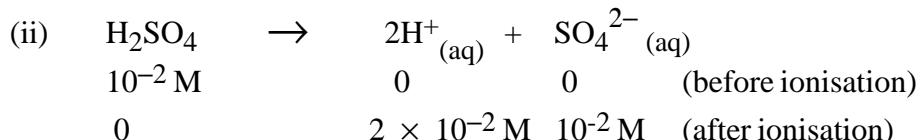
Example :2 Calculate pH of (i) 10^{-2} N HCl (ii) 10^{-2} M H_2SO_4 and (iii) 10^{-2} N H_2SO_4

Solution : We know, strong acids on dilution ionises completely.



$$\therefore [\text{H}^{\oplus}] = 10^{-2} \text{ N} = 10^{-2} \text{ M}$$

$$\therefore pH = -\log[\text{H}^{\oplus}] = -\log [10^{-2}] = 2.0$$

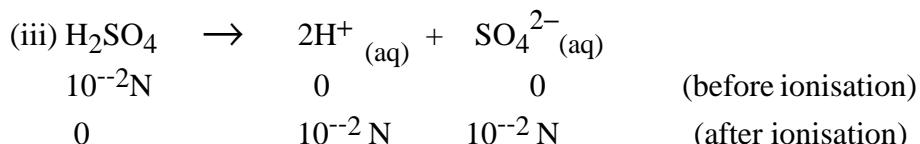


$$\therefore [\text{H}^{\oplus}] = 2 \times 10^{-2} \text{ M} \quad (1 \text{ mole of } \text{H}_2\text{SO}_4 \text{ gives 2 moles of } \text{H}^{\oplus} \text{ ion})$$

$$pH = -[\log \text{H}^{\oplus}] = -\log [2 \times 10^{-2}]$$

$$= -\log 2 + 2 \log 10$$

$$= 1.6989$$



1 equivalent of H_2SO_4 gives 1 equivalent of H^{\oplus} ion.

$$\therefore [\text{H}^{\oplus}] = 10^{-2} \text{ M}$$

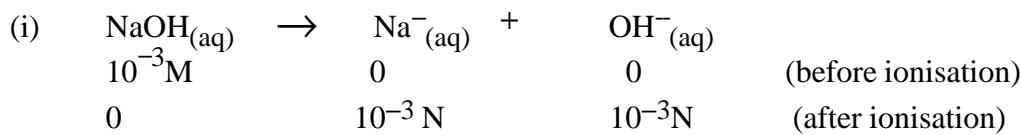
$$\therefore pH = -\log [\text{H}^{\oplus}] = -\log [10^{-2}] = 2.0$$

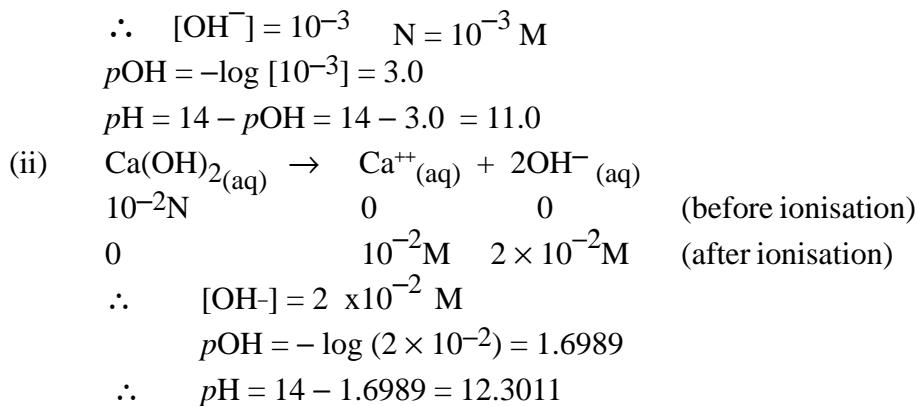
Example : 3

Calculate the pH value of (i) 0.001N NaOH and (ii) 0.01M $\text{Ca}(\text{OH})_2$

Solution :

Since NaOH and $\text{Ca}(\text{OH})_2$ are strong bases, they ionise completely on dilution.



**Example : 4**

2 gms of NaOH are dissolved in water to make 1 litre solution. What is *pH* of the solution?

Solution :

$$\text{Molarity of NaOH} = \frac{2.0}{40 \times 1} = 0.05 \text{ M} = 5 \times 10^{-2} \text{ M}$$

$$\therefore [\text{OH}^-] = 5 \times 10^{-2} \text{ M}$$

$$\text{or, } p\text{OH} = -\log [\text{OH}^-] = -\log [5 \times 10^{-2}] = 1.3010$$

$$\therefore p\text{H} = 14 - p\text{OH} = 14 - 1.3010 = 12.6989$$

Example : 5

3.2 gms of hydrogen chloride dissolved in 1 litre of water. What is *pH* of the solution ?

Solution :

$$\text{Molarity of HCl} = \frac{3.2}{36.5} = 0.089 \text{ M} = 8.9 \times 10^{-2}$$

$$\therefore [\text{H}^+] = 8.9 \times 10^{-2} \text{ M}$$

$$\text{or, } p\text{H} = -\log [\text{H}^+] = -\log [8.9 \times 10^{-2}] = 1.2138$$

Example 6

Calculate the *pH* value of a solution containing 3.65 gms of hydrochloric acid per litre of the solution.

Solution :

$$\text{Molecular mass of HCl} = 36.5$$

$$36.5 \text{ gms of HCl per litre} = 1.0 \text{ M solution}$$

$$3.65 \text{ gms of HCl per litre} = 0.1 \text{ M solution}$$

$$\therefore [\text{H}^+] = 0.1 \text{ M} = 10^{-1} \text{ M}$$

$$\text{Hence, } p\text{H} = -\log [\text{H}^+] = -\log[10^{-1}] = 1.0$$

Example 7

How many grams of KOH must be dissolved in one litre of solution to give it a *pH* value of 12.0.

Solution :

Strength of KOH = ?

pH value of solution = 12.0

We know, $pH = -\log [H^+]$

or, $12.0 = -\log [H^+]$

$$\text{or, } [H^+] = 10^{-12} \text{ moles/litre.}$$

$$\text{At } 25^\circ\text{C}, K_w = [H^+] [OH^-] = 1.0 \times 10^{-14}$$

$$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-12}} = 1.0 \times 10^{-2} \text{ moles/litre.}$$

Since KOH is a strong base,

$$[KOH] = [OH^-] = 1.0 \times 10^{-2} \text{ M.}$$

We know, Strength = Molarity \times Molecular mass of solute.

Molecular mass of KOH = 56

$$\therefore \text{Strength of KOH} = 56 \times 10^{-2} = 0.56 \text{ gms/litre}$$

Hence, 0.56 gms of KOH must be dissolved in one litre of the solution to give it a *pH* value of 12.0.

9.12 **BUFFER SOLUTION**

Hydrogen ion concentration of aqueous solution changes largely by the addition of very small amount of an acid or a base to it. It is very often necessary to have solutions, whose *pH* value does not change much on addition of small amount of strong acid or alkali to it. Such solutions are known as **buffer solution** or simply **buffer**.

For example, take a solution of NaCl in water. Its *pH* value is 7.0. When 1 ml of 1N, HCl is added to 1 litre of NaCl solution, the *pH* of resulting solution decreases from 7.0 to 3.0

But when the same amount of acid or alkali is added to ammonium acetate solution (having *pH* value 7.0), the *pH* value of the resulting solution does not undergo an appreciable change. Thus, ammonium acetate solution is a buffer solution.

Statement : A **buffer solution** may be defined as a solution, whose *pH* value does not change appreciably by the addition of a small amount of either acid or alkali from outside sources.

Illustrations :

(a) Why aqueous solution of NaCl does not act as buffer ?

NaCl on dilution dissociates completely giving Na^+ and Cl^- ions in aqueous solution.

(i) Let $HCl_{(aq)}$ be added to NaCl solution. By the addition of $HCl_{(aq)}$, H^+ ion and Cl^-

ion concentration in the solution increases. The increase in concentration of Cl^- ion in the solution does not affect the $p\text{H}$ value. But the increase in concentration of H^+ ion, decreases the $p\text{H}$ value.

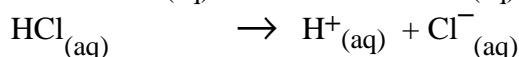
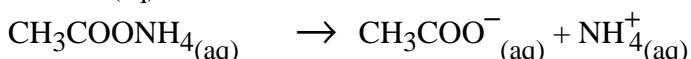
- (ii) Let $\text{NaOH}_{(\text{aq})}$ be added to NaCl solution. Here, by the addition of $\text{NaOH}_{(\text{aq})}$, Na^+ ion and OH^- ion concentration in the solution increases. The increase in concentration of OH^- ion decreases the concentration of H^+ ion, Hence, $p\text{H}$ value increases. Therefore, NaCl solution is not a buffer.

(b) Why aqueous solution of $\text{CH}_3\text{COONH}_4$ acts as a buffer ?

Ammonium acetate on dilution dissociates completely as follows;

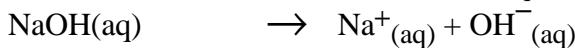
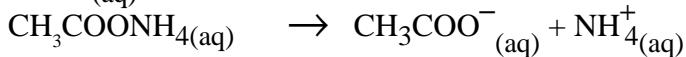


- (i) Let $\text{HCl}_{(\text{aq})}$ be added to ammonium acetate solution.



Here, the H^+ ions furnished by acid combine with the acetate ions to form acetic acid molecules. Since acetic acid is a weak electrolyte, it dissociates to a very small extent. Hence, H^+ ion concentration inside the solution increases very slightly. hence, its $p\text{H}$ value does not change appreciably. The increase in the concentration of Cl^- ions does not affect the $p\text{H}$ value.

- (ii) Let $\text{NaOH}_{(\text{aq})}$ be added to ammonium acetate solution.



Here, the OH^- ions furnished by the base combine with NH_4^+ ions to form ammonium hydroxide molecules. Since ammonium hydroxide is a weak base, it dissociates to a very small extent. Hence, OH^- ion concentration inside the solution does not increase appreciably. So, the $p\text{H}$ value of the solution does not increase appreciably.

Hence, buffer solutions are considered to have reserve acidity and reserve alkalinity. For example, $\text{CH}_3\text{COONH}_4$ has reserve acidity due to the presence of NH_4^+ ions and reserve alkalinity due to CH_3COO^- ions.

Type of buffers :

Buffers are of two types

- (i) Simple buffer.
- (ii) Mixed buffer.

- (i) Simple buffer :** Simple buffer solution can be prepared by mixing salt of weak acid and weak base with water.

For example : $\text{CH}_3\text{COONH}_4$, NH_4CN can act as simple buffer.

(ii) **Mixed buffer :** These are of two types.

- (a) Acidic buffer
- (b) Basic buffer.

(a) **Acidic buffer :** An acidic buffer is an equimolar mixture of a weak acid and its salt of strong base.

For example, a mixture containing one mole of CH_3COOH and one mole of CH_3COONa forms an acidic buffer. Its $p\text{H}$ value is 4.75.

(b) **Basic buffer :** A basic buffer is an equimolar mixture of a weak base and its salt of strong acid.

For example, a mixture of one mole of NH_4OH and one mole of NH_4Cl forms a basic buffer. Its $p\text{H}$ value is about 9.25.

Characteristics of Buffer solution :

Buffer solutions have the following characteristics.

- (i) Its $p\text{H}$ value is fixed.
- (ii) Its $p\text{H}$ value does not change either keeping it for a long time or on exposure to atmosphere or by dilution to a small extent.
- (iii) The addition of a little amount of even strong acid or alkali does not change the $p\text{H}$ value appreciably.

Buffer solution of a mixture of weak acid and its salt. (Acid Buffer)

A very common buffer is prepared by mixing equimolar solution of CH_3COOH and CH_3COONa . CH_3COONa is completely dissociated. The mixture, thus contains CH_3COO^- , Na^+ and CH_3COOH molecule.

When a strong acid is added:

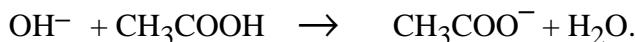
The H^+ ions will be taken up by CH_3COO^- ions forming CH_3COOH which is weakly ionising.



Thus, $p\text{H}$ value remains almost unaffected.

When a strong base is added :

The OH^- ions added are neutralised by CH_3COOH present in the mixture.



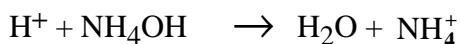
Thus, again the $p\text{H}$ value remains unaltered.

Here the reserve acidity is due to the presence of CH_3COOH and reserve alkalinity is due to CH_3COO^- ions.

Buffer solution of a mixture of weak base and its salt. (Basic Buffer)

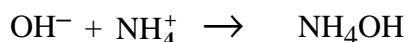
A mixture containing equimolar solution of NH_4OH and NH_4Cl constitutes another good buffer. The mixture contains NH_4^+ , Cl^- ions and undissociated NH_4OH .

When a strong acid is added : H^+ ions are neutralised by NH_4OH .



When a strong base is added :

OH^- ions are neutralised by NH_4^+ ions forming weakly dissociated NH_4OH .



Here, the reserve acidity is due to NH_4^+ ions and reserve alkalinity is due to NH_4OH .

Henderson Equation for Acid and Basic Buffers (Henderson - Hasselbalch equation)

I. pH of Acid buffers (Buffers mixture of weak acid & its salt)

Let HA be the weak acid and NaA be the salt of weak acid (highly ionised)

Since HA is a weak acid, it is slightly ionised.



Applying law of chemical equilibrium

$$K_a = \frac{[H^+][A^-]}{[HA]} \dots \dots \dots (1)$$

$$\text{or, } [\text{H}^+] = \frac{\text{K}_a[\text{HA}]}{[\text{A}^-]} \dots \dots \dots \quad (2)$$

Again, NaA is completely ionised.



So, in presence of NaA, the ionisation of HA is further suppressed due to the presence of common ion A⁻. This is **common ion effect**. We have thus,

[Acid] = [HA]; [Salt] = [A⁻]

Taking logarithm of both sides of equation (2),

$$\log [H^+] = \log K_a + \log [HA] - \log [A^-] \dots \dots \dots \quad (3)$$

$$\text{or, } -\log [\text{H}^+] = -\log K_a - \log [\text{HA}] - \log [\text{A}^-] \dots\dots\dots (4)$$

This equation (6) is known as **Henderson - Hasselbalch equation** or simply **Henderson equation**. This helps in calculation of pH of a buffer solution made by mixing a known quantity of weak acid and its salt.

II. pH of Basic buffers (Buffer mixture of weak base and its salt)

Let BOH be the weak base and BA be the salt of weak base (highly ionised). Since BOH is weak base, it is slightly ionised.



$$K_b = \frac{[B^+][OH^-]}{[BOH]} \dots \dots \dots (7)$$

Again, BA is completely ionised.



So, in presence of BA the ionisation of BOH is further suppressed due to the presence of the common ion B⁺ (Common ion effect)

We have thus,

[Base] = [BOH], [Salt] = [B⁺]

Taking logarithm of both sides of equation (8), we have

$$\log [\text{OH}^-] = \log [K_b] + \log [\text{BOH}] - \log [B^+] \dots \quad (9)$$

$$\text{or, } \text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \dots \dots \dots \quad (12)$$

Equation (12) is known as **Henderson - Hasselbalch equation** or simply **Henderson equation**. It helps in calculation of pH value of the buffer obtained by mixing a known quantity of weak base and its salt.

Since $\text{pH} = 14 - \text{pOH}$ or, $\text{pOH} = 14 - \text{pH}$

Equation (12) may be represented as

$$14 - \text{pH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or, } \text{pH} = 14 - \text{pK}_b - \log \frac{[\text{Salt}]}{[\text{Base}]} \dots \dots \dots \quad (13)$$

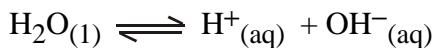
Applications of Buffers :

Buffer solutions are used in –

- (a) qualitative analysis of mixtures.
- (b) quantitative analysis or estimations.
- (c) Industrial process such as manufacture of paper, dyes, inks, paints, drugs etc.
- (d) digestion of food.
- (e) preservation of foods and fruits.
- (f) agriculture and dairy products preservation.

9.13 HYDROLYSIS OF SALTS

Water dissociates to a small extent producing H^+ and OH^- ions.



In pure water, concentration of H^+ ions and OH^- ions are equal. Hence, pure water is neutral.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely giving +vely charged ions (cations) and - vely charged ions(anions). The anions and cations of the salt react with H^+ ions and OH^- ions furnished by water to form either acidic or basic or even neutral solution.

Statement :

Hydrolysis is a phenomenon of the interaction of anions and cations of the salt with H^+ and OH^- ions furnished by water producing acidic, basic or neutral solution.

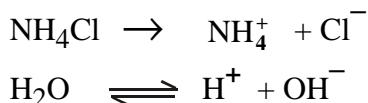
So, hydrolysis is the reverse of neutralisation. Neutralisation involves the combination of H^+ ions and OH^- ions to form water, while hydrolysis results in the formation of H^+ ions and OH^- ions.

The salts are classified into the following four types;

- (a) Salts of strong acids and strong bases.
- (b) Salts of strong acids and weak bases.
- (c) Salts of weak acids and strong bases.
- (d) Salts of weak acids and weak bases.

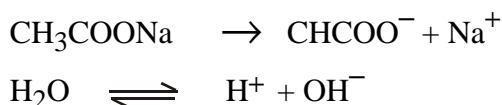
Here, we will discuss the hydrolysis of different types of salts .

- (a) **Salts of strong acids and strong bases :** The salts of this type are $NaCl$, KCl , KNO_3 etc. This type of salts do not undergo hydrolysis. The reason is that, the possible products of hydrolysis are strong electrolytes and themselves get fully ionised. Thus, the number of hydrogen ions remains equal to the hydroxyl ions in solution. Such a solution is neutral in character.
- (b) **Salts of strong acids and weak bases :** The examples of such salts are ammonium chloride, calcium nitrate etc. Consider the hydrolysis of ammonium chloride in water.



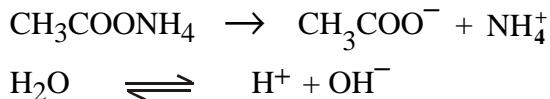
NH_4Cl dissociates fully to form NH_4^+ ions and Cl^- ions and water dissociates slightly giving H^+ ions and OH^- ions. The OH^- ions of water associate with the NH_4^+ ions of the salt to form NH_4OH . NH_4OH is a weak electrolyte, and it dissociates to a very small extent. As OH^- ions are taken up, more of water ionises to maintain the constant value of K_w . Due to this, the concentration of H^+ ions in solution becomes more than OH^- ion concentration. Therefore, such a solution will be acidic in character.

(c) **Salts of weak acids and strong bases:** The examples of such salts are sodium acetate, potassium carbonate etc. Consider the hydrolysis of sodium acetate in water.



Sodium acetate dissociates completely to form sodium ions and acetate ions. Water ionises slightly. The H^+ ions of water attack the CH_3COO^- ions to form acetic acid, which is a weak acid and dissociates to a very small extent. As H^+ ions are taken up, more of water ionises to maintain the constant value of K_w . Due to this, the concentration of OH^- ions in solution becomes more than the H^+ ion concentration. Therefore, such a solution will be basic in character.

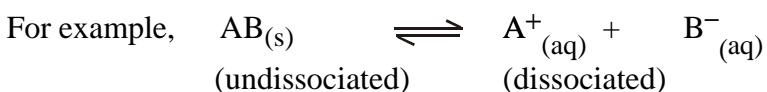
(d) **Salts of weak acids and weak bases :** An example of such a salt is ammonium acetate. Consider its hydrolysis.



Ammonium acetate on dissociation gives CH_3COO^- ions and NH_4^+ ions. Water being a weak electrolyte, dissociates slightly giving H^+ ions and OH^- ions. The acetate and ammonium ions are attacked by H^+ ions and OH^- ions of the water to form CH_3COOH and NH_4OH . Since, both CH_3COOH and NH_4OH are weak electrolytes, they dissociate to a very small extent, giving rise to equal number of H^+ ions and OH^- ions. Such a solution will be neutral in character.

9.14 SOLUBILITY PRODUCT

If a small quantity of a sparingly soluble salt is shaken with water, an equilibrium is established between the solid phase and the ions in solution.



This is heterogeneous equilibrium in which the ions A^+ and B^- have variable concentrations. Therefore, only these will be taken into consideration. Suppose a small amount of silver

chloride is added to water. Since it is a sparingly soluble salt, a very small amount of it passes into solution. Whatever amount of silver chloride which passes into solution will exist as Ag^+ and Cl^- ions. The state of equilibrium can be represented as,



Applying the law of chemical equilibrium, we have,

$$K = \frac{[\text{Ag}^+] [\text{Cl}^-]}{[\text{AgCl}_{(\text{s})}]}$$

The concentration of the solid (AgCl in this case) is taken as constant.

$$\text{Hence, } K [\text{AgCl}] = [\text{Ag}^+] [\text{Cl}^-]$$

$$\text{or, } K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$$

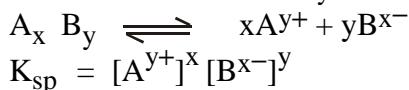
K_{sp} is another constant and is called **solubility product**, which is temperature dependent.

Consider the case of lead chloride, which is also a sparingly soluble salt. The equilibrium between the ions and the undissolved salt is written as,



$$\therefore K_{\text{sp}} = [\text{Pb}^{2+}] [\text{Cl}^-]^2$$

In general, if a salt of type $A_x B_y$ is considered,



Hence, the **solubility product** of a sparingly soluble substance may be defined as *the product of the molar concentrations of its ions raised to the power equal to the number of times each ion occurs in the equation representing the dissociation of the substance at a given temperature.*

Relation between Solubility and Solubility product :

Let us suppose that the solubility of a sparingly soluble salt $A_x B_y$ is ' S ' mol/L. Then we have,

$$\begin{aligned} A_x B_y &= xA^{y+} + yB^{x-} \\ (\text{'S moles}) &= (\text{xS moles}) + (\text{yS moles}) \end{aligned}$$

$$\text{Thus, } [A^{y+}] = xS \text{ and } [B^{x-}] = yS$$

$$\begin{aligned} \therefore K_{\text{sp}} &= [A^{y+}]^x [B^{x-}]^y \\ &= [xS]^x [yS]^y \\ &= x^x S^x y^y S^y \\ &= x^x y^y S^{x+y} \end{aligned}$$



$$x = 2, y = 1$$

$$\therefore K_{\text{sp}} = 2^2 \cdot 1^1 \cdot S^{2+1} = 4S^3$$

This relationship between solubility and solubility product can be used for the calculation of solubility product.

Difference between Ionic product and Solubility product :

Solubility product is constant for a given electrolyte at a given temperature. But ionic product, which is the product of the concentration of ions, can be varied by changing the concentrations of the ions. Ionic product of an electrolyte can not exceed its K_{sp} value irrespective of the nature of the source of the ions. When the ionic product temporarily exceeds the solubility product due to the increase in concentration of either one or both types of ions, the excess ions at once combine with oppositely charged ions and the solid salt separates out.

Depending upon the values of ionic product, the solutions can be classified into three different categories as follows :

- (i) If ionic product = K_{sp} , the solution is just saturated and no precipitation takes place .
- (ii) If ionic product > K_{sp} , the solution is super saturated and precipitation takes place.
- (iii) If ionic product < K_{sp} , the solution is unsaturated and more of the solute can dissolve.

9.15 COMMON ION EFFECT

The phenomenon in which degree of dissociation of a weak electrolyte is suppressed by addition of a substance having an ion common to weak electrolyte.

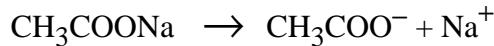
Consider the dissociation of a weak electrolyte, say, acetic acid,



The equilibrium constant of weak acid K_a is given by

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Now, suppose sodium acetate is added to this solution.



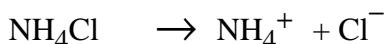
By the addition of sodium acetate, the concentration of CH_3COO^- ions in solution increases. Thus, in order to keep K_a constant, H^+ ions concentration must decrease or concentration of undissociated acetic acid must increase. In other words, the dissociation of acetic acid is suppressed by addition of CH_3COONa to its solution. Here, CH_3COO^- ion acts as the common ion.

Similarly, the dissociation of NH_4OH , which is a weak electrolyte is suppressed by the addition of NH_4Cl to it.



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

If NH_4Cl is added to it,



By the addition of NH_4Cl , the concentration of NH_4^+ ion increases.

Thus, in order to keep K_b constant, OH^- ions concentration must decrease or concentration of undissociated NH_4OH must increase. This indicates that, by the addition of NH_4Cl to NH_4OH solution (having NH_4^+ ion in common), the dissociation of weak electrolyte (NH_4OH) is further suppressed.

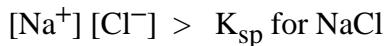
Application of the common ion effect and solubility product principle :

(a) Recovery of pure NaCl from sea water :

The crude salt obtained by the evaporation of sea water contains mainly sodium chloride along with impurities like CaCl_2 , KBr etc. For obtaining pure NaCl, HCl gas is passed through or conc. HCl is added to it. Hence, all impurities remain in solution and pure NaCl is precipitated out.



The ionic product, $[\text{Na}^+] [\text{Cl}^-]$ in the new system on passing HCl, exceeds the solubility product of NaCl.



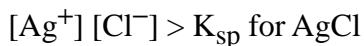
Hence, pure NaCl separates out and then purified by recrystallisation.

(b) In qualitative analysis :

The qualitative analysis of mixture is based on the principle of solubility product. Following are some of the important applications in mixture analysis which involve the principles of solubility product as well as the common ion effect.

(a) Precipitation of Group - I radicals (Pb^{2+} , Ag^+ and Hg^{2+})

The group reagent is dil. HCl. The Group- I radicals are precipitated out by dil HCl because the ionic products of the chlorides of these exceed their corresponding solubility products.



No other radicals are precipitated out because the ionic products of their chlorides do not exceed the corresponding solubility products.

(b) Precipitation of Group - II radicals by H_2S in presence of dil. HCl

Hydrochloric acid suppresses the ionisation of weakly dissociated H_2S (Group II reagent) $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$. Thus, only the ionic products of the sulphides of Group II radicals exceed their corresponding solubility products and hence only these are precipitated out leaving the sulphides of Group III, IV etc. in solution because their solubility products are high.

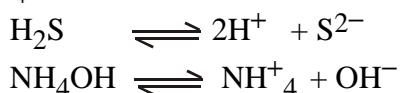
It is important to note that dil. HNO_3 and dil. H_2SO_4 may also suppress the ionisation of H_2S but these are not used because these are oxidising agents and oxidise hydrogen sulphide to sulphur.

(c) Precipitation of Group III A radicals by NH₄OH in presence of NH₄Cl :

Addition of NH₄Cl in Group - III A further suppresses the ionisation of NH₄OH. As a result of which, the ionic products of only the Group III A radicals exceed their corresponding solubility products. Hence, other group (III B, IV etc.) radicals remain in solution phase while Group III A radicals (Fe³⁺, Al³⁺ and Cr³⁺) are precipitated out as their hydroxides.

(d) Precipitation of Group III B radicals by H₂S in presence of NH₄OH :

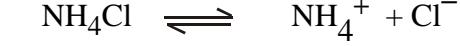
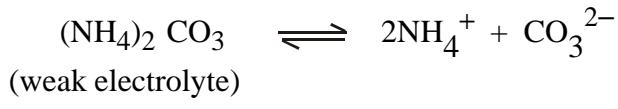
The Group-IIIB radicals are Co²⁺ Ni²⁺, Mn²⁺ and Zn²⁺. The group reagent is H₂S in presence of NH₄OH.



OH⁻ ions furnished by NH₄OH combine with the H⁺ ion furnished by H₂S to form unionisable water. As a result of which more H₂S is ionised to maintain the equilibrium according to Le-Chatelier's principle. Thus, the concentration of S²⁻ ions will be high in the solution and a stage will be reached when the ionic products of Group-III B radicals and sulphide ions exceed the corresponding solubility products and Group III B radicals are precipitated out.

(e) Precipitation of Group IV radicals :

The group reagent is ammonium carbonate in presence of NH₄Cl.



(strong electrolyte)

Due to common ion (NH₄⁺) effect, ionisation of (NH₄)₂CO₃ is suppressed. Thus, only the Group - IV radicals precipitate out as carbonates, which have low solubility products.

CHAPTER (9) AT A GLANCE

1. **Buffer solution :** Buffer solution may be defined as solution, whose pH value does not change appreciably upon the addition of small amounts of either acids or bases or even water from outside source.
2. **Common ion effect :** It is an effect due to which the ionisation of a weak electrolyte is further suppressed when a salt having common ion is added to it.
3. **Equilibrium :** A system is said to be in a state of equilibrium if the rate of the forward reaction is equal to that of the backward reaction.
4. **Hydrolysis :** It is defined as a process in which a salt reacts with water to form an acid and a base.
5. **Law of Mass Action :** The rate of reaction is proportional to the product of the concentration of reactants each raised to the power equal to the number of moles of the reactant species involved in the chemical equation.
6. **Le- Chatelier's Principle :** If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of such a change.
7. **pH :** It is defined as the negative logarithm of hydrogen ion concentration.

$$pH = -\log [H^+]$$
8. **Solubility Product :** The solubility product of a sparingly soluble substance is defined as the product of the molar concentrations of its ions raised to power equal to the number of times each ion occurs in the equation for the dissociation of a substance at a given temperature.
9. **Henderson equation :** for acid buffers : $pH = pK_a + \log \frac{[Salt]}{[Acid]}$
 : for basic buffers : $pOH = pK_b + \log \frac{[Salt]}{[Base]}$
 and $pH = 14 - pK_b - \log \frac{[Salt]}{[Base]}$

QUESTIONS

Very short type questions - (1 mark each)

1. What do you call the state of a chemical reaction when the forward and the backward rates are equal ?
2. According to Bronsted theory, what is a base ?
3. What is the pH of 0.01(N) HCl ?
4. Calculate the pH of 0.001(N) HCl
5. What is the pH value of pure water ?
6. Which catalyst is used in contact process for manufacture of sulphuric acid ?
7. What is the basicity of sulphuretted hydrogen ?
8. What is the effect of pressure on the solubility of a solid ?
9. What substance on mixing with ammonium hydroxide forms a buffer solution ?
10. Which catalyst is used in the manufacture of ammonia by Haber's Process.
11. What substance on mixing with weak acid forms buffer solution ?
12. In which reaction, the value of ΔH will be negative ?
13. The pH of an acidic solution will be more or less than 7.0 ?
14. What is the pH of 0.0001 M NaOH ?
15. Give two examples of Lewis acid.
16. What is the pH of 1N HCl ?
17. What is active mass ?
18. What is the relation between equilibrium constant for forward reaction and equilibrium constant for backward reaction in a reversible process ?
19. What happens to the solubility of calcium acetate if temperature increases.
20. Whether CO_2 is a Lewis acid or base?
21. What is the pH of 1M HCl solution?
22. Write the relation between K_p & K_c of the following reaction.

$$\text{PCl}_5 \text{ (g)} \rightleftharpoons \text{PCl}_3 \text{ (g)} + \text{Cl}_2 \text{ (g)}$$
23. In which condition the rate of forward and backward reactions are equal?
24. Arrange the following solutions in water in increasing pH
 $\text{CaCl}_2, \text{NaOAc}, \text{KCl}, \text{NaOH}$
25. What is the relation between pH & pOH?
26. Write the relation between K_p & K_c of the following reaction.

$$\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \rightleftharpoons 2\text{HI}_{(\text{g})}$$

Short Answer Questions (2 marks each)

1. Under what conditions of temperature and pressure would you get the maximum yield of ammonia in the following reaction ?



2. What do you mean by the equilibrium constant of a reaction ? Does it change with temperature?

3. (a) Explain the term buffer solution.

- (b) Give two examples of buffer solution.

4. For a general reaction



What is the expression for the equilibrium constant ?

5. The solubility product of AgCl is 1.7×10^{-10} at 298K. What will be its solubility at that temperature in a 1M aqueous solution of hydrochloric acid ?

6. Arrange the following aqueous solutions in the increasing order of their pH values.

- (a) 0.1 N sodium chloride

- (b) 0.1 N hydrochloric acid.

- (c) 0.1 caustic soda

7. When silver nitrate solution is added to a mixture of chloride and iodide ions in solution, silver iodide precipitates first followed by the silver chloride. Give reasons for that in brief.

8. How do you define an acid in the modern concept ? Give one example.

9. Define solubility product. How the idea of solubility product is used for purification of common salt ?

10. Why it is necessary to add excess of NH₄OH before passing H₂S for precipitation of Group III B cations ?

11. Give Bronsted and Lowry concept of an acid.

12. Calculate the solubility of AgCl in moles per litre, if the solubility product constant for AgCl is 1.0×10^{-10} .

13. What is the role of ammonium chloride in the precipitation of Group III A radicals in the qualitative analysis ?

14. Why is sodium carbonate solution alkaline ?

15. 10 ml of N/5 alkali is mixed with 20ml of N/10 acid. What is the pH of the resultant solution ?

16. Why is the pH of a solution of cupric sulphate solution less than 7.0 ?

17. What will be the value of ΔH, when a reaction at constant temperature and pressure is at equilibrium ?

18. Which substance makes a buffer with acetic acid ? What happens to the pH when a small quantity of HCl is added to such a mixture ?

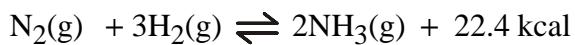
19. Why it is necessary to add dilute HCl before passing H₂S for precipitating Group. II cations ?
20. Name one factor which influences the solubility of a solid in a solvent ?
21. Write the conjugate acid of OH⁻ and NH₃.
22. Distinguish between ionic product and solubility product.
23. Why is it necessary to add solid NH₄Cl before adding excess of NH₄OH for precipitations Group IIIA cations ?
24. Explain why the change of pressure in the reaction H₂ + I₂ ⇌ 2HI will not affect the equilibrium constant ?
25. Write the conjugate base of H₂SO₄ and HCO₃⁻
26. What happens to H⁺ ion concentration when temperature increases and why?
27. Synthetic clothes dry up quicker than cotton clothes. Give reasons.
28. Give two applications of pH.
29. Calculate the pH of a solution containing 0.365g of HCl per litre of the solution.
30. Explain what happens when HCl gas is passed through conc NaCl solution.
31. Give one example each of acid buffer and basic buffer.
32. Write the Lewis structure of H₂SO₄ molecule.
33. Calculate the pH of 0.001N NaOH solution.
34. How is pure NaCl recovered from sea water?

Short Answer Questions (3 marks each)

1. Discuss equilibria in physical processes with reference to solid ⇌ liquid equilibrium with example.
2. Discuss equilibria in physical processes with reference to liquid ⇌ vapour equilibrium with example.
3. Discuss solid ⇌ vapour equilibrium with example.
4. Write a note on ionisation of polybasic acid with example.
5. What are the factors that affect the acid strength. Discuss with example.

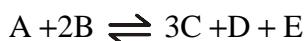
Long Questions (7 marks each)

1. State and explain Le-Chatelier's principle. Discuss the effect of change of temperature and pressure on the following system at equilibrium:



2. What is meant by equilibrium reaction ?
State Le-Chatelier's principle and discuss its applications to synthesis of ammonia
3. State law of mass action. Explain the law with three examples.

4. What is common ion effect ? Explain giving examples.
5. State Law of mass action. Explain the law with one example. Derive the expression for equilibrium constant of reaction,



6. Name the basic radicals of Group III B of qualitative analysis. What is the group reagent ?
7. Write shorts notes on :

- (a) Buffer solution
- (b) Le-Chatelier's principle
- (c) Theories of acids and bases
- (d) Common ion effect.
- (e) Solubility product

8. Define and explain law of mass action. What is an equilibrium constant ?
9. State Le-Chatelier's principle. How is it applied to the synthesis of ammonia ?

Give the expression for K_c and K_p for such reaction.

ADDITIONAL QUESTIONS

1. Describe the various postulates of the Arrhenius theory of acids and bases. What are the limitations of this theory ?
2. Discuss in detail the phenomenon of hydrolysis of salts.
3. Discuss in detail the Lowry-Bronsted theory of acids and bases. What is meant by a conjugate pair?
4. Write the importance of solubility product in qualitative analysis .
5. What is buffer solution ? Write the types of buffer solution with example. What are the applications of buffer solutions ?
6. The molar concentration of A and B are 0.80 mole litre⁻¹ each. On mixing them, the reaction starts to proceed as $A + B \rightleftharpoons C + D$ and attain equilibrium . At equilibrium molar concentration of C is 0.60 mole litre⁻¹. Calculate K_c of the reaction ? (Ans : $K_c = 9.0$)
7. A mixture of 3 moles of H₂ and 1 mole of N₂ react at constant pressure of 100 atmosphere. At equilibrium 0.5 mole of ammonia is formed. Calculate the value of K_p for the equilibrium reaction

$$\frac{3}{2} H_2 + \frac{1}{2} N_2 \rightleftharpoons NH_3$$
 (Ans : $K_p = 0.005$ atm)
8. The value of K_p for dissociation of 2HI \rightleftharpoons H₂ + I₂ is 1.84×10^{-2}
If the equilibrium concentration of H₂ is 0.4789 mole litre⁻¹, Calculate the conc. of HI at equilibrium. (Ans : 3.53 mole litre⁻¹)
9. K_{sp} of AgCl is 2.8×10^{-10} at 25°C. Calculate solubility AgCl in pure water
(Ans : S = 1.673×10^{-5} mole litre⁻¹)

MULTIPLE CHOICE QUESTIONS

1. Irreversible reaction is one which :
 - (a) proceeds in one direction only.
 - (b) proceeds in both the direction.
 - (c) is instantaneous reaction.
 - (d) is slow reaction.
2. When rate of forward reaction is equal and opposite to the rate of backward reaction, the state is said to be :
 - (a) Reversible state
 - (b) Equilibrium.
 - (c) Chemical equilibrium.
 - (d) None of the above.
3. Which of the following reactions will be favoured by low pressure ?
 - (a) $H_2 + I_2 \rightleftharpoons 2HI$
 - (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
 - (c) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
 - (d) $N_2 + O_2 \rightleftharpoons 2NO$
4. Which of the following factor will be useful in manufacture of ammonia by Haber's process ?
 - (a) High pressure.
 - (b) Low pressure.
 - (c) High temperature.
 - (d) Increase in the concentration of ammonia.
5. The reaction in which heat is absorbed is known as :
 - (a) Exothermic.
 - (b) Endothermic.
 - (c) Reversible.
 - (d) None of the above.
6. The rate at which a substance reacts is proportional to its active mass. This statement is :
 - (a) Le-Chatelier's principle.
 - (b) Faraday's Law.
 - (c) Law of multiple proportions.
 - (d) Law of mass action.
7. When chemical equilibrium is reached the
 - (a) Reaction stops.
 - (b) Rate of forward reaction is equal to the rate of backward reaction.
 - (c) Rate of forward reaction is more than that of backward reaction.
 - (d) None of the above.

8. In a reversible reaction if there is no change in total number of molecules, the reaction will be favoured by
- High pressure.
 - Low pressure
 - High temperature.
 - Higher concentration of a reactant.
9. Which of the following will be favoured by high pressure ?
- $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$
 - $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$
 - $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 - $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$
10. Chemical equilibrium is
- Stationary
 - Dynamic
 - Inertness
 - State of rest.
- 11.(i) For the reaction, $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, the K_p and K_c are related as
- $K_p = K_c (RT)^2$
 - $K_p = K_c (RT)^0$
 - $K_p = K_c (RT)^{-2}$
 - $K_p = K_c (RT)^{-1}$
- (ii) In which of the following reactions $K_p = K_c$?
- $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$
 - $2\text{NOCl} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$
 - $\text{I}_{2(s)} + \text{H}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$
 - $\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2\text{HCl}(g)$
12. The partial pressure of PCl_3 , Cl_2 and PCl_5 are 0.1, 0.2 and 0.008 atmosphere respectively for a reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. The value of K_p is
- 2.5
 - 5.0
 - 0.25
 - 25

13. For which of the following reactions the value of K_p is greater than K_c ?
- $N_2 + O_2 \rightleftharpoons 2NO$
 - $2SO_2 + O_2 \rightleftharpoons 2SO_3$
 - $2NO_2 \rightleftharpoons N_2O_4$
 - $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
14. For the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the forward reaction at constant temperature is favoured by :
- Introducing an inert gas at constant volume.
 - Introducing chlorine gas at constant volume.
 - Introducing an inert gas at constant pressure.
 - Increasing the volume of the container.
15. Lewis acids are
- Electron acceptors
 - Proton acceptors
 - Electron donors.
 - Proton donors.
16. The pH of solution containing 0.4 gm NaOH per litre is,
- 2.0
 - 12.0
 - 10.0
 - 11.0
17. Conjugate base of HCO_3^- ion is
- | | |
|---------------|-----------------|
| (a) CO_2 | (c) CO_3^{2-} |
| (b) H_2CO_3 | (d) HCO_3^- |
18. Aqueous solution of $FeCl_3$ is
- Acidic
 - Basic
 - Amphoteric
 - Neutral
19. When 1.0 ml of dil H_2SO_4 is added to 100ml of a buffer solution of pH 7.2, the pH
- becomes 7.0
 - is less than 7.0
 - is more than 7.0
 - does not change

20. What is the pH of 0.01M NaOH assuming complete ionisation ?
(a) 0.01
(b) 2.0
(c) 12.0
(d) 14.0
21. The pH of the solution is 3.0. If its pH is changed to 6.0, then the $[H^+]$ of the original solution has to be
(a) Doubled
(b) Halved.
(c) Increased 1000 times.
(d) Decreased 1000 times.
22. The compound that is not a Lewis acid is
(a) BF_3
(b) $AlCl_3$
(c) $BeCl_2$
(d) $SnCl_4$
23. The conjugate acid of NH_2^- is
(a) NH_3
(b) NH_2OH
(c) NH_4^+
(d) N_2H_4
24. An acidic buffer can be prepared by making solution of
(a) HCl and NaCl
(b) NaOH and NaCl
(c) HCOOH and HCOONa
(d) NH_4Cl and NH_4OH
25. A compound is precipitated when its
(a) Ionic product exceeds the solubility product
(b) Ionic product is less than its solubility product.
(c) Ionic product is equal to the solubility product.
(d) None of the above.

26. A basic buffer can be prepared by mixing
- CH_3COONa and CH_3COOH
 - Na_2SO_4 and H_2SO_4
 - NaOH and NaCl
 - NH_4Cl and NH_4OH
27. Which of the following solutions has the maximum pH value.
- Solution of caustic soda.
 - Pure water
 - Water saturated with CO_2 gas
 - Solution of sodium chloride.
28. Hydrolysis is regarded as interaction between
- H^+ and OH^- ions.
 - Ions of acid with ions of base
 - Ions of salt with ions of water.
 - Acid and base.
29. Which of the following solutions have pH close to 1.0 ?
- 100 ml of M/10 HCl + 100 ml of M/10 NaOH
 - 55 ml of M/10 HCl + 45 ml of N/10 NaOH
 - 10 ml of M/10 HCl + 90 ml of M/10 NaOH
 - 75 ml of M/10 HCl + 25 ml of M/5 NaOH
30. The decrease in the ionisation of H_2S in the presence of HCl is due to
- Solubility product.
 - Dilution
 - Common ion effect
 - Saturation

ANSWER TO MULTIPLE CHOICE QUESTIONS

- | | | | | | |
|------|-------|-----------------|-------|--------|-------|
| 1. a | 6. d | 11.(i) b (ii) d | 16. b | 21. d | 26. d |
| 2. c | 7. b | 12. a | 17. c | 22. c. | 27. a |
| 3. c | 8. d | 13. d | 18. a | 23. a | 28. c |
| 4. a | 9. c | 14. d | 19. d | 24. c | 29. d |
| 5. b | 10. b | 15. a | 20. c | 25. a | 30. c |

UNIT – VIII

CHAPTER - 10

REDOX REACTION

The transformation of matter into one or more new substances by means of any chemical change is termed as Chemical Reaction.

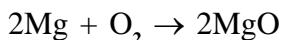
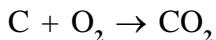
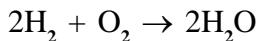
10.1 REDOX REACTIONS :

Chemical reactions such as burning of coal, sulphur, magnesium, rusting of iron etc. fall under a specific category called **oxidation reduction reactions** or simply **redox reaction**. Redox reactions form the basis of electrochemical and electrolytic cells.

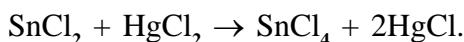
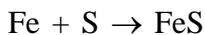
OXIDATION :

Classical concept : In a classical sense oxidation is a chemical process involving

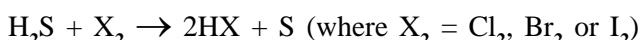
- (a) **Addition of oxygen :** When hydrogen combines with oxygen water is formed. Carbon burns in air or oxygen forming carbon dioxide. Magnesium burns in oxygen producing magnesium oxide.



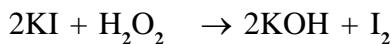
- (b) **Increase in the proportion of electronegative element or radical :** Iron combines with electronegative element sulphur forming ferrous sulphide. Similarly, cuprous chloride is oxidised by chlorine to give cupric chloride, where the proportion of electronegative radical (Cl^-) is increased. Stannous chloride is oxidised by mercuric chloride to form stannic chloride.



- (c) **Removal of hydrogen** – When HCl is heated with MnO_2 , Cl_2 is liberated. Thus hydrogen is removed from HCl. Similarly, S is liberated from H_2S by halogens.



- (d) **Decrease in the proportion of electropositive element or radical** – Hydrogen peroxide liberates I_2 from KI. Conversion of Cu_2O to CuO involves decrease in the proportion of electropositive element Cu.

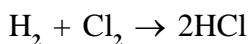
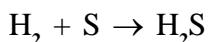


Thus, in a limited sense oxidation is a process of addition of oxygen or increase in the proportion of the electronegative elements or groups in an element or a compound or removal of hydrogen or decrease in the proportion of electropositive elements or groups in a compound.

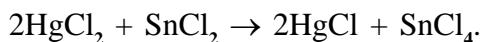
REDUCTION :

Classical concept : Reduction is a chemical process just opposite to oxidation involving :

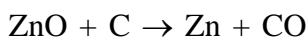
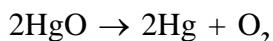
- (a) **Addition of hydrogen :** When sulphur is heated in an atmosphere of hydrogen, hydrogen sulphide is formed. Similarly, hydrogen combines with chlorine in presence of sunlight producing hydrogen chloride. In these cases hydrogen is directly added to sulphur and chlorine.



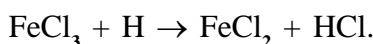
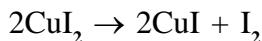
- (b) **Increase in the proportion of electropositive element :** When $CuCl_2$ is heated with Cu, $CuCl$ is formed where there is increase in the proportion of Cu. Similarly $HgCl_2$ is reduced by $SnCl_2$ to give $HgCl$.



- (c) **Removal of oxygen :** Oxygen is removed from HgO when heated, Similarly, ZnO is reduced to Zn by heating with carbon.



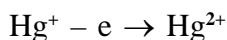
- (d) **Decrease in the proportion of electronegative element :** Cupric iodide decomposes to give cuprous iodide where there is decrease in the proportion of the electronegative element. Similarly, ferric chloride is reduced to ferrous chloride by nascent hydrogen.



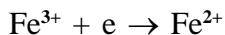
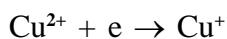
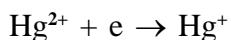
Thus, reduction is the process of addition of hydrogen or increase in the proportion of electropositive element or groups in an element or a compound or removal of oxygen or decrease in the proportion of electronegative elements or groups in a compound.

Oxidation and Reduction in the light of Electronic theory :

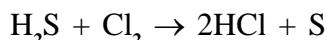
According to electronic theory **oxidation** is the loss of electrons by an atom or group of atoms participating in a chemical reaction. When electrons are lost, there is increase in the positive charge or decrease in the negative charge of the atom or ion.



Reduction is the gain of electrons by an atom or group of atoms participating in a chemical reaction. When electrons are gained, there is increase in the negative charge or decrease in the positive charge of the atom or ion.

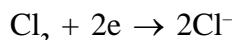


Oxidising Agent : A substance which can oxidise another substance and is itself reduced is termed as an oxidising agent.

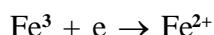
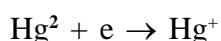


Cl_2 is an oxidising agent which oxidises H_2S to S and is itself reduced to HCl.

According to the electronic concept, an oxidising agent or **oxidant** is one which can accept electrons readily. In the above reaction, Cl_2 is an oxidant because it accepts electrons readily forming Cl^- .

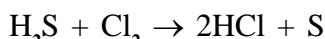


Similarly, Sn^{4+} , Hg^{2+} , Fe^{3+} ions are oxidants since they accept electrons as



Common oxidising agents are H_2O_2 , O_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , HNO_3 , Cl_2 etc.

Reducing Agent : A substance which can reduce another substance and is itself oxidised is termed as a reducing agent. In the reaction



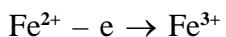
H_2S is a reducing agent because it reduces Cl_2 to HCl and is itself oxidised to S.

According to the electronic concept a reducing agent or **reductant** is one which can donate electrons readily.

In the above reaction S^{2-} donates 2 electron and is converted to elementary S.

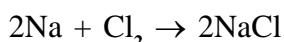


Similarly, Fe^{2+} , Sn^{2+} ions are reducing agents since they readily donate electron like

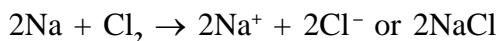


Some common reducing agents are H_2 , C, CO, SO_2 , H_2S , SnCl_2 , HgCl , etc.

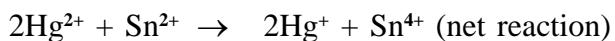
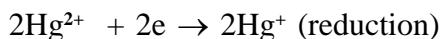
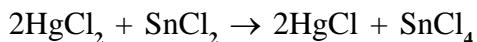
Oxidation and Reduction occur simultaneously : Oxidation involves loss of electrons whereas reduction involves gain of electrons. It is evident that if one substance loses electrons, another substance at the same time must gain the electrons, because electron can not be produced in a chemical change and the net reaction is electrically neutral. Thus, whenever a substance is oxidised, another substance must be correspondingly reduced. Consider the reaction between Na and Cl_2 to form NaCl .



In this reaction Na loses electron and behaves as a reducing agent and chlorine acts as an oxidising agent since it gains electrons.

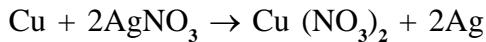


When SnCl_2 solution is added to HgCl_2 solution, a white precipitate of HgCl is obtained. In this case, mercuric chloride is reduced to mercurous chloride while stannous chloride is oxidised to stannic chloride simultaneously.

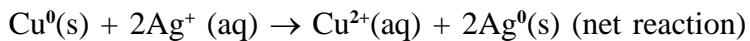
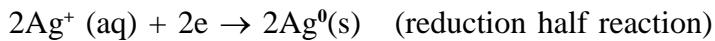


The reaction involving simultaneous oxidation and reduction is referred to as **redox reaction**. A redox reaction comprises of oxidation half and reduction half reaction as shown above.

When copper is dipped in AgNO_3 solution, the following reaction takes place.

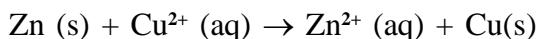


This can be written as two half reactions,



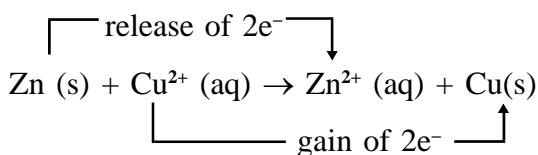
10.2 COMPETITIVE ELECTRON TRANSFER REACTIONS :

When a strip of metallic zinc is placed in aqueous copper nitrate solution and left for an hour, the blue colour of the solution disappears and reddish metallic copper gets deposited on the zinc strip. The reaction between metallic zinc and the aqueous solution of copper nitrate is :

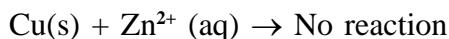


When H_2S gas is passed through the resulting colourless solution formation of white precipitate of ZnS confirms the presence of Zn^{2+} ion.

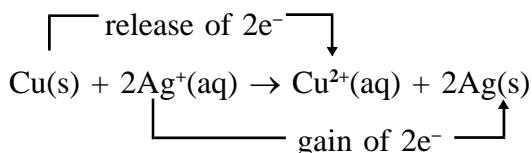
In this electron transfer reaction zinc is oxidised, releasing two electrons and copper ion is reduced by gaining electrons from zinc.



In contrast if copper rod is placed in aqueous solution of zinc sulphate for hours together no visible reaction is noticed. On passing H_2S gas through the solution we do not get a black precipitate of copper sulphide.



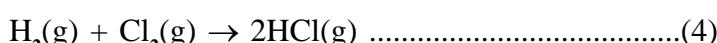
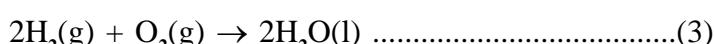
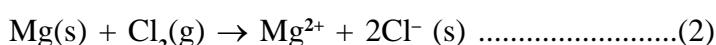
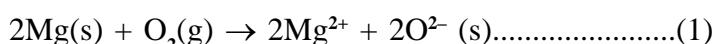
Now, if another experiment is performed by placing copper rod in silver nitrate solution, the solution develops a blue colour. when H_2S gas is passed through it a black precipitate is obtained, thus revealing the presence of Cu^{2+} ions in the solution



A comparision of the above two cases draws our attention towards a new field, i.e. competition between metals to release electrons. The electron releasing tendency of the above metal is in the order : $Zn > Cu > Ag$. Of course, Electro-chemical series or metal activity series is a list of metals arranged in the order of their electron releasing tendency.

10.3 OXIDATION NUMBER OR OXIDATION STATE :

Consider the following reaction :



In the reactions (1) and (2) Mg atoms are oxidised to form Mg^{2+} . Reactions where ions are not formed can also be called oxidation reactions. Reactions (3) and (4) where hydrogen reacts with oxygen forming water and with chlorine forming hydrogen chloride are also oxidation reactions. Here, hydrogen atoms form covalent bonds with oxygen atom and chlorine atom respectively. Oxidation of magnesium differs from oxidation of hydrogen in the sense that in the former case ionic compounds are formed and in the latter covalent compounds are formed. Application of the same term oxidation seems to be unwise. Chemists, therefore, developed a new definition of oxidation to include all these reactions under one category which is based upon a concept of **oxidation number**.

Oxidation number of an element in a compound is the charge positive or negative which would be assigned to the atoms of that element in the compound, if all the bonds were ionic bonds. Though all the bonds are not ionic, for convenience, it is arbitrarily assumed that all the compounds are ionic while computing oxidation number.

Oxidation number is different from valency. Valency expresses the combining capacity of an element and does not display positive and negative nature of the atom in the compound. But oxidation number expresses the positive and negative nature of atoms in the compound along with their combining capacity. The value of the oxidation number and valency of an atom in a compound may not be same. For example, the valency of carbon is always 4 but the oxidation numbers of carbon in various compounds of carbon are different.

Table 10.1 Oxidation number of carbon

Compounds	Oxidation number of carbon
CH_4	- 4
CH_3Cl	- 2
CH_2Cl_2	0
$CHCl_3$	+2
CCl_4	+4
CO_2	+4

Unlike valency, oxidation number can be fraction also. For ascribing positive or negative oxidation number to an atom in the compound the electronegative scale is used. The more electronegative element of a pair is arbitrarily given a negative oxidation number and less electronegative is given a positive oxidation number.

Table 10.2 Pauling's electronegativity scale

Element	Electronegativity	Element	Electronegativity
F	4.0	C	2.5
O	3.5	Se	2.4
Cl	3.0	Te	2.1
N	3.0		
Br	2.8	H	2.1
I	2.5	P	2.1
S	2.5	As	2.0

Fluorine has the highest electronegativity (4.0) and therefore, in all its compounds, fluorine is given negative oxidation number. Next in the scale is oxygen and is therefore assigned negative oxidation number in all its compounds except in oxygen - fluorine compounds. For example, in OF_2 , oxygen being less electronegative than fluorine is assigned positive oxidation number.

The following general rules are adopted for the assignment of oxidation numbers.

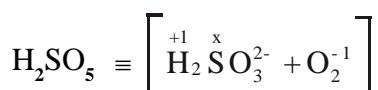
1. The oxidation number of an element in the free state or elementary state is always zero. Thus, oxidation number of H in H_2 is zero, Cl in Cl_2 is 0 and so on. They are represented as H^0 , Cl^0 , S^0 , Na^0 etc.
2. The oxidation number of hydrogen in its compound is always +1 except in metallic hydrides where hydrogen has the oxidation number – 1. In NaH , Na has the oxidation number + 1 and hydrogen, – 1.
3. All alkali metals have oxidation number of +1, alkaline earth metals have oxidation number of +2, Aluminium has oxidation number of +3, in their compounds.
4. Oxygen has the oxidation number – 2 in all its compounds except in peroxides where it is –1, in OF_2 where it is + 2, in O_2F_2 where it is + 1 and in superoxide, KO_2 , RbO_2 , CsO_2 where it is – 0.5.
5. The oxidation number of a monoatomic ion in an ionic compound is equal to its electrical charge. For a polyatomic ion the algebraic sum of the oxidation numbers of all the atoms is equal to the charge on the ion. For example. Cl^- has the oxidation number –1. In SO_4^{2-} , the algebraic sum of the oxidation numbers of sulphur and four oxygen atoms is equal to – 2.
6. In all compounds formed by the combination of a metal and a non-metal, the oxidation number of the metal atom is always positive and that of the non-metallic atom is negative. In KCl , K has always the positive oxidation number (+1) and Cl, the negative oxidation numbers (–1).

7. In compounds formed by two non-metallic atoms, the atom with lower electronegativity is assigned positive oxidation number and the atom with higher electronegativity is assigned a negative oxidation number. In CH_4 , H being less electronegative is assigned positive oxidation number (+1) and C, being more electronegative is assigned a negative oxidation number (-4)
8. Fluorine has an oxidation number of -1 in all its compounds. Chlorine, Bromine and Iodine also have an oxidation number of -1, when they occur as halide ions in their compounds. Cl, Br and I when combine with oxygen i.e. in oxoacids and oxoanions, have positive oxidation numbers.
9. The algebraic sum of the oxidation numbers of all the atoms in a molecule is zero. In KClO_4 , the oxidation number of K is +1, Cl is +7 and oxygen is -2, so that the algebraic sum of the oxidation number is zero. $[+1 + 7 + (-2 \times 4) = 0]$

IMPORTANT NOTE :

1. Metal can have zero oxidation number as in their nitrosyls and carbonyls.
2. The maximum oxidation number of an element can not exceed its group number in the periodic table. Thus, while calculating the O.N. of S in Peroxymonosulphuric acid, H_2SO_5 (Caro's acid) and peroxydisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (Marshall's acid) by the basic rule, it has been found that the O.N. of S is 8 and 7 respectively. This is absurd, since the maximum O.N. of S should be 6 because S belongs to Group VI (A) of the periodic table.

H_2SO_5 is a peroxyacid and has one peroxy linkage ($-\text{O}-\text{O}-$) i.e. O_2^{2-} , where the O.N. of Oxygen is -1. If the O.N. of S is x, then

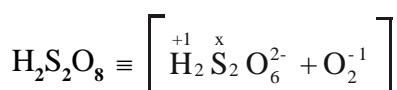


$$\text{Hence, } 2 \times (+1) + x + (-2 \times 3) + (-1) \times 2 = 0$$

$$\text{or, } x - 6 = 0 \text{ and } x = +6$$

Thus, the O.N. of S is +6 which is compatible with the above rule.

Again, $\text{H}_2\text{S}_2\text{O}_8$ another peroxy acid of sulphur containing one peroxy linkage O_2^{-1} Thus,



$$\text{Hence, } (+1) \times 2 + (x \times 2) + (-2) \times 6 + (-1) \times 2 = 0$$

$$\text{or, } 2x = +12 \text{ and } x = +6$$

Therefore, O.N. of S in this compound is +6, compatible with the fact that O.N. of S can be +6 at the maximum.

Method for calculating oxidation numbers :

For calculating the oxidation number of an atom in the molecule, the following procedure may be adopted.

- (i) Write down the formula of the molecule or ion with oxidation numbers (positive or negative) written on the top of each atom except for the atom whose oxidation number is to be determined.
Let x be the oxidation number of that atom.
- (ii) Find out the algebraic sum of the oxidation numbers of all the atoms in the molecule (x being written as the oxidation number of the atom in question)
- (iii) Equate it to zero in case of a neutral molecule or to the charge in case of an ion.
- (iv) Solve for the value of x to get the oxidation number.

Example 1 Calculate the oxidation number of Cr in $K_2Cr_2O_7$.

Solution Let x be the oxidation number of Cr.

O.N. of K = + 1 and O has the O.N = - 2.

+1 x -2

$K_2Cr_2O_7$

$$(1 \times 2) + 2x + (-2 \times 7) = 0$$

$$\text{or, } 2x = 14 - 2 = + 12$$

$$\text{or, } x = + 6$$

Hence, oxidation number of Cr in $K_2Cr_2O_7$ is + 6

Example 2 Find out the oxidation number of S in $Na_2S_4O_6$.

Solution Let x be the O.N of S.

O.N. of Na = + 1 and O = - 2.

+1 x -2

$Na_2S_4O_6$.

$$(1 \times 2) + 4x + (-2 \times 6) = 0$$

$$\text{or, } 4x = 12 - 2 = 10$$

$$\text{or, } x = + 5/2$$

Hence, the O.N. of S in $Na_2S_4O_6$ is +5/2.

Example 3 Calculate the oxidation number of chlorine in (a) $NaClO_2$ (b) Cl_2O (c) ClO_3^-

Solution Let x be the O.N of Cl.

(a) +1 x -2

$Na ClO_2$

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

$$\text{or, } x = + 3$$

Hence, O.N of Cl in $NaClO_2$ is + 3

(b) x -2

$Cl_2 O$

$$2x - 2 = 0$$

$$\text{or, } x = +1$$

Hence, O.N. of Cl in Cl_2O is +1.



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

$$\text{or, } x = +5$$

Hence, O.N. of Cl in ClO_3^- is +5.

Example 4 Calculate the oxidation number of

- (a) Ni in $\text{Ni}(\text{CO})_4$
- (b) Fe in $[\text{Fe}(\text{CN})_6]^{3-}$

Solution (a) Let x be the oxidation number of Ni

$$x = 0$$



$$x + (\text{O} \times 4) = 0 \text{ (Since CO has the oxidation number 0)}$$

Hence, oxidation number of Ni is zero

- (b) Let the oxidation number of Fe be x

$$x = -1$$

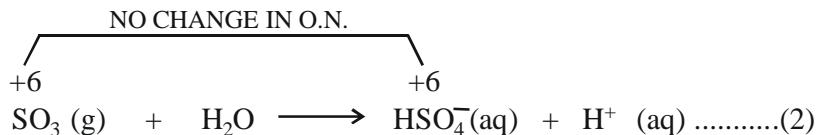
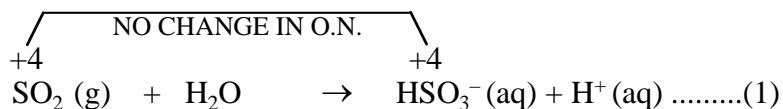


$$x + (-1 - x \times 6) = -3$$

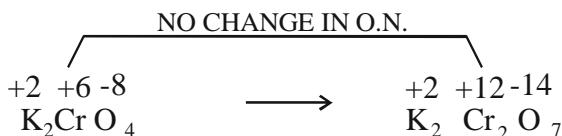
$$\text{or } x = +3$$

Hence, the oxidation number of Fe is +3.

NOTE : 1. The reaction by which SO_2 and SO_3 dissolve in water to give sulphurous and sulphuric acids respectively are not redox reactions.



- 2. Conversion of K_2CrO_4 to $\text{K}_2\text{Cr}_2\text{O}_7$ is not a redox reaction.



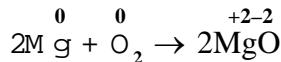
In the above examples the oxidation numbers of S and Cr do not change. Hence, they are not redox reactions.

10.4 TYPES OF REDOX REACTIONS :

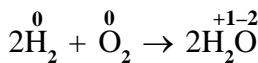
The redox reactions can be classified into different types. They are

- (1) **Synthesis :** When a new substance is formed by the direct union of simple substances, the reaction is termed as synthesis.

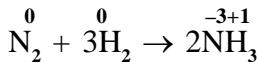
Example : Magnesium burns in oxygen or air producing magnesium oxide.



Similarly, hydrogen combines with oxygen forming water.

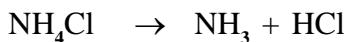
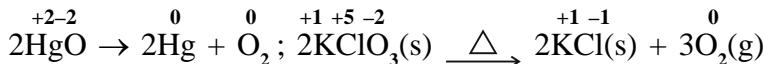


and nitrogen combines with hydrogen in presence of a catalyst under suitable conditions of temperature and pressure to produce ammonia.

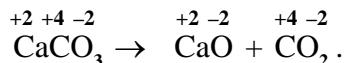


2. **Analysis or Decomposition :** This type of reaction is just the reverse of synthesis. Here the compound splits up into its constituents or simpler substances.

Example : Mercuric oxide when strongly heated decomposes to mercury and oxygen.

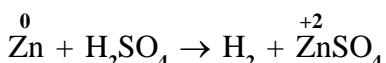


All decomposition reactions are not a redox reaction.



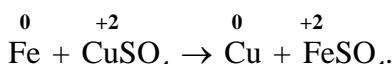
3. **Displacement or Substitution :** When one element displaces or substitutes another element from its compound the reaction is termed as displacement or substitution reaction.

Example : Zinc reacts with dilute sulphuric acid producing hydrogen and zinc sulphate.

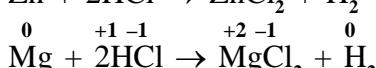
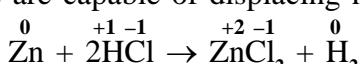


Here, zinc displaces hydrogen from H_2SO_4 .

Similarly, iron displaces copper from copper sulphate solution.

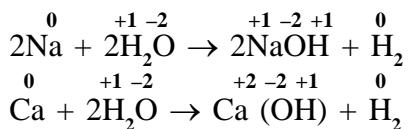


Some metals are capable of displacing hydrogen from acids.

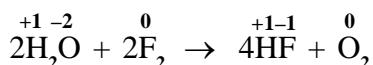


These reactions are used to prepare dihydrogen in the laboratory.

All alkali metals and some alkaline earth metals (Ca, Sr and Ba) which are very good reductants, will displace hydrogen from cold water.

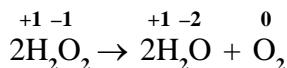


Among halogens fluorine is most reactive and can replace chloride, bromide and iodide ions in solution. In fact, fluorine can displace oxygen of water :

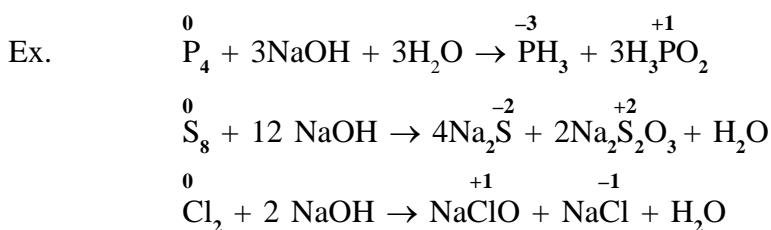


For this reason the displacement reactions of chlorine, bromine and iodine using fluorine are not carried out in aqueous solutions.

- 4. Disproportionation reactions :** This type of redox reactions involve an element in one oxidation state which is simultaneously oxidised and reduced. Decomposition of hydrogen peroxide belongs to this category.



Here the oxygen atom in hydrogen peroxide molecule is present in -1 oxidation state and decreases to -2 in water molecule whereas in oxygen molecule it increases to 0 . Non-metals like phosphorus, sulphur and chlorine undergo disproportionation in the alkaline medium.



10.5 USES OF OXIDATION NUMBER :

The concept of oxidation number is used for

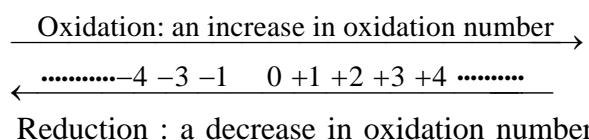
1. Writing the formula of the compounds.
2. Classifying the types of reagents or reactants in redox reactions.
3. Balancing equations for redox reactions.

- 1. Writing formulae of the compounds :** Since the algebraic sum of positive oxidation number and negative oxidation number of atoms or groups in a compound is zero, the formula of a compound can easily be written knowing the oxidation number of atoms or groups present in the compound. For example, in calcium chloride the oxidation number of Ca is $+2$ and chlorine is -1 , Hence, calcium chloride can be written as

CaCl_2 , so that the algebraic sum of oxidation numbers of Ca and Cl will be zero. Knowing the oxidation number of Al to be + 3 and of sulphate – 2, aluminum sulphate can be written as $\text{Al}_2(\text{SO}_4)_3$.

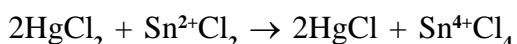
2. **Classifying the types of reagents or reactants in redox reactions :** Oxidation is a chemical reaction in which there is increase in the oxidation number of an element. When Mg burns in oxygen to form MgO , O.N. of Mg increases from 0 to +2. Therefore this is an oxidation reaction where Mg is oxidised. Conversion of CH_4 to CO_2 or CCl_4 by reaction with O_2 and Cl_2 respectively increases the oxidation number of C from – 4 to + 4 and hence they are oxidation reactions where C is oxidised.

Reduction is a chemical reaction in which there is a decrease in the oxidation number of an element. Consider the same example of the formation of MgO from Mg and oxygen. The oxidation number of oxygen decreases from 0 to – 2. Thus, oxygen is said to have undergone reduction.



Reagents which can increase the oxidation number of an element in a compound are called **oxidising agents**. In the foregoing examples, O_2 and Cl_2 are oxidising agents, because they increase the oxidation number of Mg and C respectively. The oxidation numbers of the oxidising agents are decreased.

Similarly, reagents which can lower the oxidation number of an element in a compound are called reducing agents. SnCl_2 reduces HgCl_2 to HgCl . Since the oxidation number of Hg decreases from + 2 to + 1. Therefore, SnCl_2 is a reducing agent.



The oxidation number of the reducing agent has increased (+ 2 to + 4).

The foregoing facts can be summarised as follows :

- (i) **Oxidation** = *Loss of electron* = **Increase in oxidation number**.
- (ii) **Oxidising agent** = *Electron acceptor* = **Decrease in oxidation number**.
- (iii) **Reduction** = *Gain in electron* = **Decrease in oxidation number**.
- (iv) **Reducing agent** = *Electron donor* = **Increase in oxidation number**.

3. Balancing Redox reactions :

For balancing equations for oxidation - reduction reactions, two methods are generally adopted. They are :

- (I) Oxidation number method.
- (II) Ion - electron method.

- (I) Oxidation number method :** This method is based on the fact that the total increase in the oxidation number must be equal to the total decrease in the oxidation number in the oxidation - reduction reaction. Like other chemical equations, the reactants and the products must be known.

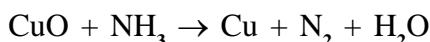
The various steps followed for balancing a redox reaction are :

- Step - 1.** Write skeleton equation representing the chemical change.
- Step - 2.** Assign oxidation numbers to all atoms in the reaction and find out which atoms undergo change in oxidation number in the reaction.
- Step - 3** Find out the increase and decrease in oxidation number for the reaction of 1 mole of reducing and oxidising agents respectively. Introduce suitable co-efficients to make the increase equal to the decrease in oxidation number.
- Step - 4** Balance the equation for all other atoms and finally balance for hydrogen and oxygen. Complete the equation.

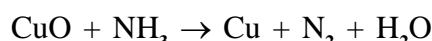
The following examples illustrate the procedure outlined.

Example 1 :

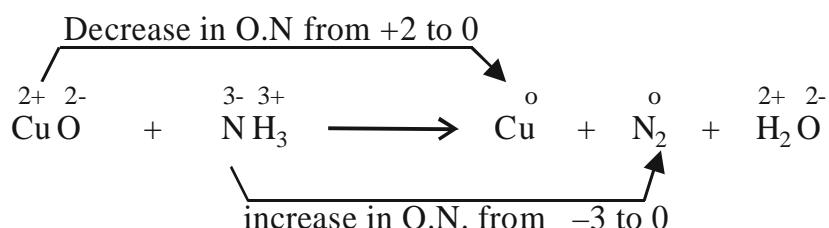
Balance the equation by oxidation number method.



- (a) Skeleton equation -



- (b) Assign oxidation number and find out the changes in oxidation number.



- (c) Balance the increase in oxidation number with decrease in oxidation number.

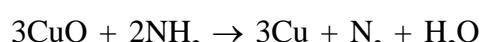
For one molecule of CuO, the O.N. of Cu reduces from +2 to 0

and for one molecule of NH₃, the O.N. of N increases from -3 to 0.

Therefore, they must react in the ratio 3 CuO : 2 NH₃.

Hence, $3\text{CuO} + 2\text{NH}_3 \rightarrow 3\text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

- and (d) Balance the hydrogen and oxygen and complete the equation.

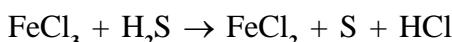


Example 2 :

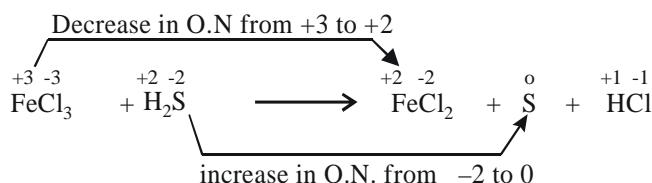
Balance the following equation by oxidation number method.



- (a) Skeleton equation

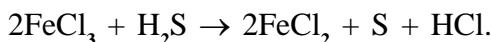


- (b) Assign oxidation number and find out the changes in O.N.



- (c) Balance the increase in oxidation number with the decrease in oxidation number.

Oxidation number of Fe decreases from + 3 to + 2 ($\text{Fe}^{+3}\text{Cl}_3 \rightarrow \text{Fe}^{+2}\text{Cl}_2$) and the oxidation number of S increases from -2 to 0 ($\text{H}_2\text{S}^{-2} \rightarrow \text{S}^0$). Therefore, 2 molecules of FeCl_3 should react with one molecule of H_2S . Hence.



- (d) Balance the number of hydrogen atoms and complete the equation.

**Example 3 :**

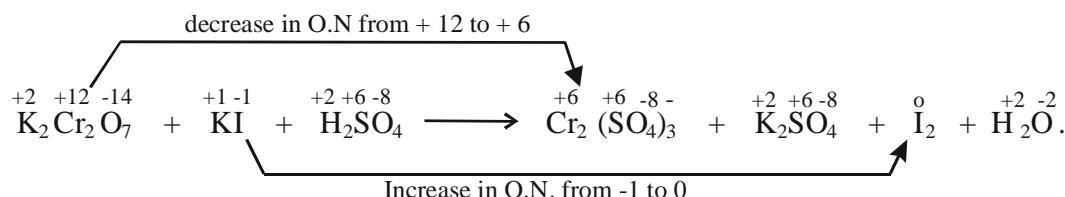
Balance the reaction between $\text{K}_2\text{Cr}_2\text{O}_7$ and KI in presence of dilute H_2SO_4 by oxidation number method.



- (a) Skeleton equation



- (b) Assign oxidation numbers and find out changes in O.N.

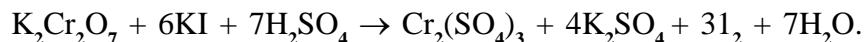


- (c) Balance the increase in O.N. with the decrease in O.N. For each molecule of $\text{K}_2\text{Cr}_2\text{O}_7$, there is 6 units of reduction of O.N.

$(\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Cr}_2^{+6}(\text{SO}_4)_3)$ and for each molecule of KI, there is one unit of oxidation. Therefore, for balance, one molecule of $\text{K}_2\text{Cr}_2\text{O}_7$ must react with 6 molecules of KI. Hence, the equation will be



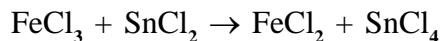
- (d) Balance the number of hydrogen and oxygen atoms and complete the equation. Since the reaction is carried out in acidic medium, $14H^+$ must be added on the reactant- side which means $7 H_2SO_4$ molecules must be required.



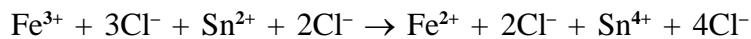
- (II) Ion - electron method :** In 1927. Jette and La Mer developed this method for balancing redox reactions. The ion - electron method is based on the fact that oxidation involves loss of one or more electrons and reduction, gain of one or more electrons. The method is limited to ionic reactions in aqueous solutions. Ionic equations can be converted to molecular equations and *vice versa*.

The equation is divided into two half reactions, one representing the oxidation and the other, the reduction reaction. Though ions take part in the reaction, this method avoids the spectator ions (these which do not take part in the reaction), but molecules of H₂O are added like H⁺ in acid medium and OH⁻ in basic medium for balancing partial ionic equations. The unit change in oxidation or reduction is a change of one electron, represented by e.

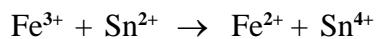
Let us consider a common redox reaction of FeCl_3 by SnCl_2 . The equation can be written as



In aqueous solution, ionic representation is



Chloride ions appear on both sides and therefore they are spectator ions and hence omitted. Only those ion taking part in the reaction are taken into account. Thus, a simplified equation can be written as :



This reaction can be divided into two half reactions.

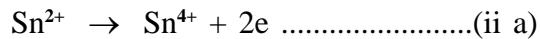
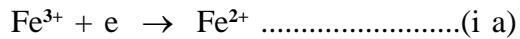


representing reduction reaction and

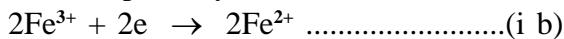


representing the oxidation reaction.

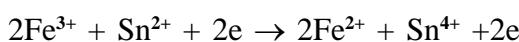
Equation (i) and (ii) must now be balanced not only with regard to the number of atoms, but also with respect to electrical charges on both sides of the equation. Therefore,



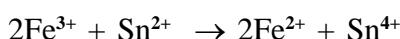
Both the partial equation (i – a) and (ii – a), though balanced with regard to the number of atom, are not balanced electrically, since on adding both the partial equations there is the residual charge on the right hand side. Therefore, the whole equation (i – a) must now be multiplied by 2 and we have,



Adding (i - b) and (ii - b), we obtain



and by cancelling the electrons common to both the sides, we have,



Example 1 :

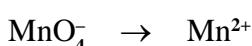
Oxidation of concentrated hydrochloric acid by potassium permanganate.



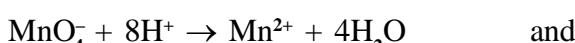
Eliminating the spectator ions, the equation can be written as



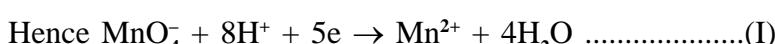
The partial half reaction for reduction is



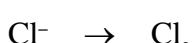
To balance this in respect of atoms, we need $8H^+$. Then,



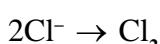
to balance it electrically, 5e⁻ will be required since O.N of Mn changes from +7 to +2.



The partial half reaction for oxidation is



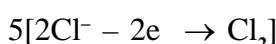
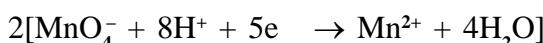
To balance it in respect of atoms, 2Cl^- will be necessary.



and to balance it electrically, $2e^-$ will be taken out since $\text{Cl}^- \rightarrow \text{Cl}^0$ needs removal of one e^- . Hence,



The above two partial equations are to be adjusted in such a way that the gain of electron is equal to the loss of electron. This is done by multiplying (i) by 2 and (ii) by 5.

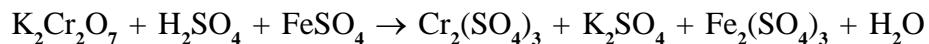


On adding, $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$

is obtained as the balanced equation.

Example 2 :

Oxidation of ferrous sulphate by potassium dichromate in presence of sulphuric acid



Eliminating the spectator ions, we find that $\text{Cr}_2\text{O}_7^{2-}$, Fe^{2+} and H^+ are taking part in the reaction and in the product side we have Cr^{3+} , Fe^{3+} and H_2O .

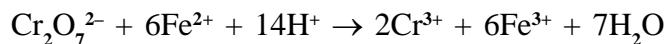
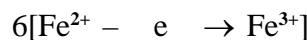
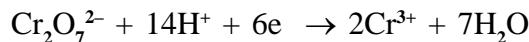
Balancing the reduction reaction atomically and electrically, we have



Balancing the oxidation reaction atomically and electrically. we have,



One dichromate ion utilises 6e and ferrous ion liberates 1e, hence partial equation (i) and (ii) must be in the ratio 1 : 6.



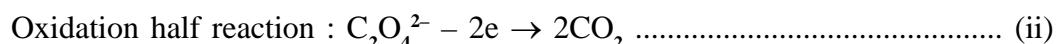
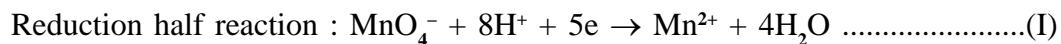
is the balanced equation.

Example 3:

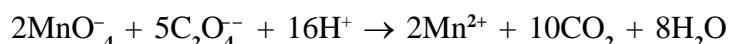
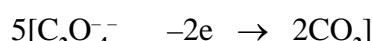
Oxidation of sodium oxalate by potassium permanganate in presence of sulphuric acid.



Ions involved in the reaction are MnO_4^- , $\text{C}_2\text{O}_4^{2-}$ and H^+ .



To make the final equation electrically neutral, multiply (i) by 2 and (ii) by 5.

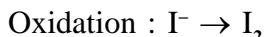


Example 4

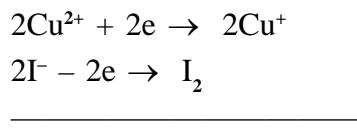
Redox reactions involved in iodometric estimation of copper.

- (a) $\text{CuSO}_4 + \text{KI} \rightarrow \text{CuI} + \text{K}_2\text{SO}_4 + \text{I}_2$
 (b) $\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + \text{NaI}$

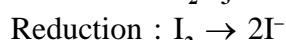
- (a) The ions involved are Cu^{2+} and I^- and the two half reactions are



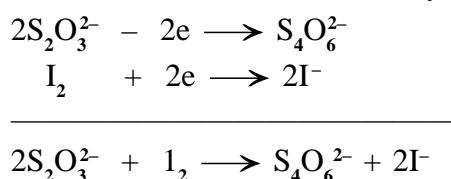
Balancing both the half reaction atomically and electrically, we have



- (b) The reactants involved are I_2 and $\text{S}_2\text{O}_3^{2-}$. The two half reactions are

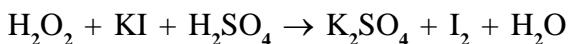


Balancing both the half reaction atomically and electrically,

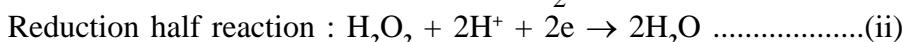
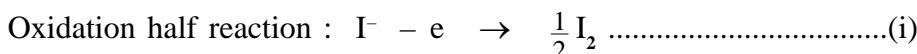


Example 5 :

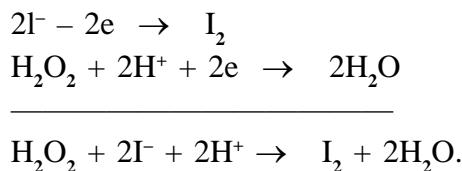
Reaction of hydrogen peroxide with potassium iodide in presence of sulphuric acid.



Ions and molecules involved are I^- , H^+ and H_2O_2

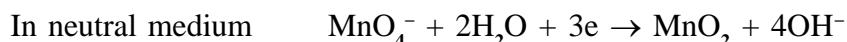


The two partial equation (i) and (ii) must take place in the ratio 2 : 1 to make the equation electrically neutral. Therefore,



Some of the common half reactions for oxidising and reducing agents are given below.

Oxidising agents :



- (ii) $\text{K}_2\text{Cr}_2\text{O}_7$: In acidic medium $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.
- (iii) Halogens X_2 : ($\text{X} = \text{Cl}, \text{Br}$ or I). $\text{X}_2 + 2\text{e} \rightarrow 2\text{X}^-$
- (iv) H_2O_2 : $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O}$
- (v) NaOCl : $\text{ClO}^- + \text{H}_2\text{O} + 2\text{e} \rightarrow \text{Cl}^- + 2\text{OH}^-$
- (vi) HNO_3 :
 (a) Concentrated. $\text{NO}_3^- + 2\text{H}^+ + \text{e} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$
 (b) Mod. Conc. $\text{NO}_3^- + 4\text{H}^+ + 3\text{e} \rightarrow \text{NO} + 2\text{H}_2\text{O}$
 (c) Dilute. $\text{NO}_3^- + 10\text{H}^+ + 8\text{e} \rightarrow \text{N}_2\text{O} + 5\text{H}_2\text{O}$

Reducing agents :

- (i) $\text{H}_2\text{C}_2\text{O}_4$: $\text{C}_2\text{O}_4^{2-} - 2\text{e} \rightarrow 2\text{CO}_2$
- (ii) HI : $2\text{HI} \rightarrow \text{I}_2 + 2\text{H}^+ + 2\text{e}$
- (iii) H_2O_2 : $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}$
- (iv) $\text{Na}_2\text{S}_2\text{O}_3$: $2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}$
- (v) H_2S : $\text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S} + 2\text{e}$
- (vi) SO_2 : $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}$
- (vii) H_2SO_3 : $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}$

Equivalent mass of Oxidants and Reductants

The equivalent mass of an oxidising agent or oxidant and a reducing agent or reductant can be calculated from the change in oxidation number or from the change in the number of electrons per ion in any redox reaction.

Equivalent mass of an oxidising agent or oxidant

$$\begin{aligned} &= \frac{\text{Molecular mass of the oxidising agent}}{\text{Change in oxidation number per mole}} \\ &= \frac{\text{Molecular mass of the oxidising agent}}{\text{No. of electrons gained per mole}} \end{aligned}$$

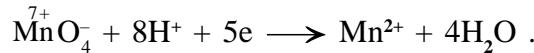
Similarly, Equivalent mass of a reducing agent or reductant

$$\begin{aligned} &= \frac{\text{Molecular mass of the reducing agent}}{\text{Change in oxidation number per mole}} \\ &= \frac{\text{Molecular mass of the reducing agent}}{\text{No. of electrons lost per mole}} \end{aligned}$$

Example 1 :

Calculate the equivalent mass of KMnO_4 in acid medium.

The partial ionic equation for the reaction can be written as



Here; the O.N of Mn changes from +7 to + 2. Thus change in O.N = 7 – 2 = 5.

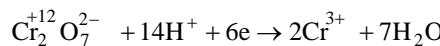
The number of electrons gained by MnO_4^{-} is 5. Therefore,

$$\text{Equivalent mass of } \text{KMnO}_4 = \frac{\text{Mol mass of } \text{KMnO}_4}{5} = \frac{158}{5} = 31.6$$

Example 2 :

Calculate the equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ in acid medium.

The above reaction can be ionically represented as



Here, the change of O.N per mole = 12 – 6 = 6. the number of electron gained by $\text{Cr}_2\text{O}_7^{2-}$ is 6. Therefore,

$$\text{Eq. mass of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol mass of } \text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{294}{6} = 49$$

Example 3 :

Find out the equivalent mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in acid medium.

FeSO_4 is oxidised to $\text{Fe}_2(\text{SO}_4)_3$ in acid medium by oxidising agents like $\text{K}_2\text{Cr}_2\text{O}_7$, or KMnO_4 . This can be represented as $\text{Fe}^{2+} - \text{e} \rightarrow \text{Fe}^{3+}$

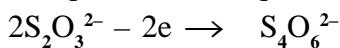
Here, change of O.N is from + 2 to +3 i.e 1 per mole of Fe^{2+} . Therefore,

$$\begin{aligned} \text{Eq. mass of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} &= \frac{\text{Mol. mass of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O}}{1} \\ &= \frac{278}{1} = 278. \end{aligned}$$

Example 4 :

Find out the equivalent mass of $\text{Na}_2\text{S}_2\text{O}_3$.

The partial ionic equation for the reaction can be written as



Here, the number of electrons lost is 2 per 2 moles of thiosulphate. Therefore,

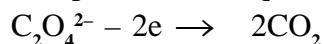
$$\begin{aligned} \text{equivalent mass of sodium thiosulphate} &= \frac{2 \text{ Molecular mass of sod. thiosulphate}}{2} \\ &= \frac{\text{Mol. mass of sod. thiosulphate}}{1} \end{aligned}$$

Hence, the equivalent mass of sodium thiosulphate is same as its molecular mass.

Example 5 :

Find out the equivalent mass of sodium oxalate in acid medium.

The partial ionic equation for the reaction can be represented as



Here, the number of electrons lost is 2 per 2 mole of oxalate. Therefore, equivalent mass of $\text{Na}_2\text{C}_2\text{O}_4$ is equal to the molecular mass of $\text{Na}_2\text{C}_2\text{O}_4$ divided by 2. In otherwords,

$$\text{Equivalent mass of } \text{Na}_2\text{C}_2\text{O}_4 = \frac{\text{Mol. mass of } \text{Na}_2\text{C}_2\text{O}_4}{2}$$

10.6 APPLICATIONS OF REDOX REACTIONS :

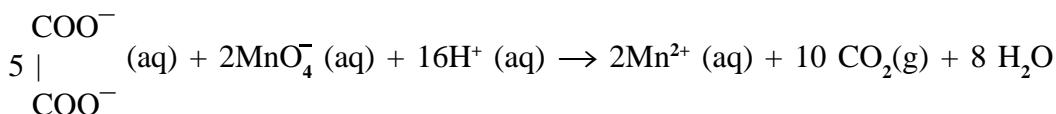
Redox reactions have vast applications in chemistry, in industry and also in our daily life.

10.6.1. Quantitative analysis : Titration involving Redox Reactions.

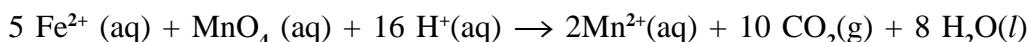
Redox reactions are very useful in quantitative analysis. Redox titrations involve the reactions between oxidants and reducing agents and help in the estimation of unknown substances in solution.

(a) Potassium permanganate titrations :

As discussed earlier KMnO_4 acts as an oxidising agent in acidic, alkaline and neutral medium. It is violet in colour in Mn^{+7} state and changes to colourless compound in Mn^{+2} state. So it is used as a *self-indicator*. When it is used against reducing agents like oxalic acid, ferrous sulphate, oxalates etc, just beyond the equivalence point the first lasting tinge of pink colour due to MnO_4^- appears, which enables it to be used as a self-indicator.



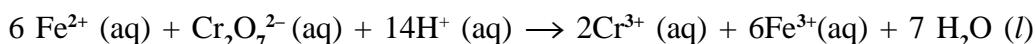
Oxalate ion permanganate ion



Ferrous ion Permanganate ion

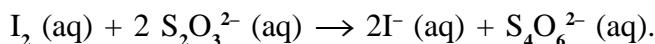
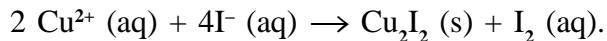
(b) Potassium dichromate titrations :

In potassium dichromate titrations indicators like diphenyl amine or N-phenyl anthranilic acid are used. At the end point diphenylamine changes colour from bluish green to purple or to intense blue. In this method strength of reducing agents like FeSO_4 , Mohr's salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ is determined.



(c) Iodometric titrations :

These titrations are carried out in two steps. In the first step, oxidising agents like KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CuSO_4 , peroxides etc. are treated with an excess of KI when I_2 is liberated quickly and quantitatively. In the second step, the liberated iodine is titrated against standard sodium thiosulphate solution using starch as indicator. At the end point the blue colour disappears.

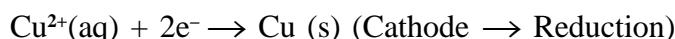
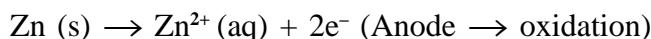


10.6.2 Redox Reactions and Electrode Processes :

An electrochemical cell or battery is a device which converts chemical energy to electrical energy. These are widely used in our daily life to run a number of small and big gadgets and equipments. In these cells redox reactions take place.

Ex : Galvanic Cell.

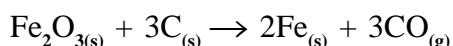
In this cell Zn rod dipped in ZnSO_4 solution and Cu rod dipped in CuSO_4 solution serve as anode and cathode respectively.



Here, electrons flow from anode to cathode thereby causing flow of electric current in the reverse direction (i.e. from cathode to anode)

10.6.3 Redox Reactions and Extraction of metals:

By using a suitable reducing agent, oxides of metals are reduced to metals. For example, ferric oxide Fe_2O_3 is reduced to iron in the blast furnace using coke as the reducing agent.

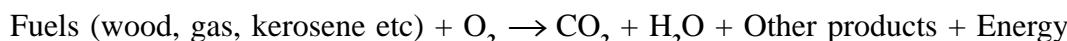


Similarly, Al_2O_3 is reduced to Al by cathodic reduction in an electrolytic cell.

Other metals like Li, Na, K, Mg, Ca etc. are also obtained commercially by electrolytic reduction methods.

10.6.4 Redox Reaction and supply of energy :

The energy required in our daily life is obtained by the oxidation of fuels. For example, oxidation of fuels like wood, gas, kerosene, petrol etc. produces a large amount of energy required for various purposes in our life.



Human body needs energy for proper functioning. This is obtained by the oxidation of glucose in our body to CO_2 and H_2O .



10.6.5 Redox Reaction and Photosynthesis :

Green plants convert water and carbondioxide into carbohydrate in presence of chlorophyll and the process is defined as photosynthesis. This is represented as



We can see CO_2 is reduced to carbohydrates while H_2O gets oxidised to O_2 and hence it is a redox reaction. The energy is provided by sunlight for this reaction. This reaction is the source of food for plants and animals. It also maintains a constant supply of 21% of O_2 by volume in the atmosphere required for combustion of fuels and breathing of all the living creatures in the world.

Other important applications include production of chemicals which are based on redox reactions. Chemicals like caustic soda, chlorine etc. are commercially produced by redox reactions in electrolytic cell.

10.7 THEORETICAL ASPECTS OF ACID-BASE TITRATION : VOLUMETRIC ANALYSIS-TITRATION

Determination of Strength and Equivalent Mass of Acid and Base

The equivalent mass of an acid or base can be determined by the volumetric method, known as *titration*. The progressive addition of an acid to a base or *vice versa* is termed as **titration** which provides a sensitive method of determining the strength of one when the strength of the other is known. This is carried out in presence of an **indicator**.

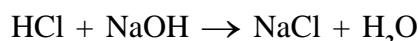
An indicator is a substance which indicates the end point or neutralisation point by a colour change. The indicator shows different distinct colours in different media. The following table shows the change of colour of different indicators in different media.

Table 10.3 Colour change of some indicators

Indicator	Colour in basic medium	Colour in neutral medium (at the end point)	Colour in acid medium
Methyl orange	Yellow	Orange	Red
Methyl red	Yellow	Red	Red
Litmus	Blue	Violet	Red
Phenolphthalein	Pink	Colourless	Colourless

The choice of indicator will depend upon the nature of the acid and alkali. For example, in the titration of a strong acid with a strong base, any indicator can be used. In the titration of strong acid and weak base (NH_4OH), methyl orange and methyl red are suitable. In the titration of weak acid (acetic acid) and strong base, phenolphthalein is suitable. It is important to note that **no titration is possible if both the acid and base are weak**.

The principle underlying titration is that an acid and a base react in the ratio of their gram-equivalents for complete neutralisation. Consider the reaction



36.5 g 40 g

From the equation we find that 36.5 g of HCl will completely neutralise 40 g of NaOH (36.5 and 40 are the equivalent mass of HCl and NaOH respectively).

Thus, 1000 ml of (N) HCl will completely neutralise 1000 ml. of (N) NaOH, since they contain one gram - equivalent of the substance in the given volume of the solution.

In other words,

$$1000 \text{ ml of (N) HCl} \equiv 1000 \text{ ml of (N) NaOH}$$

$$\text{or, } 10 \text{ ml of (N) HCl, } \equiv 10 \text{ ml of (N) NaOH.}$$

$$\text{or } 10 \text{ ml of (N/10) HCl } \equiv 10 \text{ ml of (N/10) NaOH.}$$

Suppose V_1 ml of acid of strength S_1 in terms of normality require V_2 ml of alkali of strength S_2 in terms of normality for complete neutralisation.

$$\text{Then strength of the acid } S_1 = \frac{\text{no. of gram-equivalents of acid}}{\text{volume in litres}} =$$

$$\frac{\text{no. of gram-equivalents of acid}}{V_1 / 1000}$$

(in terms of normality)

$$\therefore \text{Number of gram - equivalents of acid} = S_1 \times V_1 / 1000$$

$$\text{Similarly, no. of gram - equivalents of alkali} = S_2 \times V_2 / 1000$$

Since acid and alkali react in the ratio of their gram - equivalents for complete neutralisation.

$$\frac{S_1 \times V_1}{1000} = \frac{S_2 \times V_2}{1000}$$

$$\text{or, } S_1 \times V_1 = S_2 \times V_2$$

Therefore, **Strength of acid (in terms of normality) × Volume of acid (in ml) = Strength of alkali (in terms of normality) × Volume of alkali (in ml).**

In this equation, if three factors are known, the fourth factor can be calculated.

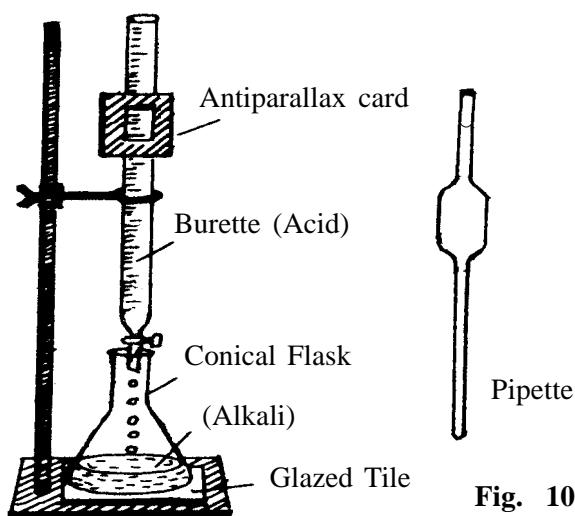


Fig. 10.1 A Volumetric titration.

The determination of equivalent mass of acids and bases involves the following steps :

- (i) For the determination of the equivalent mass of the acid, the standard solution of the base is required and *vice versa*.
- (ii) A solution of the acid or base is prepared by dissolving an accurately weighed quantity of acid or base in the solvent and making up to a known volume.
- (iii) The acid is taken in a burette and a known volume of the alkali, in a conical flask with a drop or two of a suitable indicator. Acid is added from the burette till the neutralisation point is reached as indicated by the change of colour of the indicator.
- (iv) Volume of acid, added from the burette is accurately known. A known volume of alkali is taken in the conical flask. If the strength of the acid is known, the strength of the alkali and *vice versa* can be calculated using the relation, $V_1 S_1 = V_2 S_2$.

where V_1 = Volume of the acid (in ml)

S_1 = Normality of the acid

V_2 = Volume of the alkali (in ml)

S_2 = Normality of the alkali.

- (v) The strength in grams per litre is divided by the normality to give the equivalent mass.

In general, Grams/litre = Normality × Equivalent mass.

Fundamental Principles in Titration :

$$1. \quad V_1 \times S_1 = V_2 \times S_2$$

Volume of acid (in ml) × Strength of acid (in terms of normality)

= Volume of alkali (in ml) × Strength of alkali (in terms of normality)

2. Acid and alkali solutions of the same strength in terms of normality neutralise one another in equal volumes.

3. Grams per litre = normality × equivalent mass.

Acidimetry is a method by which the strength of an alkali is determined by titrating it against a standard acid.

Alkalimetry is a method by which the strength of an acid is determined by titrating against a standard alkali.

Problem 1 :

25.2 ml. of dilute sulphuric acid is completely neutralised by 24.0 ml of 0.105 (N) NaOH solution. Find out the mass of sulphuric acid per litre of the solution. (U.U. I.D, 1978)

Solution : Suppose V_1 = volume of H_2SO_4 = 25.2 ml

$$S_1 = x \text{ (N)} = \text{Strength of } \text{H}_2\text{SO}_4$$

$$V_2 = \text{Volume of NaOH} = 24.0 \text{ ml}$$

$$S_2 = 0.105 \text{ (N)} = \text{Strength of NaOH.}$$

$$\text{By applying, } V_1 S_1 = V_2 S_2$$

$$S_1 = \frac{V_2 S_2}{V_1}$$

$$\text{or } x \text{ (N)} = \frac{24 \text{ ml} \times 0.105 \text{ (N)}}{25.2 \text{ ml}} = 0.1 \text{ (N)}$$

Hence, normality of the acid is 0.1.

$$\begin{aligned} \text{Grams per litre of } \text{H}_2\text{SO}_4 &= \text{Normality} \times \text{Equivalent mass} \\ &= 0.1 \times 49 \text{ (since eq mass of } \text{H}_2\text{SO}_4 = 49) = 4.9. \end{aligned}$$

Hence, mass of H_2SO_4 per litre of the solution = 4.9 g.

Problem 2

How many mililiters of 1.1 (N/10) HCl will react with 1 g of marble ?

(Ca = 40, C = 12, O = 16) (U.U.I.Sc., 1981 S)

Solution : Marble is CaCO_3 and its molecular mass = 100



$$100 \quad 2 \times 36.5$$

Thus, 100 g of CaCO_3 require (2×36.5) g of HCl for complete reaction = 2000 ml of (N) HCl

Therefore, 1 g of CaCO_3 will require $\frac{2000}{100}$ ml of (N) HCl = 20 ml of (N) HCl

$$\begin{aligned} \text{Suppose } 20 \text{ ml of (N) HCl} &= x \text{ ml of } 1.1(\text{N}/10) \text{ HCl} \\ &= x \text{ ml of } 0.11 \text{ (N) HCl} \end{aligned}$$

$$\therefore x = \frac{20}{0.11} \text{ ml} = 181.8 \text{ ml.}$$

Hence, 181.8 ml of 1.1 (N/10) HCl will react with 1 g of marble.

Problem 3 :

How many mililitres of concentrated sulphuric acid of specific gravity 1.84 containing 98% H_2SO_4 by mass are required to prepare 200 ml of 0.5 (N) H_2SO_4 ?

(H = 1, O = 16 and S = 32)

Solution : Eq. mass of $\text{H}_2\text{SO}_4 = \frac{\text{Mol.mass}}{\text{basicity}} = \frac{98}{2} = 49$

1000 ml of (N) H_2SO_4 contain 49 g of H_2SO_4

$$\begin{aligned} 200 \text{ ml of } 0.5(\text{N}) \text{ H}_2\text{SO}_4 \text{ will contain } & \frac{49 \times 200 \times 0.5}{1000} \text{ g} \\ & = 4.9 \text{ g of } \text{H}_2\text{SO}_4. \end{aligned}$$

The given acid contains 98% H_2SO_4 by mass, which means 98 g of H_2SO_4 is present in 100 g of H_2SO_4 solution.

$$\therefore 4.9 \text{ g of } \text{H}_2\text{SO}_4 \text{ will be present in } \frac{100 \times 4.9}{98} \text{ g} = 5 \text{ g of acid.}$$

$$\text{Specific gravity} = \frac{\text{mass}}{\text{volume}} = 1.84$$

$$\text{Hence, volume of acid required} = \frac{\text{mass}}{\text{sp.gr.}} = \frac{5}{1.84} = 2.72 \text{ ml.}$$

Problem 4

20 ml of a solution containing 3 g per litre of a dibasic acid neutralises 10 ml of a solution of Na_2CO_3 containing 5.3 g per litre. Calculate the molecular mass of the acid. (Na = 23, C = 12, and O = 16) (U.U., ISc., 1981)

$$\text{Solution : Equivalent mass of } \text{Na}_2\text{CO}_3 = \frac{106}{2} = 53$$

53 g of Na_2CO_3 per litre gives (N) solution

\therefore 5.3 g of Na_2CO_3 per litre will give (N/10) solution.

Let the strength of the dibasic acid be $S_1(N)$.

20 ml of $S_1(N)$ dibasic acid \equiv 10 ml of (N/10) Na_2CO_3 solution.

$$\therefore S_1(N) = \frac{10 \times N}{10 \times 20} = 0.05(N)$$

Thus, normality of the acid = 0.05

Gms/litre = Normality \times Eq mass, of the dibasic acid.

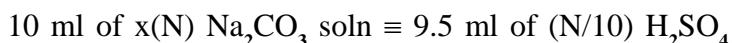
$$\therefore \text{Equivalent mass of the dibasic acid} = \frac{3}{0.05} = 60$$

Molecular mass of the dibasic acid = Eq. mass basicity = $60 \times 2 = 120$

Problem 5 :

6 g of impure sodium carbonate is present in one litre of solution. 10ml of the resulting solution on titration against a (N/10) solution of H_2SO_4 neutralises 9.5 ml of the latter. Calculate the percentage of purity of Na_2CO_3 . (Equivalent mass of $\text{Na}_2\text{CO}_3 = 53$) (U.U.I. Sc. 1981 S)

Solution : Let x = Normality of Na_2CO_3 solution.



$$\text{Therefore, } x(\text{N}) = \frac{9.5 \text{ (N)}}{10 \times 10} = 0.095 \text{ (N)}$$

. Normality of Na_2CO_3 soln. = 0.095.

Equivalent mass of Na_2CO_3 = 53

$\text{g/litre of Na}_2\text{CO}_3$ = Normality \times Eq.mass = $0.095 \times 53 = 5.035$

i.e. 5.035g of pure Na_2CO_3 is present per litre of solution.

6g impure Na_2CO_3 contain 5.035 g of pure Na_2CO_3

100 g of impure Na_2CO_3 will contain $\frac{5.035 \times 100}{6} = 83.92$ g of pure Na_2CO_3 .

Hence, purity of Na_2CO_3 is 83.92 %.

Problem - 6 :

1.575 g of $(\text{COOH})_2 \text{ xH}_2\text{O}$ crystals are dissolved in water and the volume made up to 250 ml. 8.34 ml of this solution is required for complete neutralisation of 10 ml of (N/12) KOH solution. Calculate the number of water molecules associated with the molecule of the acid.

$$\text{Solution : g/litre of } (\text{COOH})_2 \text{ xH}_2\text{O} = \frac{1.575 \times 1000}{250} = 6.3$$

If S_1 = normality of the acid and S_2 = normality of KOH

and V_1 = volume of the acid and V_2 = volume of KOH,

Then, $V_1 S_1 = V_2 S_2$

$$S_1 \times 8.34 = 10 \times 1/12$$

$$\text{or, } S_1 = \frac{10}{12 \times 8.34} = 0.099 = 0.1 \text{ (approx)}$$

$$\therefore \text{Eq mass of acid} = \frac{\text{g/litre}}{\text{normality}} = \frac{6.3}{0.1} = 63.00$$

Basicity of the acid = 2

Molecular mass = Eq. mass \times basity = $63 \times 2 = 126$.

As per formula, molecular mass of acid $(\text{COOH})_2 \text{ xH}_2\text{O}$

$$= (12 + 32 + 1) 2 + 18x = 90 + 18x$$

$$90 + 18x = 126$$

$$\text{or, } x = \frac{126 - 90}{18} = 2$$

Hence, x = no of water molecules in a molecule of acid is 2.

Problem 7 :

3.5 g of a mixture of NaOH and KOH were dissolved and made up to 250 ml. 25 ml of this solution were completely neutralised by 17 ml of (N/2) HCl solution. Calculate the percentage of KOH in the mixture.

(Na = 23, K = 39, Cl = 35.5, O = 16)

Solution : Suppose the amount of NaOH in the mixture = x g.

∴ Amount of KOH = (3.5 - x) g.

25 ml of alkali solution ≡ 17 ml of (N/2) HCl.

or, 250 ml of alkali solution ≡ 170 ml of (N/2) HCl

1000 ml of (N) HCl contain 36.5 g of HCl

170 ml of $\frac{N}{2}$ HCl will contain $\frac{36.5 \times 170}{1000 \times 2} = 3.1025$ g of HCl.

Eq mass of NaOH = 40 and that of KOH = 56

40 g of NaOH require 36.5 g of HCl

x g of NaOH will require $\frac{36.5 \times x}{40}$ g of HCl

Similarly, 56 g of KOH require 36.5 g of HCl

(3.5 - x) g of KOH will require $\frac{36.5(3.5-x)}{56}$ g of HCl

Thus, $\frac{36.5x}{40} + \frac{36.5(3.5-x)}{56} = 3.1025$ of HCl.

or, x = 3.15 g = Amount of NaOH in the mixture

∴ Amount of KOH = (3.5 - 3.15)g = 0.35 g.

3.5 g of the mixture contain 0.35 g of KOH

100 g of the mixture will contain $\frac{0.35 \times 100}{35} = 10$ g of KOH.

Hence, % of KOH = 10.

Problem 8.

Two acids A and B are titrated separately each time with 25 ml of (N) Na_2CO_3 solution and require 10 ml and 40 ml respectively for complete neutralisation. What volume of A and B would you mix to produce one litre of normal acid solution ?

Solution : For acid A

If, V_1 = Volume of acid in ml

S_1 = Strength of acid in normality

V_2 = Volume of Na_2CO_3 solution in ml

S_2 = strength of Na_2CO_3 solution in normality

$$V_1 S_1 = V_2 S_2$$

$$10 \text{ ml} \times S_1 = 25 \text{ ml} \times (N)$$

$$\text{or, } S_1 = \frac{25}{10} (N) = 2.5 (N) = \text{Strength of acid A.}$$

Similarly, for acid B,

$$\text{Strength of acid B} = \frac{25}{40} (N) = 0.625(N)$$

Suppose, x ml of acid A is mixed with y ml of acid B to give 1000 ml of (N) acid. According to the question,

$$x \text{ ml} \times 2.5(N) + y \text{ ml} \times 0.625(N) = 1000 \text{ ml} \times (N)$$

$$\text{or, } 2.5x + 0.625y = 1000 \dots\dots\dots(1)$$

$$\text{Again, } x + y = 1000 \dots\dots\dots(2)$$

(Since the total volume = 1000 ml)

From (1) and (2), $0.75 y = 600$ or, $y = 800$ ml.

Hence, $x = (1000 - 800)$ ml = 200 ml.

Therefore, 200 ml of acid A and 800 ml of acid B are to be mixed to produce 1000 ml of (N) acid solution.

CHAPTER (10) AT A GLANCE

1. **Oxidation :** Process in which an atom or group of atoms loses one or more electrons.
2. **Reduction :** Process in which an atom or group of atoms gains one or more electrons.
3. **Redox reaction :** Oxidation and reduction always occur simultaneously. The overall reaction which involves oxidation and reduction is termed as redox reaction.
4. **Oxidation Number :** Oxidation number of an element in a compound is the charge positive or negative which would be assigned to the atoms of that element in the compound, if all the bonds were ionic bonds. Oxidation number can be a fraction also. The oxidation number of an element can not exceed its group number in the periodic table.
5. **Equivalent mass of oxidising agent :** $\frac{\text{Molecular mass of the oxidising agent}}{\text{Number of electrons gained per mole}}$
6. **Equivalent mass of reducing agent :** $\frac{\text{Molecular mass of the reducing agent}}{\text{Number of electrons lost per mole}}$
7. **There are four types of redox reactions**
 - (a) Combination redox reaction
 - (b) Decomposition redox reactions
 - (c) Displacement redox reaction
 - (d) Disproportionation reactions
8. **Applications of redox reactions**
 - (a) Quantitative analysis
 - (b) Electrode processes
 - (c) Extraction of metals
 - (d) Supply of energy
 - (e) Photosynthesis
 - (f) Production of chemicals
9. **Equivalent mass of acid :** How many parts by mass of the acid contain one part by mass of replaceable hydrogen. Number of replaceable hydrogen = Basicity.
10. **Titration :** Progressive addition of acid to a base or vice versa.
11. **Indicator :** Substance which indicates the neutralisation point or end point by a colour change.
12. **Principles in Titration :**
 - (a) $V_1 \times S_1 = V_2 \times S_2$
where V_1 = Volume of acid in ml.
 S_1 = Strength of acid in terms of normality.
 V_2 = Volume of alkali in ml.
 S_2 = Strength of alkali in terms of normality.
 - (b) Acids and alkali solutions of the same strength in terms of normality neutralise one another in equal volumes.
 - (c) Grams/litre = Normality \times Equivalent mass.

QUESTIONS

PART - A

(A) Short Answer type Questions : (1 mark each).

1. Calculate the oxidation number of the underlined elements in the following compound:

- | | | |
|--|--|---|
| (i) $\text{Na}_2\text{S}_2\text{O}_3$ | (ii) $\text{K}\underline{\text{Mn}}\text{O}_4$ | (iii) $\text{K}_2\underline{\text{Mn}}\text{O}_4$ |
| (iv) $\text{K}_2\text{Cr}_2\text{O}_7$ | (v) $\underline{\text{N}}_2\text{H}_4$ | (vi) $\text{Na}_2\underline{\text{S}}\text{O}_4$ |
| (vii) $\text{Na}\underline{\text{H}}$ | (viii) $\underline{\text{Cl}}_2\text{O}_7$ | (ix) $\text{Na}_2\underline{\text{S}}\text{O}_3$ |
| (x) $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$ | (xi) $\underline{\text{Cr}}\text{O}_3$ | (xii) $\text{K}_4[\text{Fe}(\text{CN})_6]$ |
| (xiii) $\text{Ag}\underline{\text{N}}\text{O}_3$ | (xiv) $\underline{\text{Ni}}(\text{CO})_4$ | (xv) Na_2O_2 |
| (xvi) $\underline{\text{O}}\text{F}_2$ | (xvii) $\text{K}_3[\text{Fe}(\text{CN})_6]$ | (xviii) $[\text{Ag}(\text{NH}_3)]\text{Cl}$ |

2. Fill in the blanks :

- (i) Oxidation is due to —— of electron whereas reduction is due to —— of electrons.
- (ii) $\text{MnO}_4^- + \text{H}^+ + \text{——} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- (iii) $\text{Cr}_2\text{O}_7^{2-} + \text{——} + \text{——} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
- (iv) The algebraic sum of oxidation numbers of all the atoms of a neutral molecule must be ——.
- (v) Reaction in which oxidation and reduction take place simultaneously is termed as —— reaction.
- (vi) Conversion of KMnO_4 to K_2MnO_4 is a process of ——.

(B) Multiple Choice Questions : (1 mark each).

1. Oxidation involves
 - (i) Loss of electrons
 - (ii) gain of electrons
 - (iii) increase in the valency of negative part
 - (iv) decrease in the valency of positive part. (NCERT, 1971)
2. When iron is added. to copper sulphate, copper is precipitated due to
 - (i) Oxidation of Cu^{2+} .
 - (ii) Reduction of Cu^{2+} .
 - (iii) hydrolysis of CuSO_4 .
 - (iv) Ionisation of CuSO_4 .
3. The oxidation number of carbon in CHCl_3 is
 - (i) + 2 (ii) + 3 (iii) + 4 (iv) - 3.

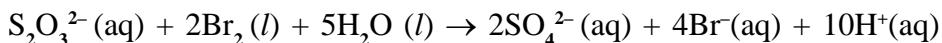
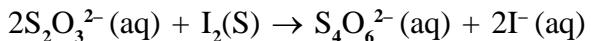
4. The process in which the oxidation number increases is called
 (i) Oxidation (ii) Reduction (iii) Auto-oxidation (iv) Neutralisation.
5. The conversion of sugar $C_{12}H_{22}O_{11}$ to CO_2 is
 (i) oxidation (ii) reduction (iii) neither oxidation nor reduction (iv) both oxidation and reduction.
6. The oxidation number of chlorine is + 5 in the compound
 (i) Cl_2O_7 (ii) ClO_3^- (iii) ClO_4^- (iv) ClO^- .
7. In the following half reaction
 $H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + X$, X is
 (i) 1e (ii) 2e (iii) 3e (iv) 4e.
8. Oxidation number of nitrogen in N_3H is
 (i) +1/3 (ii) +3 (iii) – 1 (iv) – 1/3.
9. The following reaction describes the rusting of iron.
 $4Fe + 3O_2 \rightarrow 4Fe^{3+} + 6O^{2-}$
 Which of the following statements is incorrect ?
 (i) This is an example of redox reaction.
 (ii) Metallic iron is reduced to Fe^{3+}
 (iii) Fe^{3+} is an oxidising agent.
 (iv) Metallic iron is a reducing agent.
10. Iron does not show the oxidation number of
 (i) 0 (ii) +1 (iii) + 2 (iv) + 3 (v) +8/3.

(C) Short answer type : (2 marks each).

1. Balance the following by ion-electron method.
 - (i) $Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$
 - (ii) $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + I^-$
 - (iii) $Cr_2O_7^{2-} + H^+ + I^- \rightarrow Cr^{3+} + I_2 + H_2O$
2. Balance the following equations by oxidation number method.
 - (i) $KMnO_4 + H_2SO_4 + H_2S \rightarrow K_2SO_4 + MnSO_4 + H_2O + S$
 - (ii) $K_2CrO_4 + HCl \rightarrow K_2Cr_2O_7 + KCl + H_2O$
 - (iii) $K_2KMnO_4 + HCl \rightarrow KMnO_4 + MnO_2 + KCl + H_2O$
 - (iv) $HNO_3 + I_2 \rightarrow HIO_3 + NO_2 + H_2O$
 - (v) $H_2S + HNO_3 \rightarrow H_2O + NO + S$
 - (vi) $MnO_4^- + SO_2 \rightarrow Mn^{2+} + H_2SO_4$

(D) Short answer type : (3 marks each).

1. Consider the reactions :



Why does the same reductant, thiosulphate react differently with iodine and bromine?

2. Sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agent in their reactions. Why ?
3. Determine the volume of M/8 KMnO_4 solution required to react completely with 20 Cm^3 of M/4 FeSO_4 solution in acidic medium.
4. Which of the following species, do not show disproportionation reaction and why ?



Also write reaction for each of the species that disproportionates.

ANSWERS

- A. (1) (i) +2, (ii) +7, (iii) +6, (iv) +6, (v) -2, (vi) +6, (vii) -1, (viii) +7, (ix) +4, (x) +6, (xii) +2, (xiii) +5, (xiv) 0, (xv) -1, (xvi) +2, (xvii) +3, (xviii) +1
 (2) (i) loss, gain (ii) 5e^- (iii) $6\text{e}^- + 14\text{H}^+$ (iv) zero (v) redox (vi) reduction

QUESTIONS

PART - A

(A) Short Answer type Questions

1. What is the oxidation number of S in $\text{Na}_2\text{S}_2\text{O}_3$?
2. What is the oxidation of Mn in K_2MnO_4 and KMnO_4 ?
3. What is the oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ and N in N_2H_4 ?
4. What is the oxidation number of nitrogen in nitrous oxide ?
5. What is the oxidation number of sulphur in SO_4^{2-} ?
6. What is the oxidation number of hydrogen in sodium hydride ?
7. Balance the following equation :
 - (a) $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{S}^{2-} \rightarrow 2\text{Cr}^{3+} + \text{S} + \text{H}_2\text{O}$
 - (b) $\text{MnO}_4^- + \text{Cl}^- + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{Cl}_2 + \text{H}_2\text{O}$
 - (c) $\text{MnO}_4^- + \text{H}^+ + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{Fe}^{3+}$
 - (d) $\text{Cr}_2\text{O}_7^{2-} + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cr}^{3+} + \text{Cl}_2 + \text{H}_2\text{O}$
 - (e) $\text{MnO}_4^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{2+} + \text{O}_2 + \text{H}_2\text{O}$
8. What is the oxidation number of oxygen in hydrogen peroxide ?
9. Balance the following by ion - electron method :
 - (a) $\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow \text{Fe}^{2+} + \text{Sn}^{4+}$
 - (b) $\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + \text{I}^-$
 - (c) $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{I}^- \rightarrow \text{Cr}^{3+} + \text{I}_2 + \text{H}_2\text{O}$
10. (a) Balance the equation and identify the oxidising and reducing agent in the reaction.

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{H}_2\text{O}.$$
(b) In the following reaction what is oxidised and what is reduced ?

$$3 \text{ CuO} + 2\text{NH}_3 \rightarrow 3\text{Cu} + \text{N}_2 + 3\text{H}_2\text{O}$$
11. Fill in the blanks :
 - (a) Oxidation is due to _____ of electron whereas reduction is due to _____ of electron.
 - (b) $\text{MnO}_4^- + \text{H}^+ + \text{_____} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.
 - (c) $\text{Cr}_2\text{O}_7^{2-} + \text{.....} + \text{.....} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
12. Balance the following equations by oxidation number method.
 - (a) $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{S} \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{H}_2\text{O} + \text{S}$
 - (b) $\text{K}_2\text{CrO}_4 + \text{HCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + \text{KCl} + \text{H}_2\text{O}$
 - (c) $\text{K}_2\text{MnO}_4 + \text{HCl} \rightarrow \text{KMnO}_4 + \text{MnO}_2 + \text{KCl} + \text{H}_2\text{O}.$
 - (d) $\text{HNO}_3 + \text{I}_2 \rightarrow \text{HIO}_3 + \text{NO}_2 + \text{H}_2\text{O}$
 - (e) $\text{H}_2\text{S} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO} + \text{S}$
 - (f) $\text{MnO}_4^- + \text{SO}_2 \rightarrow \text{Mn}^{2+} + \text{H}_2\text{SO}_4$.

13. Give atleast six oxidation states of nitrogen with one example for each state.
14. Why is decolourisation of KMnO_4 by oxalate accompanied by effervescence whereas no effervescence takes place when KMnO_4 is decolourised by FeSO_4 ?
15. State the reason whether HCl can be used in place of H_2SO_4 in titration involving KMnO_4 .
16. Calculate the oxidation number of the underlined elements in the following compounds :
- $\underline{\text{Cl}}_2\text{O}_7$, $\text{Na}_2\underline{\text{S}}\text{O}_3$
 - $\text{K}_2\underline{\text{Cr}}_2\text{O}_7$, $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$, $\underline{\text{Cr}}\text{ O}_3$
 - $\text{K}_4[\underline{\text{Fe}}(\text{CN})_6]$, $\text{K}\underline{\text{Mn}}\text{O}_4$, $\text{Ag}\underline{\text{N}}\text{O}_3$.
 - $\text{H}\ \underline{\text{N}}_3$, $\text{K}_2\underline{\text{Mn}}\text{ O}_4$
17. State whether the following statements are *true* or *false*.
- The oxidation number of S in H_2SO_4 is + 8.
 - The equivalent mass of KMnO_4 in neutral medium is M/3.
 - The reaction $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$ is a redox reaction.
 - Conversion of K_2CrO_4 to $\text{K}_2\text{Cr}_2\text{O}_7$ is a redox reaction.
 - Oxidation and reduction take place simultaneously.
 - Oxidation number of an element in a compound can be a fraction.
- (Ans : (i) False (ii) True (iii) False (iv) False (v) True (vi) True)
18. **Fill in the blanks :**
- The algebraic sum of oxidation numbers of all the atoms of a neutral molecule must be _____.
(CHSE, 1999 I)
 - The oxidation number of oxygen in Na_2O_2 is _____.
(c) Reduction is _____ of electron.
(d) Reaction in which oxidation and reduction take place simultaneously is termed as _____ reaction.
(e) Conversion of KMnO_4 to K_2MnO_4 is a process of _____.
(f) In Cl_2O , the oxidation number of oxygen is _____.
(g) In OF_2 , the oxidation number of oxygen is _____.
(h) Oxidation is _____ of electron.
19. What is the oxidation number of iron in potassium ferricyanide ?
20. What is the oxidation number of S in H_2SO_4 ?
- B. Very short question (1 mark)**
- What is the change in oxidation number of marked element in the following ?
(i) $\text{K}_2\underline{\text{Cr}}\text{O}_4 \rightarrow \text{K}_2\underline{\text{Cr}}_2\text{O}_7$ (ii) $\text{Na}_2\underline{\text{S}}_2\text{O}_3 \rightarrow \text{Na}_2\underline{\text{S}}\text{O}_4$
 - What is the Oxidation number of oxygen in OF_2 ?

3. What is the oxidation number of silver in $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$?
 4. What is the oxidation number of nickel in $\text{Ni}(\text{CO})_4$?

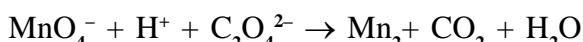
C. Short question type (2 marks)

1. Write the ion-electron equation for the following



2. Give two examples of oxidation reduction reaction ?

3. Balance the following equation by ion-electron method



4. Balance the following equation :



ANSWER

- A. 1. +2 , 2. +6 & +7 , 3. +6 & -2 , 4. +1 , 5. +6 , 6. -1 , 9. 53 , 11. -1
 10 (a). $\text{Cr}_2\text{O}_7^{2-}$ - oxidising agent , Fe^{2+} – reducing agent
 (b) NH_3 is oxidised (-3 to 0) , CuO is reduced (+2 to 0)
 11. (a) loss, gain (b) 5e (c) 6e, 14H⁺
 13. +5 : N_2O_5 , HNO_3 +2 : NO , +4 : N_2O_4 HNO_2
 $+ \frac{1}{2} : \text{N}_2\text{O}$, +3 : N_2O_3 , -3 : NH_3 , -2 : N_2H_4 , $-\frac{1}{3} : \text{N}_3\text{H}$
 14. With oxalate, effervescence is due to evolution of CO_2 whereas with Fe^{2+} , it is only converted to Fe^{3+} . No gas is evolved.
 15. HCl chemically reacts liberating Cl_2 gas – $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$.
 16. (i) +7, +4 (ii) +6, +6, +6, (iii) +2, +7, +5 (iv) $-\frac{1}{3}$, +6.
 17. (i) False, (ii) True, (iii) False, (iv) False, (v) True, (vi) True
 18. (a) Zero, (b) -1, (c) gain, (d) redox, (e) reduction (f) -2, (g) +2 (h) loss.
 19. +3. 20. +6
- B.** 1. (i) + 6 to +6 (ii) +2 to +6
 2. + 2 3. +1 4. 0

MULTIPLE CHOICE QUESTION

1. (i)

2. (ii)

3. (i)

4. (i)

5. (i)

6. (ii)

7. (ii)

8. (iv)

9. (ii)

10. (ii)

QUESTIONS**PART-B****A. Short questions type (2 marks)**

1. Calculate the normality of the following
 - (a) 0.585 g NaCl / 100 cc soln.
 - (b) 0.49 g H₂SO₄ / 1000 cc soln.
2. Calculate the normality of the resulting solution obtained by mixing 10cc of N/2 HCl with 30cc of N/10 H₂SO₄ ?
3. Indicate the type of chemical reaction from the following equations.
 - (a) NaNO₃ → NaNO₂ + O₂
 - (b) C + O₂ → CO₂
 - (c) NaCl + AgNO₃ → AgCl + NaNO₃
 - (d) BiCl₃ + H₂O → BiOCl + 2HCl
 - (e) NH₄CNO → NH₂CONH₂
 - (f) Cu + 2AgNO₃ → Cu(NO₃)₂ + 2Ag.
4. How many ml of 1 M H₂SO₄ would be required to neutralise 100 ml of 1 N sodium hydroxide solution ?
5. A solution containing 10.5 g of an alkali is completely neutralised by 500 ml of 0.5 N acid. What is the equivalent mass of the alkali ? (CHSE, 1990 S)
6. 10ml of 0.1 N NaOH solution is titrated against HCl solution of 0.05 N strength. How much HCl will be required to get the end point ?
7. State whether the following statement, are *true or false*.
 - (i) Standard solution contains one gram equivalent mass of the solute per litre of the solution.
 - (ii) The reaction of an acid with equivalent quantity of a base gives a solution which is always neutral.
 - (iii) If X ml of an N/2 solution completely react with 2x ml of an unknown solution the normality of the latter is 1.
 - (iv) The molecular mass and equivalent mass of a monobasic acid are equal.
 - (v) The equivalent mass and normality of an acid are X and N respectively. Its solution contains X/N g of it per litre.
 - (vi) Sodium carbonate solution can be titrated with acetic acid using phenolphthalein as indicator.

(Ans : (i) False (ii) False (iii) False (iv) True (v) False (vi) True)

B. Long questions :

1. Write notes on :

Molality of a solution

Oxidation number

2. What are different types of chemical reactions ? Explain giving one example in each case.
3. What is the equivalent mass of a base ?

3 grams of a mixture of NaOH and NaCl were dissolved in water and volume was made 250 ml. 25 ml of this solution required 23 ml of N/10 HCl for neutralisation. Calculate the percentage composition of the mixture. (CHSE, 1990 A, 2001 IER) Ans. 30.66% NaOH, 69.34% NaCl

4. Define 'molality' of a solution and explain it with an example.

2.7 grams of a mixture of NaOH and KCl is dissolved in water and the volume made up to 500 ml. 10 ml of this solution required 9 ml of decinormal HCl for neutralisation. Calculate the percentage composition of the mixture. (CHSE, 1992 S, 2001 R) Ans. 66.67%, NaOH, 33.33% KCl

5. Define : (a) Equivalent mass of an acid
 (b) Normal solution.

50 ml of H_2SO_4 of unknown strength was mixed with 25 ml of 1.28 (N/10) NaOH and the mixture was diluted to 100 ml. 10 ml of this diluted solution which was acidic required 8.5 ml of 0.8 (N/10) NaOH for complete neutralisation. Find out the strength of the original H_2SO_4 solution. Ans. 0.2(N)

6. A sample of organic acid weighing 3.0 g was dissolved in water. Using suitable indicator, it was titrated with 0.5 (N) NaOH. solution. Exactly 40 ml were required for neutralisation. What is the equivalent mass of the acid ? Ans. 150
7. (a) 0.4 g of a metal was dissolved in 500 ml of (N/10) H_2SO_4 . When the reaction was over, the excess required was 150 ml (N/15) alkali for complete neutralisation. Calculate the equivalent mass of the metal. Ans. 10
- (b) 0.12gm of Magnesium was dissolved in 500 ml of 0.1 N acid. What volume of N/2 NaOH solution will neutralise the resultant solution ? Ans : 80 ml]
8. A 0.50 g sample of impure $CaCO_3$ is dissolved in 50 ml of 0.985 (N) HCl. After the reaction is complete the excess HCl requires 6.0 ml of 0.105 (N) caustic soda for neutralisation. Find the percentage of $CaCO_3$ in the sample. Ans. 42.95%

9. Acid is generated in the stomach when the concentration of the acid goes up, a man suffers from acidity. The doctor prescribes him antacid. By taking 3 antacid tablets, the strength decreases from N/10 to N/200. If the fluid material is 100 ml, calculate the amount of base present per antacid tablet. (Equivalent mass of base in antacid = 100).

Ans. 3.179

C. Multiple choice questions :

1. Which of the following in aqueous solution is basic in character ?
(i) NaCl (ii) Na_2CO_3 (iii) H_2CO_3 (iv) FeSO_4 . Ans. (ii)
2. The mixture of 100 ml of 0.5 (N) HCl and 500 ml of 0.1 (N) NaOH is
(i) acidic (ii) alkaline (iii) neutral Ans. (iii)
3. 0.45 g of the acid of molecular mass 90 was neutralised by 20 ml of 0.5 (N) caustic potash. The basicity of the acid is
(i) 1 (ii) 2 (iii) 3 (iv) 4. Ans. : (ii)
4. The volume of 0.05 M H_2SO_4 needed to completely neutralise 15 ml of 0.1 M NaOH is
(i) 15 ml (ii) 75 ml (iii) 30 ml (iv) 7.5 ml Ans (i)



UNIT – IX

CHAPTER - 11

HYDROGEN

11.1 POSITION OF HYDROGEN IN THE PERIODIC TABLE

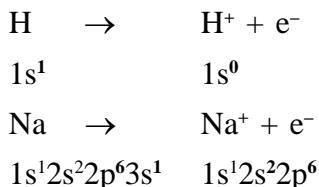
Hydrogen is the lightest and smallest element of the periodic table having atomic number one. It contains one proton in its nucleus and only one electron in 1s orbital of K shell. The hydrogen atom therefore has equal tendency to lose this electron to form H^+ or gain one electron thereby forming H^- . When hydrogen atom loses its one electron it resembles alkali metals (Group 1) in some of its properties and when it gains an electron its other properties resemble those of halogens (Group 17). Hydrogen also differs from both alkali metals and halogens in some other respects. Further, it shows resemblance with carbon (Group 14) in certain respects.

Resemblance with Alkali Metals :

1. **Electronic configuration :** Like alkali metals hydrogen has only one electron in its outermost shell.

Hydrogen	: 1s ¹
Lithium	: 1s ² 2s ¹
Sodium	: 1s ² 2s ² 2p ⁶ 3s ¹

2. **Electropositive character :** Hydrogen like alkali metals tends to lose its only electron to form H^+ ion.



3. **Affinity for non-metals :** Hydrogen and alkali metals both have great affinity for non-metals :

H_2O :	Na_2O, K_2O
H_2S :	Na_2S, K_2S
HCl :	$NaCl, KCl$

- 4. Oxidation state :** Both hydrogen and alkali metals exhibit an oxidation state of +1 in their compounds :



- 5. Reducing character.** Just like alkali metals hydrogen acts as a reducing agent as shown in the following reactions :

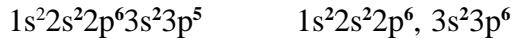


Resemblance with Halogens :

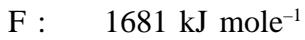
- 1. Electronic configuration.** Hydrogen atom like halogen atoms requires one electron to attain the electronic configuration of the next inert gas.



- 2. Electronegative character :** Like halogen atoms hydrogen atom has tendency to gain one electron to form hydride ion (H^-).



- 3. Ionisation energy :** The ionisation energy of hydrogen atom is quite comparable with those of halogens as given below :



- 4. Oxidation state :** Hydrogen like halogens shows an oxidation state of -1 in some of its compounds :



- 5. Combination with metals :** With alkali and alkaline earth metals hydrogen forms hydrides similar to that of halogens.



- 6. Combination with nonmetals.** Just like halogens hydrogen forms covalent compounds with non-metals such as carbon, silicon, germanium etc.



- 7. Atomicity.** Like halogens hydrogen exists as a diatomic molecule under ordinary condition.



Dissimilarity with Alkali Metals and Halogens :

Hydrogen also differs from both alkali metals and halogens in the following respects :

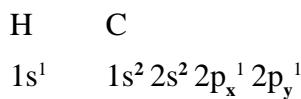
1. Hydrogen is less electropositive than alkali metals and less electronegative than halogens.
2. Unlike alkali metals and halogens, hydrogen has only one proton in its nucleus and only one electron in the extra nuclear part.
3. Oxide of hydrogen e.g. H_2O is neutral whereas the oxides of alkali metals and halogens are basic and acidic respectively.



Similarity with Carbon :

Hydrogen also shows resemblance with carbon in the following respects :

1. **Half filled outer shell.** Outer shells of hydrogen and carbon are half-filled.

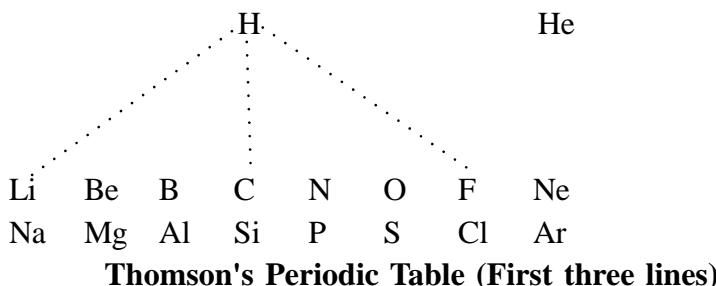


2. **Electronegativity.** Both the elements have similar values of electronegativity.

$$\text{H} = 2.1 \quad \text{and} \quad \text{C} = 2.5$$

3. **Formation of covalent compounds.** Both form covalent compounds such as HCl and CCl_4 .

In the light of the above discussion it is difficult to allot a proper place to hydrogen in the periodic table. Thomson however allotted a special position to hydrogen in his periodic table as shown below.



Electropositive Character of Hydrogen

Hydrogen atom having atomic number one has the simplest electronic configuration $1s^1$. When the hydrogen atom loses its only electron, H^+ ion is formed which shows electropositive character like alkali metals.

Hydrogen combines with electronegative elements like oxygen, chlorine and sulphur forming compounds such as H_2O , HCl and H_2S respectively. Similarly, sodium also forms Na_2O , NaCl and Na_2S with oxygen, chlorine and sulphur respectively. This indicates the electropositive character of hydrogen.

When hydrogen halides (e.g. HCl , HBr etc) or oxide (e.g. H_2O) are electrolysed hydrogen is liberated at the cathode. This also shows that hydrogen has electropositive character.

Electronegative character of hydrogen :

Hydrogen atom has also the tendency to gain one electron, thereby attaining the stable configuration of helium ($1s^2$). H^- ion then formed exhibits electronegative character like halogens.

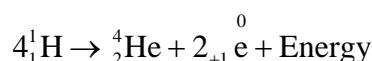
Hydrogen combines with electropositive elements such as alkali and alkaline earth metals to form hydrides (e.g. NaH , CaH_2 etc) thereby exhibiting its electronegative character.

Further, when hydrides (e.g. NaH , LiH) are electrolysed, hydrogen is liberated at the anode. This also indicates the electronegative character of hydrogen.

11.2 OCCURRENCE :

Hydrogen is the most abundant element in the universe and constitutes about 70% of total mass of it. The jovian planets like Jupiter and Saturn contain mostly hydrogen. About half of the mass of the sun and stars is composed of hydrogen.

The extremely high temperature of the sun brings about fusion of hydrogen atoms liberating large amount of energy.



Hydrogen is an essential constituent of water, coal, petroleum, clay and all animal and vegetable matter. Hydrogen gas is much less abundant (0.15% by mass) in earth's atmosphere because it is very light and earth's gravitational pull is not enough to retain it.

11.3 ISOTOPES OF HYDROGEN

Isotopes are the different forms of an element having the same atomic number but different mass numbers. Hydrogen has three isotopes having mass numbers 1, 2 and 3. These are called **hydrogen** or **protium** (${}_1\text{H}^1$), **deuterium** (${}_1\text{H}^2$) and **tritium** (${}_1\text{H}^3$).

- 1. Hydrogen or Protium.** It is represented as ${}_1\text{H}^1$ indicating thereby that this isotope of hydrogen has atomic number 1 and the mass number 1. Protium has one proton and no neutron in the nucleus and one electron in the extra nuclear part. The most abundant isotope of hydrogen is protium. Natural hydrogen contains protium to the extent of 99.984%
- 2. Deuterium or Heavy hydrogen.** It is represented by ${}_1\text{H}^2$ which indicates that this isotope of hydrogen has atomic number 1 but mass number 2. This isotope has one proton and one neutron in the nucleus and one electron in the extra nuclear part. Natural hydrogen contains 0.016% of heavy hydrogen.

3. **Tritium.** This isotope of hydrogen has one proton and two neutrons in the nucleus and one electron in the extra nuclear part. It is radioactive and unstable. It constitutes only $10^{-15}\%$ of total natural hydrogen.

Table 11.1 Isotopes of Hydrogen

	Protium	Deuterium	Tritium
Symbol	${}_1\text{H}^1$	${}_1\text{H}^2$	${}_1\text{H}^3$
Atomic number	1	1	1
Mass number	1	2	3
No. of protons in the nucleus	1	1	1
No of neutrons in the nucleus	0	1	2
No. of electrons	1	1	1
Electronic configuration	1s^1	1s^1	1s^1
Percentage of abundance	99.984	0.016	10^{-15}
Stability	Stable	Stable	Radioactive and hence unstable.

Isotopic Effect :

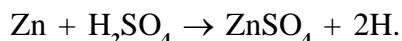
All the three isotopes of hydrogen have similar electronic configuration (1s^1) and hence they have identical chemical properties. But due to the difference in the masses of isotopes they differ appreciably from one another in the rates of their reactions and equilibrium constants for reversible reactions. They also differ in their physical properties such as melting and boiling points, latent heat of fusion, evaporation, sublimation etc. on account of differences in mass numbers. The difference in properties on account of the mass difference in isotopes of an element is known as *isotopic effect*.

Different Reactive Forms of Hydrogen :

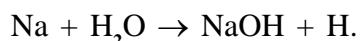
1. **Nascent Hydrogen.** Hydrogen which is just liberated as a result of chemical reaction is called *nascent* (newly born) hydrogen.

Preparation : Nascent hydrogen can be prepared by the following methods :

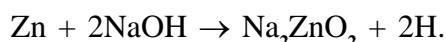
- i. By the action of zinc and dilute sulphuric acid.



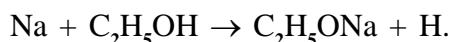
- ii. By the action of water on sodium amalgam.



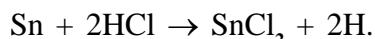
- iii. By the action of caustic soda on zinc or aluminium.



- iv. Metallic sodium reacts with absolute alcohol to form nascent hydrogen.

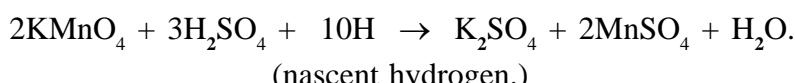
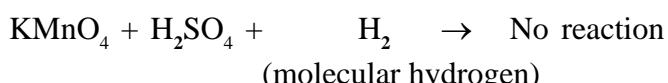


- v. Tin reacts with concentrated hydrochloric acid to form nascent hydrogen.

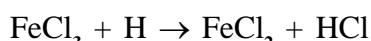


Reducing properties of nascent hydrogen :

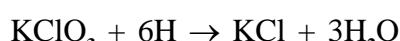
- (i) When molecular hydrogen (H_2) is passed through potassium permanganate solution acidified with dilute sulphuric acid, its pink colour is not discharged. To the same solution if some zinc pieces are added the pink colour gets discharged after some time. This is because nascent hydrogen which is just generated by the reaction of zinc and dilute sulphuric acid reduces acidified potassium permanganate solution.



- (ii) Ferric chloride solution (yellow) is reduced to ferrous chloride (light green) by adding zinc pieces and dilute hydrochloric acid. This is due to reducing property of nascent hydrogen just produced by the action of dilute hydrochloric acid on zinc.



- (iii) Nascent hydrogen generated from zinc and dilute sulphuric acid can also reduce KClO_3 to KCl .



2. Atomic Hydrogen

Preparation : Atomic hydrogen is best produced by passing molecular hydrogen through tungsten electric arc ($2000 - 3000^\circ\text{C}$) at low pressure. The dissociation of molecular hydrogen is an endothermic reaction.



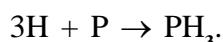
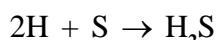
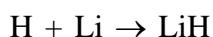
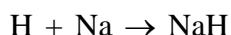
This form of hydrogen is more reactive than ordinary and nascent hydrogen.

Properties :

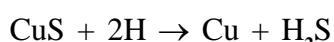
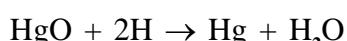
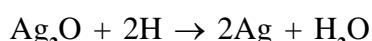
- (i) **Stability :** The life period of atomic hydrogen is only 0.03 second which can be extended to 10 seconds under special condition.
- (ii) **Recombination :** Atomic hydrogen is extremely unstable and reunites readily to form molecular hydrogen with the liberation of large amount of heat. Temperature rises to $4000 - 5000^\circ\text{C}$. Metals like Pt, Pd etc. accelerate this recombination. This is the principle under which the atomic hydrogen torch works.



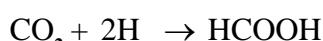
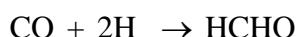
- (iii) **Formation of hydrides :** It combines with metals (such as Li, Na, K) and nonmetals (such as S, P) to give hydrides.



- (iv) **Reducing property :** It reduces oxides, chlorides and sulphides of some metals such as Cu, Ag, Hg etc. to the corresponding metals.



It also reduces carbon monoxide to formaldehyde and carbondioxide to formic acid.



3. Ortho and Para Hydrogen

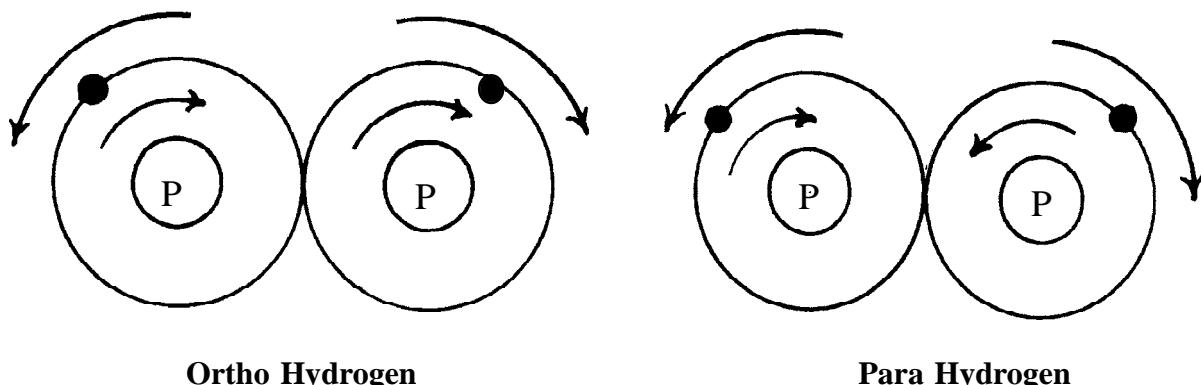
Hydrogen molecule consists of two hydrogen atoms. Each hydrogen atom in the hydrogen molecule has one proton in its nucleus and one electron revolving around the nucleus. According to Pauli's exclusion principle the spins of the two electrons should be in the opposite directions for the formation of a stable molecule. However, the spins of the protons may be either in the same direction (parallel direction) or in the opposite direction (anti - parallel direction). When the spins of the protons are in the **same direction** we get **ortho hydrogen** and when the spins of the protons are in the **opposite direction** it gives rise to **para hydrogen**.

Pure para hydrogen can be prepared by adsorbing ordinary hydrogen in activated charcoal in quartz vessel kept at a temperature of 20K for 3 to 4 hours.

Ortho hydrogen in pure form has not been prepared so far. At normal temperature, ordinary hydrogen is mixture of about 75% of ortho hydrogen and 25% of para hydrogen. As the temperature increases the proportion of ortho form increases and that of para form decreases. At the temperature of liquefaction of air the ratio of ortho and para forms is 1 : 1.

Difference between Ortho and Para Hydrogen :

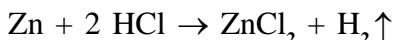
- The ortho form has higher internal energy than the para form.
- The ortho form is more stable than the para form and hence the para form has the tendency to change to ortho form.
- The two forms differ in physical properties like melting point, boiling point, thermal conductivity, specific heat etc. However, they have similar chemical properties.

**Fig 11.1 Ortho and Para forms of hydrogen****11.4 [DIHYDROGEN :]****Preparation :**

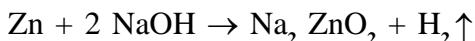
There are a number of methods for preparing dihydrogen from metal and metal hydrides.

11.4.1 Laboratory methods of preparation :

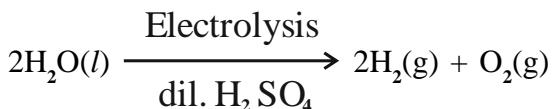
- (1) It is usually prepared by the reaction of granulated zinc with dil. hydrochloric acid.



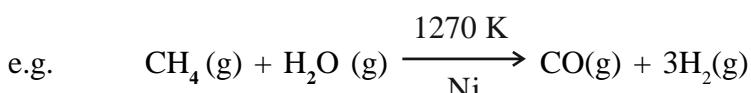
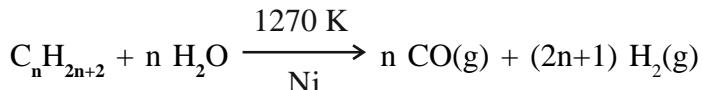
- (2) Reaction of zinc with aqueous alkali also produces dihydrogen.

**11.4.2 Commercial methods of preparation :****(1) Electrolysis of acidified water :**

Electrolysis of acidified water using platinum electrodes gives dihydrogen.

**(2) Reaction of steam on hydrocarbons :**

Reaction of steam on hydrocarbons at high temperature in the presence of catalyst yields dihydrogen.



The mixture of CO and H₂, commonly known as **water gas** or **synthesis gas** is used in the synthesis of methanol and also a number of hydrocarbons.

11.4.3 PROPERTIES

Physical Properties :

Dihydrogen is a colourless, odourless, tasteless combustible gas. It is lighter than air and insoluble in water.

Its other physical properties along with those of Deuterium and Tritium are mentioned on Table 11.2.

TABLE 11.2 Atomic and Physical Properties of Hydrogen

Property	Hydrogen	Deuterium	Tritium
Relative abundance (%)	99.985	0.0156	10^{-15}
Relative atomic mass (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 / gL^{-1}	0.09	0.18	0.27
Enthalpy of fusion / kJ mol^{-1}	0.117	0.197	-
Enthalpy of vaporization / kJ mol^{-1}	0.904	1.226	-
Enthalpy of bond dissociation / kJ mol^{-1} at 198.2K	435.88	443.35	-
Internuclear distance / pm	74.14	74.14	-
Ionization enthalpy / kJ mol^{-1}	1312	-	-
Electron gain enthalpy / kJ mol^{-1}	-73	-	-
Covalent radius / pm	37	-	-
Ionic radius (H^-) / pm	208	-	-

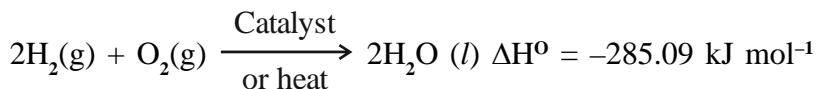
Chemical Properties :

- Action with halogens :** It reacts with halogens to give hydrogen halides.

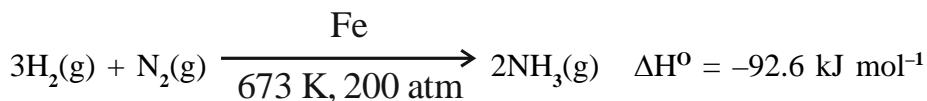


Reaction with Fluorine occurs even in dark, while with Iodine, it requires a catalyst.

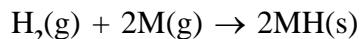
- Action with dioxygen :** It reacts with dioxygen to form water and the reaction is highly exothermic in nature.



- Action with dinitrogen :** It reacts with dinitrogen to yield ammonia and the process is known as Haber's process.



- 4. Action with metals :** Dihydrogen combines with many metals at high temperature to produce corresponding metal hydrides.



where M is an alkali metal.

- 5. Action with metals oxides :** It reduces oxides of metals (less active than iron) into corresponding metals.



- 6. Action with organic compounds :** The unsaturated hydrocarbons undergo hydrogenation in presence of suitable catalyst and hydrogen gas and produce the compounds of commercial importance.



11.4.4 Uses :

1. A starting material for manufacture of ammonia by Haber's process. and also in the preparation of highly useful chemicals like hydrogen chloride, methanol etc.
2. In the manufacture of Vanaspati ghee.
3. Manufacture of metal hydrides.
4. In the fuel cell for producing electrical energy.

11.5 [HYDRIDES :]

Almost all elements of the periodic table (except noble gases and elements of Groups 7, 8, 9) react with dihydrogen under suitable conditions forming 'Hydrides'. The general formula of these hydrides is MH_x , where 'M' stands for metal and 'x' for the number of hydrogen atoms.

Hydrides can be classified into following three categories.

- (1) Ionic hydrides
- (2) Covalent hydrides and (3) Metallic hydrides

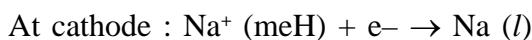
11.5.1 Ionic or Saline or Salt-like hydrides :

Dihydrogen reacts with most of the s-block elements having highly electropositive character producing stoichiometric Ionic hydrides.

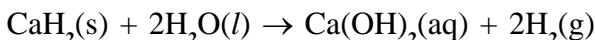
Ex. NaH , CaH_2 etc.

Properties :

1. The ionic hydrides are crystalline and non-volatile being bad conductors in their solid state.
2. In the molten state they are good conductors of electricity and produce dihydrogen gas at anode.



3. They react violently with water to produce corresponding metal hydroxide with liberation of hydrogen gas.



4. Lithium hydride forms useful complex metal hydrides such as lithium aluminium hydride (LiAlH_4) and lithium borohydride (LiBH_4). These compounds are widely used as reducing agents in organic synthesis.

11.5.2 Covalent or Molecular hydrides :

These are the compounds formed by dihydrogen with most of the p-block elements e.g. CH_4 , NH_3 . These compounds are covalent in nature.

They are further classified into following three categories according to the relative numbers of electrons and bonds in their Lewis structure.

- (a) Electron-deficient hydrides
- (b) Electron - precise hydrides
- (c) Electron - rich hydrides

- (a) Electron-deficient hydrides :** Elements of group 13 from electron-deficient hydrides. They act as Lewis acids i.e. electron acceptors.

e.g. BH_3 , AlH_3 , etc.

- (b) Electron-precise hydrides :** These compounds have the required number of electrons around the central atom. e.g. CH_4 . They show regular tetrahedral geometry. Elements of group 14 form such hydrides.

- (c) Electron-rich hydrides :** In these compounds excess electrons are present as lone pairs around the central atom. So they behave as Lewis bases. Elements of group 15-17 form such compounds. e.g. : NH_3 has 1 lone pair, H_2O has 2 lone pairs and HF has 3 lone pairs of electrons.

11.5.3 Metallic or Non-stoichiometric or Interstitial Hydrides :

The metals present in d-block and f-block (except the metal of group 7, 8 and 9) usually form metallic hydrides. These Hydrides are non-stoichiometric being deficient in hydrogen.

e.g. $\text{LaH}_{2.87}$, $\text{YbH}_{2.55}$ etc.

They not conduct heat and electricity as efficiently as their parent metals do. Metals like Platinum and Palladium can accommodate a very large volume of hydrogen and therefore used for hydrogen storage in different energy sources.

11.6 WATER

Water is the most important natural resource. A major part of all living organisms is made up of water. The estimated world water supply is given in Table 11.3

Table 11.3 Estimated World Water supply.

Source	% of total water supply
Oceans	97.33
Saline lakes and inland seas	0.008
Polar ice and glaciers	2.04
Ground water	0.61
Rivers	0.0001
Lakes	0.009
Soil moisture	0.0005
Atmospheric water vapour	0.001

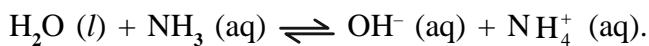
11.6.1 Physical properties of Water :

1. It is a colourless odourless and tasteless liquid.
2. H_2O possesses high values of freezing point, boiling points, heat of vaporisation and heat of fusion in comparison to hydrides of other group 16 elements such as H_2S , H_2Se , H_2Te etc., because of the presence of extensive hydrogen bonding between its molecules.
3. Water has higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant in comparison to other liquids. These properties enable water to play a vital role in biosphere.
4. Water is regarded as a universal solvent as it dissolves most of the inorganic and also covalent compounds.

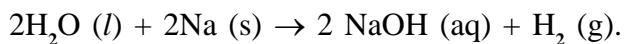
11.6.2 Chemical properties of Water :

1. **Amphoteric Nature :** Water has the ability to act as an acid as well as a base. Thus it behaves as an amphoteric substance.

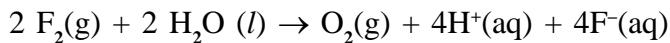
According to Brönsted – Lowry theory, it acts as an acid with NH_3 and a base with H_2S .



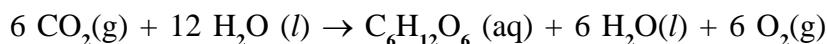
2. **Redox Reactions :** When water react with highly electropositive metals like Na, K etc. it easily gets reduced to dihydrogen and acts as an oxidising agent.



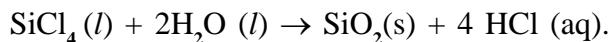
It reduces a number of electronegative elements liberating O_2 gas.



During photosynthesis water gets oxidised to O₂.



- 3. Hydrolysis Reactions :** Some ionic and covalent compounds get hydrolysed when dissolved in water.

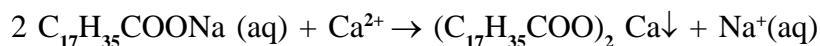


11.6.3 Hard and soft water :

Water containing soluble bicarbonate, chloride, sulphate etc. salts of calcium and magnesium is known as **Hard** water. This type of water does not give lather with soap.

Water free from soluble salts of calcium and magnesium is called **Soft** water. It gives lather with soap easily.

Hardness of water is due to the following reaction.



Hard water is harmful for boilers and also unsuitable for laundry. There are two types of hardness of water : (i) temporary hardness and (ii) permanent hardness.

Temporary hardness is due to the presence of calcium and magnesium bicarbonates. It can be removed by (a) Boiling (b) Adding calculated amount of lime.

Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium. It can be removed by

- (a) Treatment with washing soda
- (b) Adding sodium hexametaphosphate (Na₆P₆O₁₈)
- (c) Adding Zeolite (NaAlSiO₄)

11.7 HEAVY WATER :

Heavy water is deuterium oxide (D₂O). An American chemist, **Urey** established that ordinary water contains 0.016 percent of heavy water.

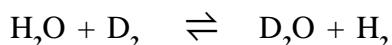
Preparation :

- 1. Multistage Electrolysis of Ordinary Water :** Heavy water is prepared on a commercial scale by multistage (continuous and prolonged) electrolysis of natural water. When ordinary water is electrolysed by passing current through it, lighter water molecules decompose more readily than D₂O or HDO molecules. On continuous and prolonged electrolysis the residue gets enriched in heavy water. The decomposition products are burnt and water then formed is transferred to the previous electrolyser.

The electrolytic cell consists of a steel tank which serves as the cathode. A perforated cylindrical sheet of nickel acts as the anode. A large number of such cells are used for electrolysis of water in several stages. The residual water in the last electrolyser is almost pure heavy water.

- 2. Fractional Distillation of Ordinary Water.** Separation of heavy water from ordinary water may be effected by fractional distillation method. This method takes the advantage of the difference in the boiling points of ordinary water (100°C) and heavy water (101.42°C). The lighter fraction (H₂O) distils over first leaving behind a residue richer in heavy water (D₂O).

- 3. Exchange Reactions :** Heavy water can also be prepared by the exchange reaction:



This reaction is catalysed by finely divided nickel.

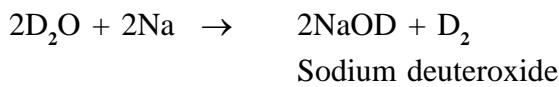
Physical Properties : Heavy water is a colourless, odourless and tasteless mobile liquid. It has slightly higher values of density, melting point and boiling point due to its higher molecular mass as compared to that of ordinary water. D_2O has a lower dielectric constant than ordinary water and hence ionic compounds are less soluble in D_2O than in H_2O .

Table 11.4 Some physical constants of Heavy Water (D_2O) and Ordinary Water (H_2O)

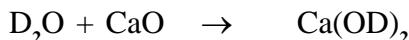
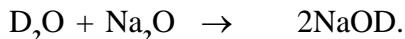
Property	Heavy Water(D_2O)	Ordinary Water (H_2O)
Density at 293 K	1.017	0.998
Melting point	276.8 K	273 K
Boiling point	374.4 K	373 K
Dielectric constant	80.5	82
Refractive index at 293 K	1.3284	1.3329
Viscosity at 293 K(milli poise)	12.6	10.09
Solubility NaCl/100 g at 298 K	30.5	35.9

Chemical Properties : Heavy water behaves like ordinary water in most of its chemical properties. However, heavy water reacts more slowly than ordinary water in chemical reactions.

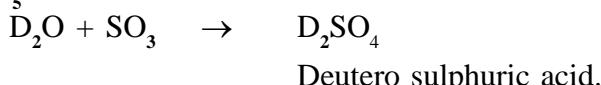
- 1. Action with metals :** D_2O reacts with alkali and alkaline earth metals liberating heavy hydrogen (D_2)



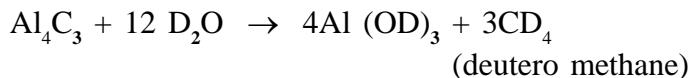
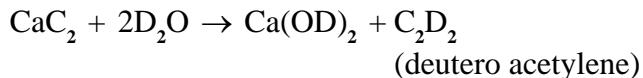
- 2. Action with metallic oxides :** D_2O reacts with basic oxides of metals like Na_2O , CaO etc. to form heavy alkalies.



- 3. Action with nonmetallic oxides :** D_2O reacts with acidic oxides of nonmetals such as SO_3 , P_2O_5 etc. to form deutero acids



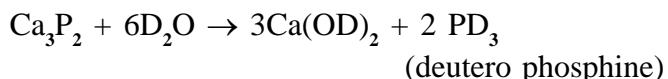
- 4. Action with metallic carbides, nitrides and phosphides :** With carbides deutero hydrocarbons are formed.



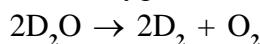
With metallic nitrides D_2O forms deutero ammonia.



D_2O reacts with metallic phosphides forming deutero phosphine.



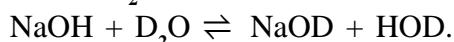
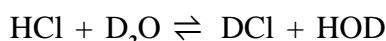
- 5. Electrolysis :** Heavy water containing dissolved P_2O_5 on electrolysis decomposes to deuterium and oxygen which are liberated at cathode and anode respectively.



- 6. Formation of deutero hydrates :** Compounds such as CuSO_4 , Na_2SO_4 , MgSO_4 , etc. when crystallised from heavy water, form crystalline salts with definite number of heavy water molecules called deutero hydrates e.g.



- 7. Exchange reaction :** Compounds containing hydrogen undergo exchange reactions with heavy water.



Summary :

D_2O	Na	NaOD
	Ca	$\text{Ca}(\text{OD})_2$
	Na_2O	NaOD
	CaC_2	$\text{Ca}(\text{OD})_2$
	SO_3	D_2SO_4
	P_2O_5	D_3PO_4
	CaC_2	$\text{Ca}(\text{OD})_2 + \text{C}_2\text{D}_2$
	Al_4C_3	$\text{Al}(\text{OD})_3 + \text{CD}_4$
	Mg_3N_2	$\text{Mg}(\text{OD})_2$
	Ca_3P_2	$\text{Ca}(\text{OD})_2$
	Electrolysis	$\text{D}_2 + \text{O}_2$
	HCl	DCl
	NaOH	NaOD + HOD

Uses of Heavy Water :

Heavy water is used

- (i) As a moderator of neutron in nuclear reactions .
- (ii) As a source for the preparation of D₂.
- (iii) As a tracer compound for studying reaction mechanism in organic chemistry.

11. 8 HYDROGEN PEROXIDE, H₂O₂

Hydrogen peroxide occurs in minute quantities in air and water. It is also present in juices of certain plants. A French chemist, Thenard in 1818 prepared hydrogen peroxide by reacting barium peroxide with dilute hydrochloric acid.

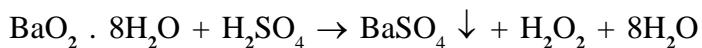
11.8.1 Preparation : Hydrogen peroxide can be prepared in the laboratory by the following methods :

1. **From Sodium peroxide :** Calculated amount of sodium peroxide is reacted with ice - cold 20% solution of sulphuric acid.



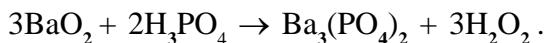
On cooling the resulting solution to 271K, most of sodium sulphate crystallises out as Na₂SO₄, 10H₂O which is removed. A 30% solution of hydrogen peroxide containing a little amount of sodium sulphate is now obtained.

2. **From Barium peroxide :** A thin paste of hydrated barium peroxide, BaO₂. 8H₂O is prepared in ice cold water and then added slowly to an ice-cold solution of 20% sulphuric acid.

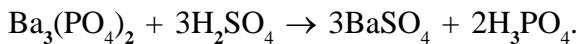


The white precipitate of barium sulphate is removed by filtration. The resulting solution contains 5% solution of hydrogen peroxide. Hydrogen peroxide prepared by this method contains some Ba²⁺ ions which catalyse the decomposition of hydrogen peroxide. Hence, the solution can not be stored for a long time.

Phosphoric acid may be used in place of sulphuric acid.

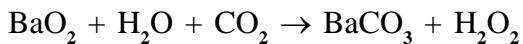


Barium phosphate is then decomposed by dilute sulphuric acid.



Insoluble barium sulphate is removed by filtration and phosphoric acid so formed is used again.

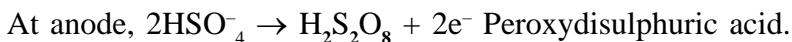
3. **Merck's Process :** Carbon dioxide is passed through a suspension of barium peroxide in ice-cold water when hydrogen peroxide and barium carbonate are formed.



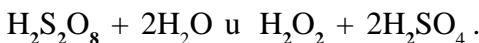
Barium carbonate is filtered and the filtrate is concentrated.

11.8.2 Manufacture of Hydrogen Peroxide :

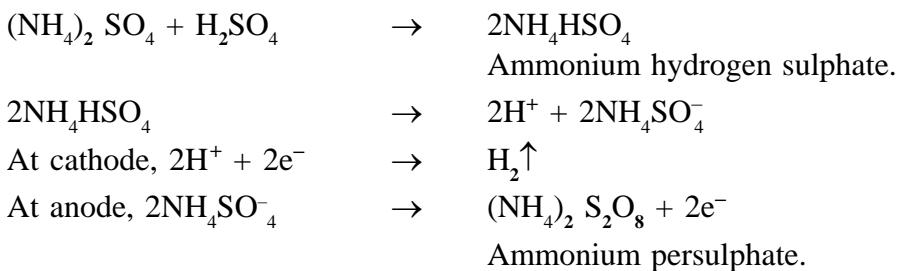
- 1. By electrolysis of 50% H_2SO_4 solution :** Hydrogen peroxide (80 – 90%) is manufactured by electrolysing a cold 50% solution of sulphuric acid in an electrolytic cell using platinum as anode and graphite as cathode. The following reactions occur.



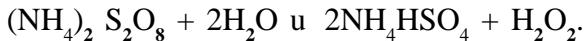
Peroxydisulphuric acid thus formed around anode is then distilled with water under reduced pressure. The low boiling hydrogen peroxide distils over leaving behind high boiling sulphuric acid which is recovered and recycled.



It has also been observed recently that equimolar mixture of sulphuric acid and ammonium sulphate on electrolysis gives a more concentrated solution of hydrogen peroxide as per the following reaction.



Ammonium persulphate thus formed is taken out and distilled with water to get hydrogen peroxide.



- 2. By Auto oxidation of Anthraquinol :** This is the most recent method widely used in America. 2 - Ethyl anthraquinone is dissolved in benzene and hydrogen gas is passed through the solution in presence of palladium catalyst. On passing air through the resulting solution (anthraquinol then formed by reduction), 20% solution of hydrogen peroxide is formed alongwith reproduction of anthraquinone derivative.

11.8.3 Concentration of Hydrogen Peroxide solution :

Hydrogen peroxide obtained by the above process is in the form of dilute solution. Concentration of dilute solution of hydrogen peroxide is undertaken by the following steps.

- i. **Slow evaporation in water bath :** Dilute solution of hydrogen peroxide is taken in an evaporating dish and evaporated carefully on a water bath until the solution contains 30% solution of hydrogen peroxide.
- ii. **Evaporation in vacuum desiccator :** The resulting solution of hydrogen peroxide obtained after the first step, is kept in vacuum desiccator over concentrated sulphuric acid. The water vapour gets absorbed by conc. H_2SO_4 . The residual solution thus obtained contains about 90% solution of hydrogen peroxide.

- iii. **Distillation under reduced pressure :** The above solution is then distilled under reduced pressure (10 – 15mm). Water distils over at 303 – 313 K leaving behind 99% of H_2O_2 solution.
- iv. **Removal of last traces of water :** This is carried out by cooling the solution in a freezing mixture consisting of dry ice (solid carbon dioxide) and ether when crystals of hydrogen peroxide separate out. These crystals are removed, dried and melted to obtain pure hydrogen peroxide.

Precautions taken for storing hydrogen peroxide :

Decomposition of hydrogen peroxide ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$) is catalysed by the presence of heavy metal ion, dust, strong bases, rough surfaces and light. Hence, the following precautions should be taken while storing hydrogen peroxide solution.

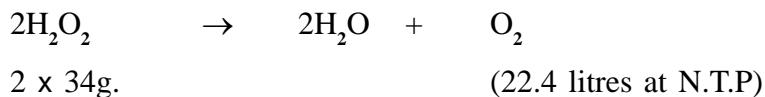
- i. It is to be stored in coloured paraffin wax coated plastic or teflon bottle. Glass bottles are not used since the rough surface of glass, alkali oxides present in it and exposure to light catalyse the decomposition of hydrogen peroxide.
- ii. Some stabilisers such as glycerine, acetanilide, phosphoric acid etc. must be used to check further decomposition of hydrogen peroxide.

Strength of Hydrogen peroxide solution :

The strength of hydrogen peroxide is expressed in terms of weight or volume.

- i. **As weight percentage.** The weight percentage of hydrogen peroxide shows the weight of H_2O_2 in 100 gms of solution. For example, a 15% solution by weight of hydrogen peroxide means 15 grams of hydrogen peroxide are present in 100 gm. of solution.
- ii. **As volume.** Hydrogen peroxide is usually available as solution labelled with a volume strength. (Example, 40 volumes H_2O_2) 40 volumes of H_2O_2 means that one litre of this solution will give 40 litres oxygen at N.T.P.

It is possible to calculate the strength of hydrogen peroxide from its volume strength. A 40 volume solution of hydrogen peroxide means one litre of the solution gives 40 litres of oxygen at N.T.P. Hydrogen peroxide decomposes as :



22.4 litres of oxygen is obtained from 68g of H_2O_2

40 litres of oxygen is obtained from $\frac{68 \times 40}{22.4}$ g of H_2O_2

So, 1 litre of H_2O_2 solution contains $\frac{68 \times 40}{22.4}$ g $\text{H}_2\text{O}_2 = 121.4$ g of H_2O_2 ,

Hence, 1 litre of 40 volume hydrogen peroxide contains 121.4 g of H_2O_2 .

Problem : Calculate the normality of 10 volume of hydrogen peroxide solution.

Solution :

Step 1.

To calculate the strength in g/litre of 10 volume H_2O_2 solution.

10 volume of H_2O_2 means that one litre of the solution liberates 10 litres of O_2 at N.T.P.

H_2O_2 decomposes as : $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 $2 \times 34 = 68\text{g}$ 22.4 litres at N.T.P.

22.4 litre of O_2 is liberated from 68g of H_2O_2 at N.T.P.

10 litres of O_2 is liberated from $\frac{68 \times 10}{22.4} = 30.357\text{g}$ of H_2O_2 at N.T.P

Hence, the strength of 10 volume of H_2O_2 solution = 30.357 g/litre

Step 2.

To calculate the equivalent mass of H_2O_2 .

32 parts by weight of O_2 are obtained from 68 parts by weight of H_2O_2 .

8 parts by weight of O_2 are obtained from $\frac{68 \times 8}{32} = 17$ parts by weight of H_2O_2 .

Equivalent mass of $\text{H}_2\text{O}_2 = 17$

Step 3.

To calculate the normality of 10 volume H_2O_2 solution

$$\text{Normality} = \frac{\text{Gms/litre.}}{\text{Equivalent mass}}$$

$$= \frac{30.357}{17} = 1.79.$$

Hence, the strength of 10 volume H_2O_2 solution = 1.79 N.

Problem : Calculate volume 1.5 N H_2O_2 solution.

Solution :

$$\text{Eq. mass of } \text{H}_2\text{O}_2 = \frac{\text{Molecular mass}}{2} = \frac{34}{2} = 17$$

$$\text{Normality} = \frac{\text{Gms/litre.}}{\text{Eq.mass}}$$

$$\therefore \text{Gms/litre.} = \text{Normality} \times \text{Eq. mass.}$$

$$= 1.5 \times 17 = 25.5$$



68 gms of H_2O_2 liberate 22.4 litres of O_2 at N.T.P.

25.5g of H_2O_2 will liberate $\frac{22.4 \times 25.5}{68} = 8.4$ litre of O_2 at N.T.P.

Hence, the strength of hydrogen peroxide solution is 8.4 volume.

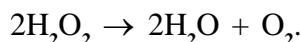
11.8.4 Properties of Hydrogen Peroxide :

Physical properties :

1. Pure hydrogen peroxide is a colourless, syrupy liquid.
2. Its aqueous solution has a bitter taste.
3. It is soluble in water, alcohol and ether in all proportions.
4. Its density is 1.448g/cm^3 at 293 K. The high density is attributed to association of its molecules by intermolecular hydrogen bonds.
5. It produces blister in contact with skin.
6. Its melting point is 272.54 K .

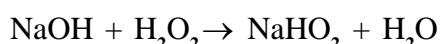
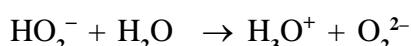
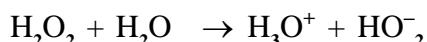
Chemical properties :

1. **Decomposition :** Pure hydrogen peroxide is not very stable and decomposes to oxygen and water on standing or on heating.



The decomposition is accelerated in the presence of heavy metal ions, dust, strong bases, light or even in contact with rough surface.

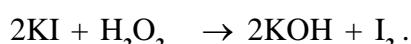
2. **Acidic nature :** Its aqueous solution behaves as weak acid. It forms two types of salts, hydroperoxide (NaO_2H) and normal peroxide (Na_2O_2) with sodium hydroxide.



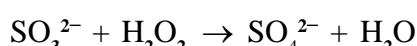
3. **Oxidising property :** Hydrogen peroxide acts as an oxidising agent (electron acceptor) in neutral, acidic and alkaline medium.

- (a) In neutral medium it oxidises iodides to iodine, sulphites to sulphates, sulphides to sulphates, nitrites to nitrates.

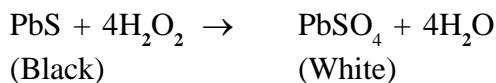
- i. Potassium iodide is oxidised to iodine.



- ii. Sodium sulphite is oxidised to sodium sulphate.

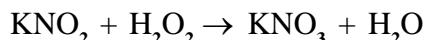
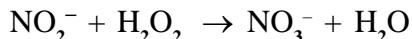


iii. Lead sulphide is oxidised to lead sulphate



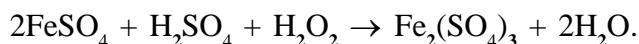
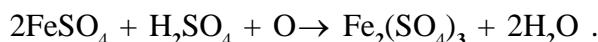
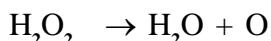
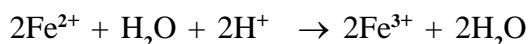
Hydrogen peroxide restores the colour of old oil paintings. In these paintings white basic lead carbonate is used which is turned black by hydrogen sulphide present in air due to the formation of PbS. By treatment with H_2O_2 is changed again to white PbSO_4 .

iv. Potassium nitrite is oxidised to potassium nitrate

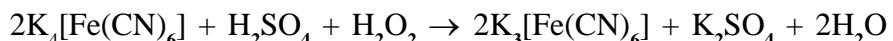
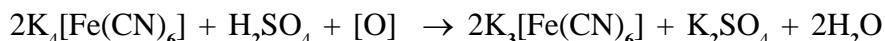
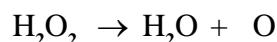


(b) In acidic medium hydrogen peroxide oxidises ferrous salts to ferric salts, ferrocyanide to ferricyanide, and dichromate to chromium pentoxide.

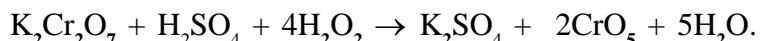
i. Ferrous sulphate in acidic medium is oxidised to ferric sulphate.



ii. Potassium ferrocyanide in acidic medium is oxidised to $\text{K}_3[\text{Fe}(\text{CN})_6]$

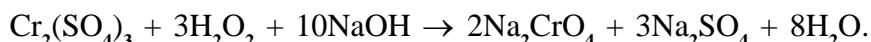


iii. Acidified potassium dichromate is oxidised to blue chromium pentoxide.



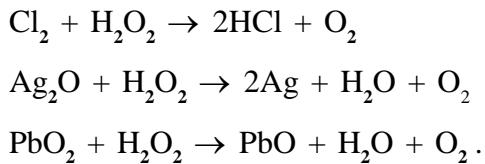
Chromium pentoxide.

(c) In alkaline medium hydrogen peroxide oxidises chromium salts and manganese salts to chromates and manganese dioxide respectively.



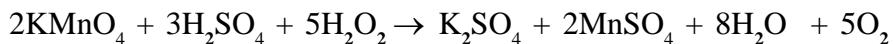
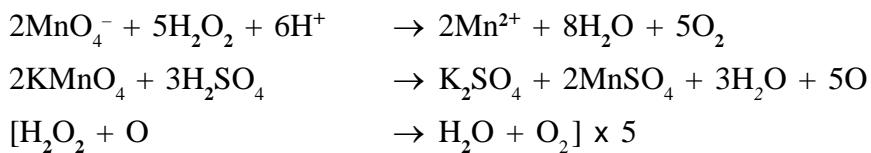
4. **Reducing property.** Hydrogen peroxide also acts as a reducing agent (electron donor) in neutral, acidic and alkaline medium.

- (a) In neutral medium it reduces halogens to halogen acids, silver oxide to metallic silver, lead dioxide to lead monoxide and ozone to oxygen.

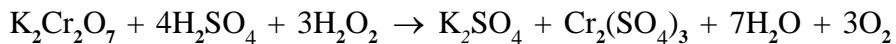
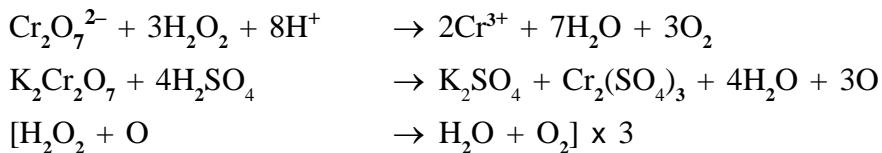


- (b) In acidic medium hydrogen peroxide reduces potassium permanganate solution, potassium dichromate solution and manganese dioxide.

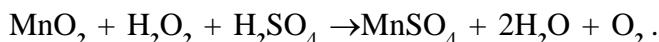
- (i) It reduces pink coloured acidified KMnO_4 solution to colourless manganous sulphate.



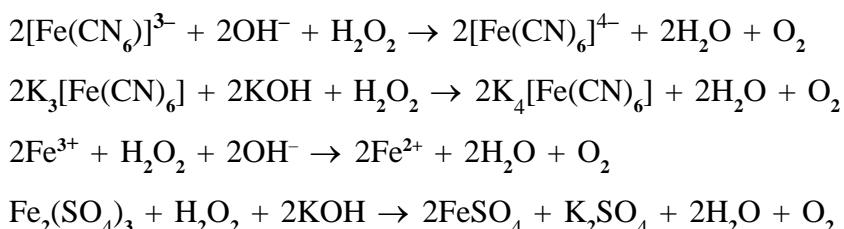
- (ii) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution (orange colour) is reduced to green chromic sulphate.



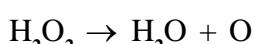
- (iii) In presence of dil. H_2SO_4 , hydrogen peroxide reduces manganese dioxide to manganous sulphate.



- c. In alkaline medium hydrogen peroxide reduces potassium ferricyanide to potassium ferrocyanide and ferric salts to ferrous salts.



5. **Bleaching action.** It acts as a bleaching agent. It bleaches delicate materials such as silk, feather, ivory etc by oxidation.



Colouring matter + O → Colourless matter.

Summary :

Δ	$\text{H}_2\text{O} + \text{O}_2$
NaOH	$\text{H}_3\text{O}^+ + \text{HO}_2^-$
KI	$\text{NaHO}_2^- + \text{H}_2\text{O}$
Na_2SO_3	$\text{KOH} + \text{I}_2$
PbS	Na_2SO_4
KNO_2	PbSO_4
$\text{FeSO}_4 / \text{H}^+$	$\text{KNO}_3 + \text{H}_2\text{O}$
$\text{K}_4(\text{Fe}(\text{CN})_6)$	$\text{Fe}_2(\text{SO}_4)_3$
$\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$	$\text{K}_3[\text{Fe}(\text{CN})_6]$
$\text{Cr}^{3+}/\text{OH}^-$	CrO_5
$\text{Mn}^{2+}/\text{OH}^-$	CrO_4^{2-}
$\text{Fe}^{3+}/\text{OH}^-$	MnO_2
Cl_2	Fe^{2+}
Ag_2O	HCl
$\text{MnO}_4^-/\text{H}^+$	Ag
$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$	Mn^{2+}
$[\text{Fe}(\text{CN})_6]^{3-}/\text{OH}^-$	Cr^{3+}
	$(\text{Fe}(\text{CN})_6)^{4-}$

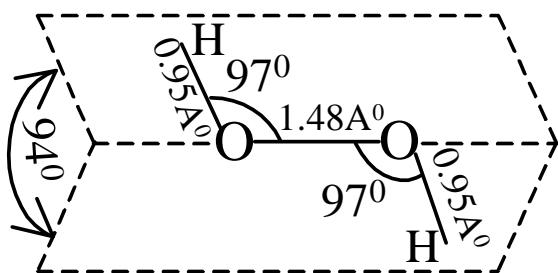
Uses of hydrogen peroxide :

It is used

- As an antiseptic for cleaning wounds, teeth and ears.
- For bleaching hair, silk, wool, ivory etc.
- For restoring the colour of lead paintings.
- In the laboratory for detection of chromium, vanadium and titanium.
- As a fuel in submarines and rockets.

Structure of Hydrogen peroxide.

Hydrogen peroxide molecule has a non-planar and non-linear structure often described as open book structure. The molecule contains a peroxy bond ($O-O$) and the two hydrogen atoms are attached to two different oxygen atoms. The $O-O-H$ remains in one plane and the other hydrogen atom remains in another plane at an angle of 94° as shown below. The $H-O-O$ bond angle is 97° . The $O-O$ bond distance is around 1.48 \AA^0 while that of each $O-H$ bad is 0.95 \AA^0 .



11.9 HYDROGEN AS A FUEL

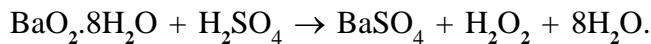
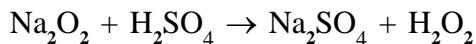
Dihydrogen on combustion produces large quantities of heat (Table 11.5). Also the pollutants released in this case are only the oxides of nitrogen (due to the presence of dinitrogen as impurity with dihydrogen) which can be minimised by injecting a small amount of water into the cylinder. However, cylinder of compressed dihydrogen is about 30 times as heavy as a cylinder containing petrol which is a great disadvantage. Liquid dihydrogen requires expensive insulated tanks made up of alloys like NaNi_5 , $\text{Ti}-\text{TiH}_2$, $\text{Mg}-\text{MgH}_2$ etc. to store it at very low temp like 20K. These limitations have prompted researchers to search for alternative techniques to use dihydrogen efficiently.

Table 11.5 Energy released by combustion of various fuels in moles, mass and volume.

Energy released on combustion in kJ	Dihydrogen (in gaseous state)	Dihydrogen (in liquid)	LPG	CH_4 gas
Per mole	286	285	2220	880
Per gram	143	142	50	53
Per litre	12	9968	25590	35

CHAPTER (11) AT A GLANCE

1. Hydrogen, due to its electronic configuration, resembles both alkali metals of Gr 1 and halogens of Gr 17.
2. There are three isotopes of hydrogen. These are protium (${}_1^1\text{H}^1$), deuterium or heavy hydrogen (${}_1^2\text{H}^2$) and tritium (${}_1^3\text{H}^3$).
3. **Heavy water** - It is deuterium oxide (D_2O). It is used as a moderator in some nuclear reactors.
4. **Isotopic effect** - The difference in properties due to the mass difference in isotopes of an element is known as Isotopic effect.
5. **Nascent hydrogen** - Hydrogen which is just liberated as a result of chemical reaction. It is represented by H.
6. **Ortho and para hydrogen** -These are two **isomers** of hydrogen. In ortho hydrogen the spins of the protons are in the same direction (parallel) whereas in para hydrogen the spins of the protons are in the opposite direction (antiparallel). Orthoform is more stable than paraform.
7. Hydrogen peroxide is a colourless, syrupy liquid, soluble in water, alcohol, ether. It is not very stable, readily decomposes to water and oxygen upon standing or heating. It acts as an oxidising and reducing agent in acidic, alkaline, neutral medium. and also a bleaching agent. The bleaching action is due to **oxidation**.
8. Hydrogen peroxide is prepared in the laboratory by the reaction of sodium or barium peroxide with 20% sulphuric acid.



9. Strength of hydrogen peroxide is expressed in terms of weight or volume.
 - (a) 15% solution of H_2O_2 means 15 gms of H_2O_2 are present in 100 gms of solution.
 - (b) 40 volumes of H_2O_2 means that one litre of this solution will give 40 litres of oxygen at NTP.
10. Hydrogen peroxide molecule has a non-planar and nonlinear structure. O – O bond length is 1.48 \AA^0 and O – H bond length is 0.95 \AA^0 . H – O – O bond angle is 97° and the interplanar angle is 94° .
11. Hydrogen on combustion produces large amount of heat and hence can be used as a fuel.

QUESTIONS

(A) Short answer type (2 marks each)

1. Old paintings of lead are generally washed with dilute solution of hydrogen peroxide in order to regain its colour. Explain.
2. What is the trade name of hydrogen peroxide used as an antiseptic ?

3. Name one compound each in which hydrogen exists in (i) positive oxidation state and (ii) negative oxidation state.
4. Which isotope of hydrogen
 - (i) does not contain neutron (ii) is radio active ?
5. Explain why H_2O_2 cannot be stored for a prolonged period ?
6. Show how can hydrogen peroxide function both as an oxidising and reducing agent.
7. What is the structure of hydrogen peroxide ?
8. Give four uses of hydrogen peroxide.
9. Why is anhydrous barium peroxide not used in the preparation of H_2O_2 ?
10. Distinguish between ortho and para hydrogen.
11. Name the isomers of hydrogen.
12. Name two isotopes of hydrogen.
13. Give the products of electrolysis of H_2O are D_2O
14. Write the formula of heavy water. What is the mass number of heavy hydrogen?
15. What is the oxidation number of oxygen in hydrogen peroxide ?
16. Give examples showing electropositive and electronegative character of hydrogen.
17. How hydrogen peroxide restores the colour of old oil paintings ?
18. Name the isotopes of hydrogen with mass numbers.
19. Name one reaction in which water acts
 - (i) as an oxidising agent and (ii) as a reducing agent.

(B) Long answer type (7 marks each)

1. Discuss the position of hydrogen in the periodic table.
2. Mention one method of preparation of hydrogen peroxide. Show with equations what happens when it reacts with
 - (a) Lead sulphide (b) Ozone (c) Potassium iodide solution.
3. Describe the preparation, properties and uses of heavy water.
4. What are ortho and para hydrogen ? How is para hydrogen isolated ? Explain the term - Isotopic effect.
5. Explain how is dilute silitution of hydrogen peroxide concentrated ? Write chemical equation for reactions of hydrogen peroxide with the following.
 - (i) Chlorine (ii) Acidified ferrous sulphate solution
6. Describe one method of preparation of hydrogen peroxide. What happens when it reacts with (a) Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution (b) FeSO_4 ? Give two of its important uses.

7. Write note on- Heavy water (5 marks)
8. Describe one method of preparation of hydrogen peroxide. Explain with example how it acts both as oxidising and reducing agent. What is meant by '10 volume' of hydrogen peroxide ?

MULTIPLE CHOICE TYPE QUESTIONS

1. In which of the following compounds does hydrogen exhibit a negative oxidation state?
(a) LiH (b) H₂O (c) HCl (d) none of these.
2. The number of neutrons in deuterium is
(a) 2 (b) 3 (c) 1 (d) 0.
3. Which of the following statements is correct ?
(a) Deuterium has two electrons.
(b) Deuterium has two protons.
(c) Deuterium has the same mass as that of hydrogen.
(d) Deuterium has the same atomic number as that of hydrogen.
4. Heavy water is
(a) Water obtained by electrolysis. (b) H₂O (c) D₂O (d) T₂O.
5. The composition of nucleus of deuterium is
(a) One electron and one proton
(b) One proton and one neutron.
(c) One neutron and one electron.
(d) Two protons and one electron.
6. Hydrogen peroxide does not act as :
(a) A reducing agent (b) an oxidising agent (c) a dehydrating agent (d) a bleaching agent.
7. The oxide that gives hydrogen peroxide on treatment with a dilute acid is
(a) PbO₂ (b) NaO₂ (c) MnO₂ (d) TiO₂.
8. Ortho hydrogen differs from para hydrogen in
(a) atomic mass (b) atomic number (c) nuclear spins.
9. Electronic configuration of deuterium atom is
(a) Is¹, (b) 2s² (c) 2s¹ (d) Is²
10. Decomposition of hydrogen peroxide is prevented by
(a) NaOH (b) MnO₂ (c) Glycerol (d) Oxalic acid
11. Which of the following is based as a moderator in nuclear reactors ?
(a) Heavy hydrogen (b) Ozone (c) Heavy water (d) Hydrogen peroxide.
12. The strength of 20 volume of H₂O₂ is per litre or 100 ml ?
(a) 13.6 g / litre (b) 60 g / litre (c) 160 g / litre (d) 20 g / litre.
13. When hydrogen peroxide is oxidised the product formed is
(a) O²⁻ (b) OH⁻ (c) HO₂⁻ (d) O₂.

14. Heavy water is manufactured by
(a) Fractional distillation of water
(b) exhaustive electrolysis of water
(c) Fractional diffusion of steam
(d) fractional crystallisation of ice.
15. Hydrogen peroxide involves
(a) polar bond. (b) Non-polar bond. (c) Semi polar bond (d) hydrogen bond.
16. Metal hydrides are ionic, covalent or molecular in nature. Among LiH, NaH, KH, RbH, CsH, the correct order of increasing ionic character is
(a) LiH > NaH > CsH > KH > RbH
(b) LiH < NaH < KH < RbH < CsH
(c) RbH > CsH > NaH > KH > LiH
(d) NaH > CsH > RbH > LiH > KH
17. The radioactive isotope of hydrogen is :
(a) Protium (b) Deuterium (c) Tritium (d) Hydronium
18. Which of the following ions will cause hardness of water sample ?
(a) Na^+ (b) K^+ (c) Ca^{2+} (d) Li^+
19. Which of the following statements are correct ?
(a) Hydrides of group 13 act as Lewis acids
(b) Hydrides of group 14 act as Lewis acids
(c) Hydrides of group 15 act as Lewis bases.
(d) Hydrides of group 14 act as Lewis bases.
20. Permanent hardness of water is due to the presence of
(a) Chlorides of Ca and Mg in water.
(b) Sulphates of Ca and Mg in water.
(c) Hydrogen carbonates of Ca and Mg in water.
(d) Carbonates of alkali metals in water.

ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS
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- | | | | |
|--------|---------|---------|------------|
| 1. (a) | 6. (c) | 11. (c) | 16. (b) |
| 2. (c) | 7. (a) | 12. (b) | 17. (c) |
| 3. (d) | 8. (c) | 13. (d) | 18. (c) |
| 4. (c) | 9. (a) | 14. (b) | 19. (a, c) |
| 5. (b) | 10. (c) | 15. (c) | 20. (a, b) |



UNIT - X

S-BLOCK ELEMENTS : ALKALI AND ALKALINE-EARTH METALS

CHAPTER - 12

ALKALI METALS

(GROUP – 1)

12.1 INTRODUCTION :

The elements belonging to Group 1 of the periodic table are called Alkali metals. The six elements are- Lithium(Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). These are called alkali metals because they readily dissolve in water to form hydroxides which are strongly alkaline in nature. They also form alkaline oxides. The element Francium (Fr) is radioactive.

Fig 12.1 - Position of the alkali metals in the periodic table.

12.2 ELECTRONIC CONFIGURATIONS

All the alkali metals have one electron in their outermost *s*- orbital preceded by the noble gas (inert gas) configuration. Thus the general configuration of alkali metals may be written as (Noble gas) ns^1 where *n* represents the valence shell. The electronic configurations of alkali metals are given below.

Table – 12.1

Element	Symbol	At. No	Electronic Configuration	Configuration of the outermost shell
Lithium	Li	3	$1s^2, 2s^1$ or [He] $2s^1$	$2s^1$
Sodium	Na	11	$1s^2, 2s^2, 2p^6, 3s^1$ or [Ne] $3s^1$	$3s^1$
Potassium	K	19	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$ or [Ar] $4s^1$	$4s^1$
Rubidium	Rb	37	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$ or [Kr] $5s^1$	$5s^1$
Caesium	Cs	55	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6,$ $4d^{10}, 5s^2, 5p^6, 6s^1$ or [Xe] $6s^1$	$6s^1$
Francium	Fr	87	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10},$ $4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^1, 6p^6, 7s^1$ or [Rn] $7s^1$	$7s^1$

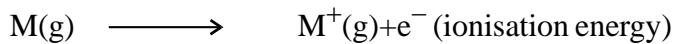
Anomalous behaviour of lithium:

Though lithium belongs to the alkali metal group (Group 1) and has most of the characteristic properties of the metals of group 1, it differs from the remaining members of the group in many respects. This is mainly due to the following reasons:

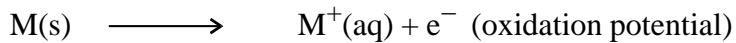
- (i) The size of the lithium atom and its ion is very small.
- (ii) It has high ionisation energy and least electropositive character.
- (iii) The polarising power of Li^+ ion is quite high due to its small size, which result in the covalent character of its compounds.
- (iv) It has no vacant d-orbital in its valence shell.
- (v) It is acting as strongest reducing agent even if it is expected to be the least reducing agent due to its high consisation energy

Reason:- This anomaly can be explained if its hydration energy is to be taken into account.

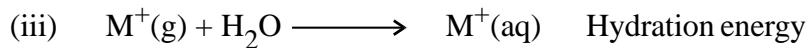
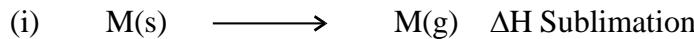
It is known that ionisation is the property of isolated atoms in the gaseous state.



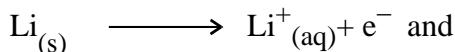
However, oxidation potential is the property when the metal goes into the solution as $M^+(aq)$ ions.



It involves several steps.



The over-all tendency for the charge depends upon the net effect of three steps. Since Li^+ has the smallest size, it gets hydrated to a maximum extent and a large amount of hydration energy is released in the third step which compensates the higher energy needed to remove electron in the second step. The net effect is that it has greater tendency to lose electrons in solution than other alkali metals. Thus, the reaction can be represented as



Therefore, Lithium is the strongest reducing agent due to greater hydration energy.

Diagonal relationship

It has been observed that some elements of second period show similarities with the elements of the third period present diagonally to each others, though belonging to different groups. This is called *diagonal relationship*.

Table 12.2

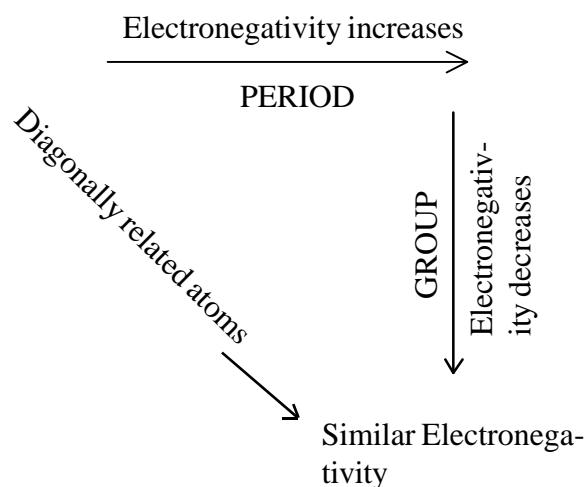
Group- 1	Group- 2	Group – 13	Group- 14
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Second period	Li	Be	B
Third period	Na	Mg	Al

For example, Lithium (Gr. 1) resembles Magnesium (Gr. 2). Similarly, Be with Al and B with Si have resemblances in respect of their physical and chemical properties.

Cause of Diagonal relationship

The cause of diagonal relationship is the similarity in properties such as electronegativity, ionisation energy, size etc. between the diagonal elements. For example, on moving from left to right across a period, the electronegativity increases, while on moving down a group, electronegativity decreases. Therefore, on moving diagonally, the two opposing tendencies almost cancel out and the electronegativity values remain almost same, thus the diagonal pairs have many similar properties.



12.3 GENERAL CHARACTERISTICS OF ALKALI METALS

Physical Characteristics :

The important physical properties of alkali metals are given below.

Table - 12.3
Physical Characteristics of Alkali metals

Property	Li	Na	K	Rb	Cs
Atomic Radius (A°)	1.23	1.57	2.03	2.16	2.35
Ionic radius (A°)	0.68	0.92	1.3	1.48	1.69
Ionization Potential(kJ/mol)	520	496	418	403	374
Electronegativity	1.00	0.9	0.8	0.8	0.7
Density(g/cm^3)	0.53	0.97	0.86	1.53	1.09
Melting Point(K)	453	371	336.5	312	301.5
Boiling Point(K)	1609	1156	1032	973	943
Abundance in Earth's Crust(ppm)	65	28300	25904	300	7

The properties of francium have not been listed in the above table, as it is a recently discovered element. A very little is known about this radioactive element.

1. Atomic and Ionic Radii

Alkali metals have the largest atomic and ionic radii in their respective periods. On moving down the group the atomic and ionic radii increase.

Explanation : The alkali metals are the first elements of each period. As we move in a period, the atomic radius and ionic radius tend to decrease due to increase in the effective nuclear charge. Therefore, the alkali metals have the largest atomic and ionic radii in their respective periods. On moving down the group there is increase in the number of shells and therefore atomic and ionic radii increase.

2. Ionisation Energies

- (i) Alkali metals have the lowest ionization energy in each period. Within the group, the ionization energies of alkali metals decrease down the group.

Explanation : The atoms of alkali metals are largest in their respective periods and therefore the valence electrons, are loosely held by the nucleus. By losing the valence electrons, they acquire stable noble gas configurations. This accounts for their ease to lose electrons and hence they have low ionization energies. On moving down the group, the atomic size increases and the magnitude of screening effect (number of inner shells) also increases and consequently, the ionization energy decreases down the group.

- (ii) The second ionization energies of alkali metals are very high.

Explanation : When an electron is removed from the atoms of alkali metals, they form monovalent cations which have very stable electronic configuration (same as that of noble gases). Therefore, it becomes very difficult to remove the second electron from the stable noble gas configurations and hence their second ionisation energy values (IE_2) are very high.

3. Melting and Boiling Points

All these metals are soft and have low melting and boiling points.

Explanation : The alkali metals have only one valence electron per metal atom and therefore the energy binding the atoms in the crystal lattice of the metal is low. Thus, the metallic bonds in these metals are very strong and consequently their melting and boiling points decrease on moving down from Li to Cs.

4. Density

The densities of alkali metals are quite low as compared to other metals. Li, Na and K are even lighter than water. The densities increase on moving down the group. However, K is lighter than Na.

Explanation : The densities of metallic elements depend upon the type of packing of atoms in metallic state and also on their size. The alkali metals have close packing of metal atoms in their lattice .Because of the large size of their atoms, they have low densities. As we move down the group from Li to Cs, there is increase in atomic size as well as atomic mass. But the increase in atomic mass is more to compensate the increase in atomic size. As a result, the densities (mass/volume) of alkali metals gradually increase from Li to Cs. However, potassium is lighter than sodium probably due to increase in atomic size of potassium.

5. Electropositive or Metallic character

All the alkali metals are strongly electropositive or metallic in character.

Explanation: The electropositive character of an element is expressed in terms of the tendency of its atom to release electrons:



As alkali metals have low ionisation energies, their atoms readily lose their valence electron. These elements are, therefore, said to have strong electropositive or metallic character. Since the ionisation energies decrease down the family, the electron releasing tendency or electropositive character is expected to increase down the family.

6. Oxidation states

All the alkali metals exhibit an oxidation state of +1 in their compounds.

Explanation: The alkali metals have only one electron in their valence shell and therefore they can lose the single valence electron readily to acquire the stable configuration of a noble gas. Thus, they form monovalent ions, M^+ (e.g., Li^+ , Na^+ , K^+ , Rb^+ , Cs^+). Since the second ionization energies are very high, they cannot form divalent ions. Thus alkali metals are univalent and form ionic compounds.

7. Characteristic Flame colouration

All the alkali metals and their salts impart characteristic flame colouration

Explanation: The alkali metals have very low ionization energies. The energy from the flame of bunsen burner is sufficient to excite the electrons of alkali metals to higher energy levels. The excited state is quite unstable and therefore when these excited electrons come back to their original energy levels, they emit extra energy, which fall in the visible region of the electromagnetic spectrum and thus appear coloured.

The following colours are given by alkali metals:

Li	Na	K	Rb	Cs
Crimson red	Yellow	Pale violet	Violet	Bluish

The different colours of the alkali metals can be explained on the basis of amount of energy absorbed for excitation of the valence electron.

8. Photoelectric effect

The alkali metals emit electrons when radiation strikes on their surfaces. This phenomenon of emission of electrons when electromagnetic radiation strikes against them is called *photoelectric effect*. Therefore, alkali metals exhibit photoelectric effect.

Explanation: Alkali metals have low ionization energies and therefore the electrons are easily ejected when exposed to light. Among alkali metals, caesium has lowest ionization energy and hence it can show photoelectric effect to the maximum extent.

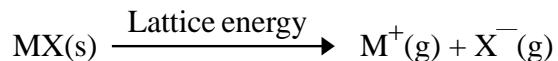
9. Nature of the compounds

The compounds of the alkali metals are ionic in nature.

Explanation: Due to the low ionization energies and large atomic sizes the atoms of alkali metals form cations readily by losing the valence electrons. Consequently, they form ionic bonds with the non-metals of the p-block.

10. Lattice energies

The alkali metal salts consist of cations and anions which are held together by strong electrostatic force of attraction. Therefore, the lattice energies of alkali metal salts are very high. The lattice energy is defined as the amount of energy required to break one mole of a crystal into its free ions



Therefore lattice energy gives a measure of the forces of attraction between the ions. Larger the forces of attraction, the greater will be lattice energy. The lattice energy also depends upon the size of the ion and its charge. For the cation of same valency the lattice energy of ionic solids having the same anion decreases with increase in size of the cation due to decrease in force of attraction between them as shown below.

Table - 12.4

Salt	Lattice energy (kJ mol ⁻¹)	Salt	Lattice energy (kJ mol ⁻¹)
LiCl	802.6	NaF	894.5
NaCl	758.7	NaCl	758.7
KCl	681.4	NaBr	714.8
RbCl	660.6	NaI	668.8
CsCl	618.7		

↓ ↓ ↓ ↓

12.4 **CHEMICAL CHARACTERISTICS :**

The alkali metals exhibit high chemical reactivity. This is due to

- (i) their low ionisation energies.
- (ii) low heat of atomisation

As the value of ionisation energy decreases down the group from Li to Cs, the reactivity of alkali metals increases from Li to Cs.

The alkali metals are highly reactive towards the more electronegative elements such as oxygen and halogens. Some of their characteristic chemical properties are given below.

1. Action with air.

All the alkali metals get tarnished on exposure to air due to the formation of oxides on the surface. They burn vigorously in air or oxygen forming oxides. Lithium forms monoxide (Li_2O), sodium forms peroxide(Na_2O_2), the other elements form superoxides(MO_2 :M = K, Rb, Cs).

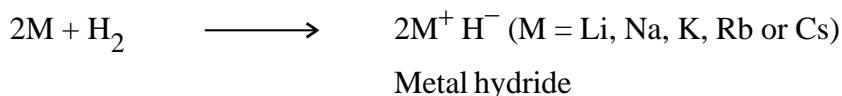


Explanation: The formation and stability of these oxides can be explained on the basis of the fact that a small cation can stabilise a small anion and a large cation can stabilise a large anion. The size of Li^+ ion is very small and it has a strong positive field around it. It can, therefore, combine with only small anion, O^{2-} ion. This results in the formation of monoxide (Li_2O). On the other hand, Na^+ ion is larger cation and has a weak positive field around it.

Therefore, Na^+ ion can stabilize a bigger peroxide ion, O_2^{2-} or $[\text{-O}-\text{O}-]^{2-}$ which has also weak negative field around it. Similarly, the other ions K^+ , Rb^+ , Cs^+ are still larger and have very weak positive field and can therefore, stabilise a bigger superoxide, O_2^- anion and form superoxides.

2. Action with hydrogen

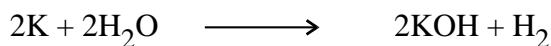
The alkali metals react with hydrogen to form hydrides which are ionic in nature ($M^+ H^-$).



- i) The reactivity of alkali metals with hydrogen increases from Li to Cs.
- ii) The ionic character of the hydrides increases from Li to Cs. This is because of decrease in ionization energy down the group so that electrons become easily available to hydrogen for forming H^- ion.
- iii) The stability of hydrides decreases from Li to Cs. This is due to the fact that as the size of alkali metal increases from Li to Cs, the $M - H$ bond becomes weak. Therefore, the stability of hydrides decreases.
- iv) The hydrides behave as strong reducing agents and their reducing nature increases down the group.

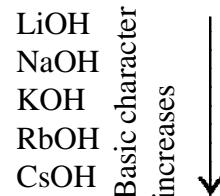
3. Action with water

Alkali metals readily react with water to form hydroxides and hydrogen gas.



Lithium reacts somewhat slowly. But sodium and the other members of the family react so rapidly with water that the hydrogen gas evolved immediately catches fire. Thus alkali metals cannot be kept either in air or in water. They are normally kept in kerosene oil.

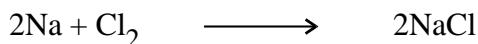
The hydroxides of alkali metals are strongly basic and the strength of the base increases down the group.



Explanation: The $M-OH$ bond in the hydroxides of alkali metals is very weak and it can easily ionize to M^+ and OH^- ions. This accounts for their basic character. Since the ionization energy decreases down the group, the bond between metal and oxygen becomes weak. Therefore, the base strength of the hydroxides increases accordingly. Thus, $NaOH$ is a stronger base than $LiOH$ and so on.

4. Action with Halogens

The alkali metals readily combine with halogens to form ionic halides M^+X^- . e.g.



The reactivity of halogen towards alkali metals increases on moving down the group. This is due to the decrease in ionisation energy or increase in the electropositive character as we move down the group.

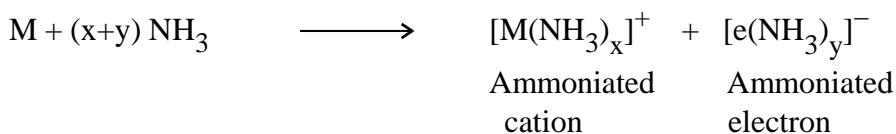
All the metal halides are ionic crystals. However, LiI is slightly covalent because of the polarisation (Li being the smallest cation has maximum polarizing power and iodide ion being largest anion can be polarised to the maximum extent).

All the alkali metal halides except LiF are soluble in water. However LiF is insoluble in water due to its high lattice energy because of small cation and small anion.

5. Solution in liquid Ammonia.

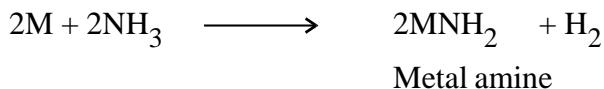
Alkali metals dissolve in liquid ammonia to give blue solutions which are conducting in nature.

Explanation: In solution the alkali metal atom readily loses the valence electron. Both the cation and the electron combine with ammonia to form ammoniated cation and ammoniated electron.



The ammoniated electron is responsible for the blue colour of the solution. Both ammoniated cation and electron make the solution conducting in nature.

On standing, the solution slowly liberates hydrogen as:



6. Hydration of Ions

The alkali metal ions are highly hydrated. The smaller the size of the ion the greater is the degree of hydration. Thus, Li^+ ion gets much more hydrated than Na^+ ion which is more hydrated than K^+ ion and so on. Therefore, the extent of hydration decreases from Li^+ to Cs^+ . As a result of larger hydration of Li^+ ions than Na^+ ion, the effective size of Li^+ ions is more than that of Na^+ ion and their ionic radii in water (called hydrated ionic radii) decrease in the order:



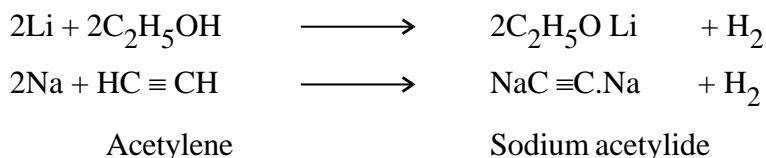
Table - 12.5

Ion	Li⁺	Na⁺	K⁺	Rb⁺	Cs⁺
Ionic radius (PM)	76	102	138	152	167
Hydrated radius(PM)	340	276	232	228	226
Ionic mobility ($\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	33.5	43.5	64.5	67.5	68.0

As a result, the hydrated Li⁺ ion being largest ion in size has the lowest mobility in water. On the other hand the hydrated Cs⁺ ion being smallest ion in size has the highest mobility in water.

7. Reducing nature

Alkali metals are strong reducing agents. This is due to their greater ease to lose electrons. This is also indicated by the larger negative values of their reduction potentials . All of them are better reducing agents than hydrogen ($E^\ominus = \text{Zero}$). Therefore, these metals react with compounds containing acidic hydrogen atoms such as alcohols and acetylene liberating hydrogen.



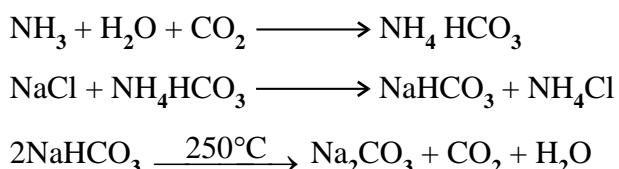
12.5 **PREPARATION AND PROPERTIES OF SOME IMPORTANT COMPOUNDS :**

1. SODIUM CARBONATE (Na₂CO₃. 1OH₂O)

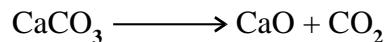
Sodium carbonate finds a lot of commercial use and is manufactured by Solvay process.

Preparation by Solvay ammonia soda process :

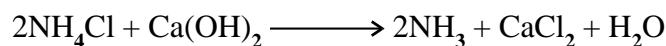
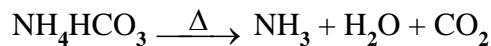
In this process, raw materials like common salt, ammonia and lime stone are used. It involves the reaction of sodium chloride and ammonium hydrogen carbonate to form sparingly soluble sodium hydrogen carbonate, where the latter decomposes on heating to yield sodium carbonate. The equations for Solvay process are



Carbon dioxide used in the carbonating tower is produced by heating lime stone.



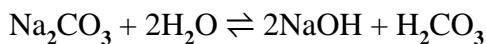
This process involves recovery of ammonia, when the filtrate from the vacuum filter containing ammonium chloride and ammonium bicarbonate are treated as follows:



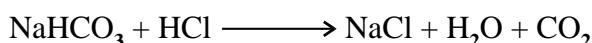
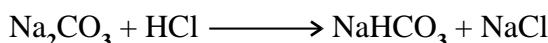
Ammonia, thus recovered, is reused in the process.

Properties :

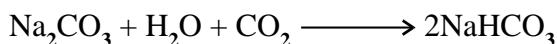
- Physical :**
- (i) Sodium carbonate is a white crystalline solid, which mostly exists as decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (washing soda)
 - (ii) The decahydrate loses its water of crystallisation on heating to form monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, which on heating changes to anhydrous form, a white powder called soda ash (M.P.852°C)
 - (iii) Na_2CO_3 dissolves fairly in water, forming an alkaline solution due to hydrolysis.



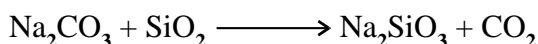
- Chemical :** (i) **Action of acids :** Acids react with evolution of CO_2



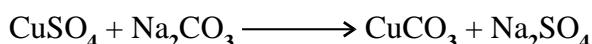
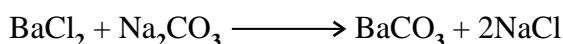
- (ii) **Action of CO_2 :** By passing CO_2 to a concentrated solution of Na_2CO_3 , Sodium hydrogen carbonate is precipitated.



- (iii) **Action of Silica :** On heating sodium carbonate with silica strongly sodium silicate, also called as water glass or soluble glass is produced.



- (iv) **Formation of metal carbonates :** Metal salts, when treated with Na_2CO_3 , form insoluble carbonates.



Uses :

- (i) It is used in softening of water and cleaning, as washing soda.
- (ii) It is used in the manufacture of glass, borax, paper and soap.
- (iii) It is used as an important laboratory reagent both in qualitative and quantitative analysis.

2. SODIUM CHLORIDE (NaCl) (Common salt)

Sodium chloride is the most common of the salts of sodium. It is widely distributed in nature. Sea water contains about 2.95% of NaCl. In the Dead sea it is found up to 9.2 percent. As rock salt it is found in England, Australia, Germany, Canada, Pakistan and in Himachal Pradesh in India.

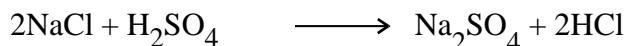
Preparation.

- 1) **From seawater:** In India and also in other tropical countries where sea water runs deep into the coast line is evaporated in tanks. The solid crust so left after evaporation is collected. The heaps of crystals of sodium chloride are given a fine spray of water which dissolves magnesium chloride. The remaining product contains about 98% of NaCl and the rest is MgCl₂, CaCl₂ etc. In very cold countries the brine is concentrated by freezing out water. The concentrated solution is then evaporated in big iron pans.

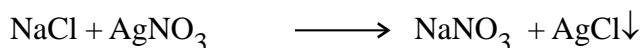
Purification: It is purified by passing hydrogen chloride through a saturated solution of the commercial common salt. Sodium chloride precipitates due to common ion effect. Only KCl is present as an impurity which is removed by repeated crystallisation.

Properties:

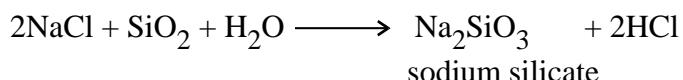
1. Sodium chloride is a white crystalline substance which is slightly hygroscopic
2. It dissolves in water with the absorption of heat. The solubility changes slightly with the change in temperature.
3. It melts at 800°C.
4. **Action of sulphuric acid-** It gives hydrogen chloride with hot concentrated H₂SO₄.



5. **Action of silver nitrate –** It gives a white precipitate with silver nitrate.



6. **Action on sand (SiO₂) –** When fused with sand in presence of moisture it gives sodium silicate. This reaction is used in salt glazing

**Uses;** it is used

- 1) As a preservative for food articles like fish, meat etc.
- 2) For the manufacture of sodium metal, caustic soda, washing soda etc.

- 3) For the salting out of soap.
- 4) In freezing mixtures.
- 5) For glazing pottery.
- 6) It is an essential constituent of food.

3. SODIUM HYDROXIDE (CAUSTIC SODA) (NaOH):

Sodium hydroxide is manufactured by the electrolysis of sodium chloride solution (brine) in a specially designed cell called Castner – Kellner cell (Fig. 12.6).

Castner – Kellner or Mercury Cathode Process.

The apparatus consists of a large rectangular iron vessel divided into three compartments by state partitions dipping into a layer of mercury which runs along the floor and is brought into circulation with the help of an eccentric wheel. The two outer compartments are filled with brine and are fitted with stout graphite electrodes which form the anodes. The middle compartment is filled with water and a little NaOH and is fitted with a bunch of iron rods serving as the cathode. By induction, mercury acts as cathode in the outer compartments and as anode in the middle compartment.

On passing electric current chlorine is liberated at the anodes in the outer compartments and escapes through the outlets. The sodium liberated dissolves in the flowing mercury forming sodium amalgam, reacts with water, forming a solution of NaOH and hydrogen escapes through an outlet above and the solution of caustic soda, the concentration of which is not allowed to exceed 20%, is taken out from time to time.

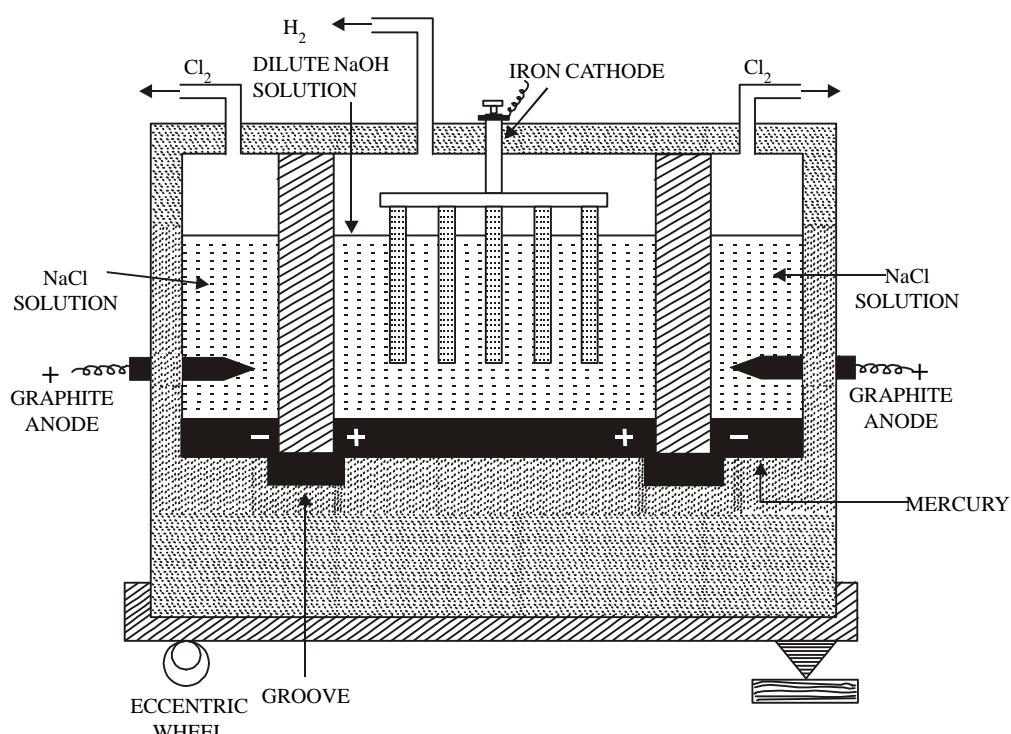
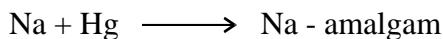
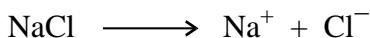


Fig. 12.6 Castner-Kellner process for the manufacture of caustic soda.

Reactions:

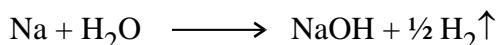
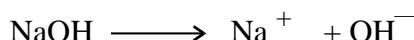
Outer compartments: In these compartments mercury layer acts as cathode by induction.



Sodium dissolves in mercury to form sodium amalgam, which due to rocking motion of the cell travels to the central compartment.

**Central compartment:**

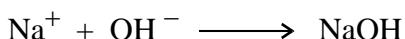
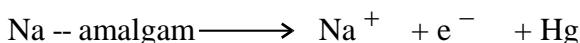
In this compartment sodium amalgam acts as anode by induction.



So at cathode hydrogen gas is liberated and sodium hydroxide is formed.

At the mercury anode:

At sodium amalgam anode, sodium undergoes oxidation and passes into solution as Na^+ ions.



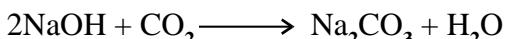
With the progress of electrolysis, concentration of NaOH in the central compartment continues to increase. When it reaches 20%, the solution is withdrawn, evaporated to dryness so that fused sodium hydroxide, is obtained. This is then cast into sticks or pellets.

Properties of NaOH :

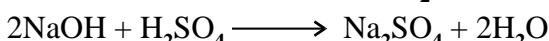
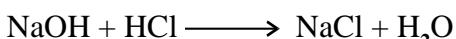
Physical properties : It is a white crystalline solid having bitter taste. It is soluble in water and is corrosive in nature. Its density is 2.13 g/ml and melting points is 318°.

Chemical properties :

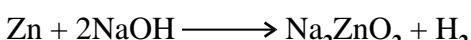
- It reacts with atmospheric carbon dioxide to form sodium carbonate



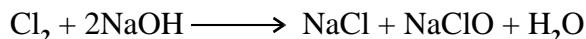
- As a strong alkali, it reacts with acids to form salts



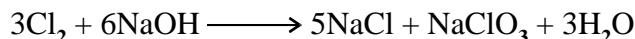
- Action on metals :** It reacts with metals like Zn, Al etc. to liberate hydrogen.



4. **Action on non-metals :** With cold and dil. NaOH, halides and hypohalites are formed, when treated with halogens.



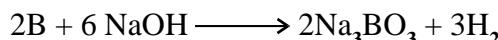
With hot and conc. NaOH solution, halogens form halates and halides



When NaOH is heated with sulphur, sodium thiosulphate is formed.

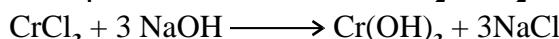
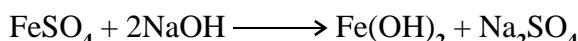


With boron, hydrogen is evolved.

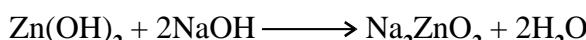


Action on Salts :

When treated with metallic salts, NaOH forms the corresponding hydroxides.



Green ppt



Sodium Zincate

Uses:

Causic soda is extensively used

1. In the manufacture of sodium in many industries such as: hard soap, paper and viscose rayon (artificial silk)
2. In the manufacture of many dye – stuffs.
3. In the petroleum industry for the bleaching and refining of oils.
4. In the manufacture of hypochlorites, chlorates and nitrates.

4. SODIUM HYDROGEN CARBONATE (BAKING SODA) (NaHCO_3) :

It is called as baking soda for its use in the preparation of cakes and pastries, because of its property to evolve CO_2 on heating.

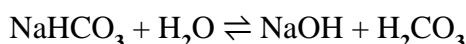
Preparation : It is prepared by passing CO_2 through the saturated solution of sodium carbonate.



Properties :

Physical : It is a white crystalline solid, sparingly soluble in water.

Chemical : (i) On hydrolysis, it forms an alkaline solution.



(ii) On heating, it forms sodium carbonate with evolution of CO_2



(iii) It reacts with metal salts to form normal carbonates



Uses : Sodium hydrogen carbonate is used :

- (i) in fire extinguishers
- (ii) for making Baking powder
- (iii) as a medicine, as mild antiseptic for skin infections and to neutralise acidity in the stomach.
- (iv) in making effervescent drinks.

12.6 ANALYTICAL TESTS FOR SODIUM

(a) Flame Test:

A thin paste of sodium salt with conc. Hydrochloric acid imparts persistent golden yellow colour to the flame. Golden yellow colour will not be visible when seen through double blue glass.

(b) (i) Action with Magnesium uranyl acetate solution:

To a little sodium salt solution, 2 ml of magnesium uranyl acetate solution is added; a yellow crystalline ppt. of sodium magnesium uranyl acetate results.

(ii) Action with Potassium pyroantimonate solution:

To a little sodium salt solution, 2ml of potassium pyroantimonate solution is added; a white ppt of sodium pyroantimonate results.

12.7 BIOLOGICAL IMPORTANCE OF SODIUM AND POTASSIUM :

An individual, averagely healthy and with normal dietary habit, seldom suffers from deficiency of sodium or potassium. Sodium and potassium occur in plants and animals as the salts (chlorides, phosphates and carbonates) of inorganic acids and salts of proteins and organic acids. Sodium ions are found outside the cells, as extracellular cations, while potassium ions are abundantly present in the cell fluids as main intracellular cations. Generally, sodium and potassium are almost totally absorbed from the gastrointestinal tracts.

Functions :

The metabolism of sodium and potassium are related to some fundamental physiological mechanism, as described below :

1. **Maintaining osmotic pressure :** Sodium and potassium function to maintain the normal osmotic pressure of the different body fluids and thus protect the body against excessive loss of fluids.
2. **Maintaining proper viscosity of blood :** Sodium and potassium chlorides present in the blood plasma help in keeping the globulins in physical solution and in regulating the degree of hydration of the plasma proteins, which is very vital in maintaining proper viscosity of blood.
3. **Secretion of digestive fluids :** Gastric HCl is derived from NaCl present in the blood, while the base in pancreatic juice and bile is derived from blood sodium and potassium salts.

Although quite similar in their chemical properties, sodium and potassium differ quantitatively in their ability to activate enzymes, in their transport mechanism and in penetrating cell membranes.

CHAPTER (12) AT A GLANCE

- | | |
|----------------------------|---|
| 1. Baking powder | - The chemical is sodium bicarbonate (NaHCO_3) |
| 2. Borax | - The chemical composition is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ |
| 3. Carnallite | - It is an ore of potassium and magnesium and its composition is $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |
| 4. Chile salt petre | - The chemical is NaNO_3 (sodium nitrate) |
| 5. Caustic soda | - The chemical is sodium hydroxide (NaOH) |
| 6. Caustic potash | - The chemical is potassium hydroxide (KOH) |
| 7. Nitre | - The chemical is potassium nitrate (KNO_3) |
| 8. Sylvinit | - Its chemical composition is $\text{NaCl} \cdot \text{KCl}$ |
| 9. Common salt | - Its chemical composition is sodium chloride (NaCl) |
| 10. Potash alum | - Its chemical composition is $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ |

QUESTIONS

Very short answer type. (1 mark each)

1. Give the electronic configuration of potassium atom.
2. Give one use of potassium chlorate.
3. (a) Write the formula of Borax.
(b) What is the composition of carnallite?
4. What happens when CO_2 gas is passed through aqueous solution of sodium carbonate?
5. Between Lithium and Sodium which is more electropositive ?
6. What is Borax? Give one use of borax.
7. Oxide of an alkali metal is – (amphoteric, basic, acidic) Hint. basic.
8. The element in which the outer most electron is held most loosely is ..(Li, Na, K, Rb)
9. Soda lime is a mixture of —— and ——.
10. Why alkali metals do not form M^{2+} ion?
11. Write the electronic configuration of Sodium.
12. Sodium metal is stored under
13. Why are alkali metals soft ?
14. Sodium nitrate on heating gives ——— gas.
15. Why sodium is less electropositive than potassium ?

16. In sodium chloride —
Sodium ion is smaller than the sodium atom
Sodium ion is larger than sodium atom
Sodium ion is larger than the chloride ion
Sodium ion and chloride ion have the same size.
17. Using *s,p,d,f* notations, write the electronic configuration of K.
18. Which one of the following is an ore of potassium ?
(Cryolite, Carnallite, Bauxite, Dolomite)
19. _____ is manufactured by Solvay process
20. Why alkali metals are used as reducing agents ?
21. What product is obtained at the anode during electrolysis of fused sodium hydride ?
22. Give one use of potassium chlorate.
23. Which is the most electropositive element among the Group IA elements ?
24. Aqueous solution of sodium bicarbonate is——
(a) acidic (b) strongly acidic (c) alkaline (d) neutral.
25. Name the elements in the group I-A of the periodic table.
26. What is the composition of carnallite?
27. Between sodium and potassium which is more electropositive?
28. Why alkali metals have low densities?
29. What is the chemical formula of washing soda?
30. Write the chemical formula of Glauber's salt.
31. Write the electronic configuration of sodium atom.

Short answer type. (2 mark each)

1. Why is the size of sodium ion less than that of potassium ion?
2. Give the principle of extraction of sodium by electrolytic method.
3. Give the principle of preparation of sodium hydroxide by Solvay's process.
4. How is Glauber's salt prepared?
5. Why is solid NaCl a bad conductor of electricity?
6. What are the products of electrolysis when an aqueous solution of sodium chloride is electrolysed?

7. What happens when NaOH is added to $\text{Al}_2(\text{SO}_4)_3$ solution drop by drop and finally in excess. Give balanced equations only.
- Hints: $\text{Al}_2(\text{SO}_4)_3 + 6\text{NaOH} \longrightarrow 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4$
 $\text{Al(OH)}_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O}$
8. In the extraction of sodium by electrolytic method, fused sodium chloride is used instead of aqueous solution of sodium chloride. What is the reason?
9. What happens when sodium bromide is heated with hot conc. H_2SO_4 ?
10. Give two uses of potassium chlorate.
11. What happens to the pH of the sodium chloride solution on electrolysis?
12. (a) Give the formula of borax (b) Give one use of potassium chlorate
(c) Give electronic configuration of potassium.
13. What happens when sodium metal is heated with ammonia gas?
Hint : - $2\text{Na} + 2\text{NH}_3 \longrightarrow 2\text{NaNH}_2 + \text{H}_2$
14. What happens when the lime water is added to sodium carbonate solution ?
Hint : - $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaOH} + \text{CaCO}_3$
15. The alkali metals are good reducing agents. How do you explain it?
16. Account for the fact that sodium metal cannot be obtained by the electrolysis of aqueous sodium chloride solution.
17. How will you obtain the following compounds from sodium chloride ?
(a) Sodium metal (b) NaOH
18. Give the uses of ach of the following.
19. How do the following properties of alkali metals vary with rise in atomic number ?
(a) Ionisation energy (b) Electropositive character.

Short answer type. (3 mark each)

1. How does metallic sodium react with
(i) Ammonia and (ii) Methyl alcohol
2. In the extraction of sodium by electrolytic method, fused sodium chloride is used instead of aqueous solution of sodium chloride. What is the reason?
3. Give the principle of preparation of sodium hydroxide by Solvay's process.
4. What happens when sodium is heated with ammonia ?
5. Give the principle of manufacture of sodium hydroxide.
6. Give the principle of extraction of sodium by electrolytic method.
7. What happens when sodium metal is exposed to moist air?
8. What happens when sodium reacts with water?
9. Name 4 elements of Group 1.

10. How Glauber salt is prepared?
11. Write one method of preparation and uses of potassium nitrate.
12. Write with equation what happens when sodium is heated with carbon dioxide gas.
13. Give the principle of manufacture of sodium carbonate.
14. “On exposure to air solid NaOH becomes a liquid and after sometime it changes to a white powder”.. Explain why it happens.
15. Give two uses of potassium cyanide.
16. Give the principle of manufacture of sodium hydroxide.
17. What happens when sodium is heated with ammonia? Give equation.
18. Give the principle of manufacture of sodium hydroxide & give one of its uses.
19. Write the chemical formula for the Chile salt petre & brown ring produced during test for Nitrate.
20. What happens when sodium reacts with water. Give equation.

Long answer type (7 marks each)

1. Name the element of Group 1 in the periodic table. Write one ore of each of Na, K, Li and also write their electronic configuration.
2. Write the principles by which sodium is extracted by electrolytic method. Mention any three properties and two uses of sodium metal.
3. Give an account of properties and uses of alkali metal.
4. What are alkali metals? Suggest a method for extraction of sodium from one of its compounds?
5. Give the principle of manufacturing sodium carbonate and sodium chlorate. Give the uses of potassium chlorate.
6. Explain why the alkali metals have low densities, are electrically conducting, good reducing agents, form monovalent ions, soluble salts and soluble hydroxides, which become stronger alkalis on descending the group.
7. Why are potassium and caesium, rather than lithium, used in photoelectric cells?
8. List some important ores of sodium ?
9. Write the preparation and uses of potassium chlorate.
10. Describe two methods for the preparation of potassium cyanide. What are its uses ?
11. Explain the following :
 - (i) Sodium metal cannot be obtained by the electrolysis of aqueous sodium chloride solution.
 - (ii) The ionization energy decreases from lithium to caesium.
 - (iii) Alkali metals are difficult to reduce.
 - (iv) The elements of Group IA are called alkali metals.

12. How is sodium isolated by Down's process ?

Sketch a diagram for the Down's cell and label the electrodes, electrolyte and the direction of flow of electrons and ions.

Write the equations for the reactions involved in the process.

13. (a) Discuss in detail the manufacture of sodium carbonate by Solvay process. What is the other important product formed in this process ? State the principle involved in the process.

(b) Why can potassium carbonate not be prepared by Solvay's process ?

14. (a) Explain any two of the following :

(i) Which is the most reactive metal of alkali metals and why ?

(ii) Sodium cannot be extracted by the electrolysis of aqueous solution of sodium chloride.

(iii) Alkali metals have low densities.

(iv) Alkali metals are strong reducing agents.

(b) Describe the Solvay process for the manufacture of washing soda. Give its two important uses.

15. (i) Write equations for the reactions involved in making sodium bicarbonate from sodium chloride.

(ii) For any two of the following state one large scale use of :

(a) Sodium metal (b) NaOH.

16. Describe the manufacture of sodium carbonate by the solvay process.

17. Discuss Solvay process.

18. (a) Sodium metal cannot be obtained by the electrolysis of an aqueous solution of sodium chloride. Why ?

(b) How is sodium hydroxide manufactured from Castner Kellner's process ?

Write the equations for the reactions which occur at each electrode ?

19. Comment on the following :

(i) Caesium is the most reactive among the alkali metals.

(ii) Alkali metals impart characteristic colours to the flame.

20. (a) Giving chemical equation state what happens when ammonia reacts on a mixture of K_2CO_3 and carbon at a high temperature.

(b) How is sodium isolated by Down's process ?

Write equations for the reactions involved. Why can sodium metal not be isolated by electrolysis of an aqueous solution of sodium chloride ?

21. Explain the following :

(a) Alkali metals are obtained by the electrolysis of their molten salts but not by the electrolysis of their aqueous solution.

- (b) The softness of Group IA metals decreases down the Group with increasing atomic number.
- (c) Aqueous solution of sodium chloride is a good conductor of electricity while solid sodium chloride is a non-conductor.
22. Give the general trends in the properties of alkali metals. Write the principle of manufacture of potassium chlorate.
23. Give the comparative account of properties of alkali metals. Write any two uses of potassium chlorate.
24. Name the elements of group 1 of the periodic table. Give the general trends in the properties of these elements. How is Glauber's salt prepared?

□□□

CHAPTER - 13

ALKALINE EARTH METALS

(GROUP - 2)

13.1 INTRODUCTION :

The elements Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra) constitute Group 2 of the periodic table. The oxides of these elements were known much earlier than the metals themselves and they were named alkaline earths since (a) they were alkaline in nature like alkali metal oxides and (b) they were found in earth's surface.

Fig 13.1 - Position of the alkaline earth metals in the periodic table.

13.2 ELECTRONIC CONFIGURATIONS :

The atoms of all the alkaline earth metals have two electrons in their valence shell preceded by the noble gas configuration. Their general configuration may be written as [Noble gas] ns^2 where n represents the valence shell (Table-13.1).

Table - 13.1

Element	Symbol	At.No.	Electronic configuration	Configuration of outermost shell
Beryllium	Be	4	$1s^2, 2s^2$ or $[\text{He}] 2s^2$	$2s^2$
Magnesium	Mg	12	$1s^2, 2s^2, 2p^6, 3s^2$ or $[\text{Ne}] 3s^2$	$3s^2$
Calcium	Ca	20	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ or $[\text{Ar}] 4s^2$	$4s^2$
Strontium	Sr	38	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6$ or $[\text{Kr}] 5s^2$	$5s^2$
Barium	Ba	56	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 6s^2$ or $[\text{Xe}] 6s^2$	$6s^2$
Radium	Ra	88	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 6s^2, 6p^6, 7s^2$ or $[\text{Rn}] 7s^2$	$7s^2$

13.3 GENERAL CHARACTERISTICS OF ALKALINE EARTH METALS (GROUP-2) :

Physical characteristics:

The important physical constants of alkaline earth metals are given below. The other physical properties are discussed thereafter.

Table - 13.2
Physical constants of Alkaline Earth Metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic radius (A^0)	1.05	1.36	1.74	1.91	1.98	-
Ionic radius (M^{++}) (A^0)	1.31	0.65	0.99	1.13	1.35	1.50
Ionisation energy E_1 (kJ mole $^{-1}$)	900	737	590	549	502	510
$(\text{kJ mole}^{-1})E_2$	1757	1450	146	1060	965	975

Density (g/cm ³)	1.86	1.75	1.55	2.60	3.59	5.00
Melting point (K)	1551	924	1116	1026	998	973
Abundance in Earth's crust (ppm)	6.00	2.1×10^4	3.6×10^4	3.0×10^2	2.5×10^2	1.3×10^{-6}

1. Atomic and ionic radii :

The atomic and ionic radii of the members of the family are smaller than the corresponding members of the alkali metals.

Explanation :

The alkaline earth metals have a higher nuclear charge and therefore, the electrons are attracted more towards the nucleus. As a result, their atomic and ionic radii are smaller than those of alkali metals. On moving down the group, the radii increase due to gradual increase in the number of the shells and the screening effect.

2. Melting and boiling points:

Alkaline earth metals have low melting and boiling points which are higher than the corresponding alkali metals in the same period due to comparatively smaller size. However, melting and boiling points do not show regular trends.

Explanation :

The atoms of alkaline earth metals have smaller size as compared to alkali metals. Therefore, they are more closely packed in their crystal lattices and hence they have higher melting and boiling points.

3. Ionisation energy :

The alkaline earth metals have low ionisation energies due to fairly large size of the atoms. Since the atomic size increases down the group, the ionisation energy decreases (Table 13.2). A comparison of the ionisation energies of the members of Groups 1 and 2 shows that the members present in the second group have higher values as compared to those of Group 1, because they have smaller size and electrons are more attracted towards the nucleus of the atoms.

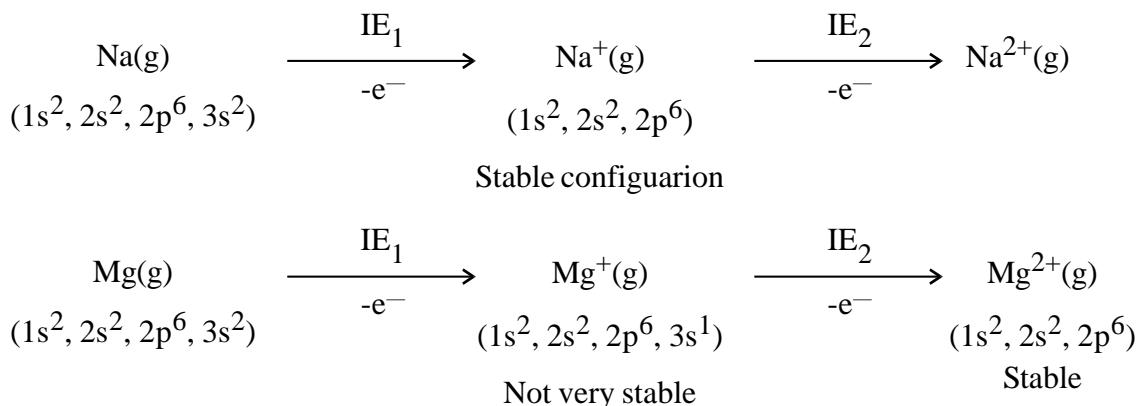
It may be noted that although I E₁ values of alkaline earth metals are higher than those of alkali metals, the IE₂ values of alkaline earth metals are much smaller than

those of alkali metals. The ionisation energy values of sodium (alkali metal) and magnesium (alkaline earth metal) are given below.

Element	IE ₁	IE ₂
Na	496 kJ mol ⁻¹	4562 kJ mol ⁻¹
Mg	737 kJ mol ⁻¹	1450 kJ mol ⁻¹

Explanation:

In case of alkali metals (i.e. Na) the second electron is to be removed from a cation which has already acquired a noble gas configuration. On the other hand, in the alkaline earth metals (i.e. Mg), the second electron is to be removed from a monovalent cation, $\text{Mg}^+ : (1s^2 \ 2s^2 \ 3s^1)$ which still has one electron in the outermost shell. Thus, the second electron in Mg can be removed easily.



The IE₃ of Mg will be very high because the electron is to be removed from stable noble gas configuration.

4. Electropositive and metallic character :

Because of the low ionisation energies of alkaline earth metals, they are strongly electropositive in nature. However, these are not as strongly electropositive as the alkali metals of Group 1 because of comparatively higher ionisation energies. The electropositive character increases down the group i.e. from Be to Ba.

5. Characteristic flame colouration :

Except Be and Mg, the alkaline earth metal salts impart characteristic colours to the flame.

Metal	Be	Mg	Ca	Sr	Ba	Ra
Colouration	—	—	Brick red	Crimson red	Grassy green	Crimson red

Beryllium and magnesium do not give any characteristic flame colour action.

Explanation :

The alkaline earth metals give characteristic flame colouration because their ionisation energies are low. Therefore the valence electrons in these atoms can be easily excited to higher energy states by the energy of flame of bunsen burner. When these excited electrons (excited state is unstable state) come back to ground state they emit radiations which fall in the visible region. Therefore, they give colours to the flame. On the otherhand, beryllium and magnesium atoms are comparatives smaller and their ionisation energies are very high. Hence the energy of the flame is not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour to bunsen flame.

6. Tendency to form bivalent ions:

The alkaline earth metals exhibit a valency of 2 as they can lose two electrons and form bivalent ions. Inspection of Table 13.2 reveals that the second ionisation energy (IE_2) of alkaline earth metals is greater than the first ionisation energy (IE_1). It, thus appears that if ionisation energy is the only factor involved in the formation of divalent ions, we would expect that alkaline earth metals would prefer to form $+1$ ions (M^+) rather than $+2$ ions (M^{2+}). Actually, they predominantly show $+2$ oxidation state e.g. Mg^{2+} , Ca^{2+} , Ba^{2+} etc.

Explanation:

This can be explained as :

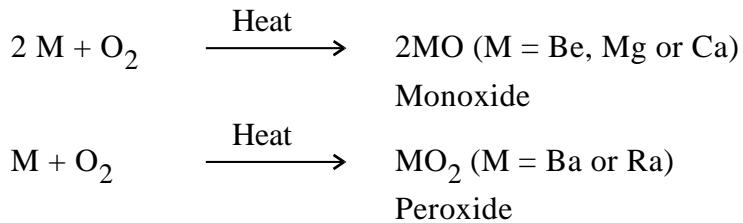
- (i) Divalent ions have the stable noble gas configuration.
- (ii) In solution, the $+2$ ions of alkaline earth metals are extensively hydrated and the high hydration energies of M^{2+} ions make them more stable than M^+ ions. It is observed that the amount of enegy released when M^{2+} ion is dissolved in water is much more than that for M^+ ion. This large amount of extra energy released in the hydration of $+2$ ions is more to compensate the second ionisation energy required for the formation of such ions.

- (iii) In the solid state, the divalent cation form stronger lattices than monovalent cations and therefore, a lot of energy called **lattice energy** is released. It is the greater lattice energy of M^{2+} ion which compensates the high second ionisation energy and is responsible for its greater stability as compared to M^+ ion.

Chemical properties :

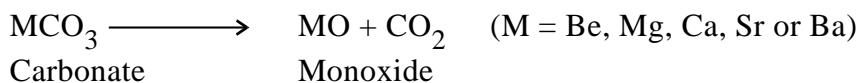
Because of their low ionisation energies and high electropositive character the alkaline earth metals have strong tendency to lose valence electrons. Therefore, they are very reactive. The reactivity of these elements increases on going down the group. However, alkaline earth metals are, in general less reactive than alkali metals. The chemistry is mainly dominated by the dipositive oxidation state (M^{2+}). Some of the general trends are discussed below.

- Action with air or oxygen - Formation of oxides :** The alkaline earth metals being less electropositive than alkali metals react with air or oxygen slowly upon heating to form oxides, MO . However, Ba and Ra form peroxides.

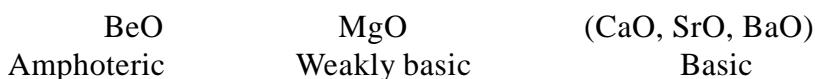


The reactivity with oxygen increases as we move down the group due to increasing electropositive character of the elements.

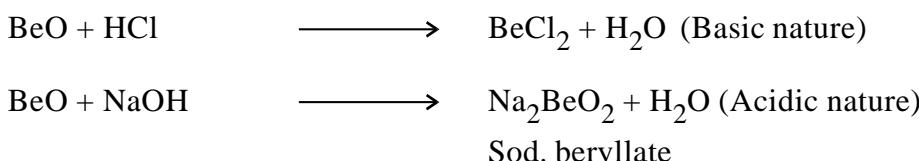
The monoxides can also be prepared by decomposition of their carbonates.



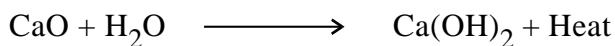
Among the oxides BeO is amphoteric while oxides of other elements are basic in nature.



The amphoteric character of BeO is supported by the fact that it reacts with acids as well as alkalies.



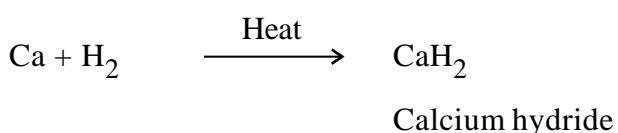
The oxides of Be and Mg (BeO , MgO) are almost insoluble in water while the oxides of rest of the metals dissolve in water to form hydroxides.



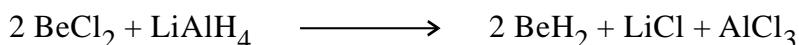
The insolubility of BeO and MgO in water is due to their large lattice energies.

2. Combination with hydrogen — Formation of hydrides :

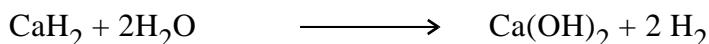
All the elements except beryllium combine with hydrogen upon heating to form ionic hydrides, MH_2 .



BeH_2 , however, can be prepared by the reaction of BeCl_2 with LiAlH_4 .

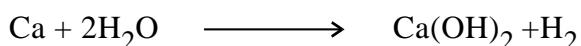


MgH_2 is covalent while all other hydrides are ionic. Calcium hydride is known as *hydrolith*. Thus, the hydrides are highly reactive with water and form hydroxides and liberate hydrogen.



3. Action with water — Formation of hydroxides :

The alkaline earth metals have lesser tendency to react with water as compared to alkali metals. They combine with water slowly to form hydroxides.



Like alkali metals, the hydroxides are basis in nature and basic strength increases down the family.

The basic character of hydroxides is due to the low ionisation energies of these metals. Because of low ionisation energies the M-O bond in MOH is weak and it can cleave to give OH^- ions in solution. Since the ionisation energy decreases down the family, the basic strength of the hydroxides increases. For example, $\text{Be}(\text{OH})_2$ is amphoteric, $\text{Mg}(\text{OH})_2$ is mildly basic while others are strong bases.

Hydroxides of Alkali & Alkaline Earth Metals

LiOH	Be(OH) ₂
	Amphoteric
NaOH	Mg(OH) ₂
	Mild base
KOH	Ca(OH) ₂
	Strong base
RbOH	Sr(OH) ₂
	Strong base
CsOH	Ba(OH) ₂
	Very strong base

BASIC CHARACTER INCREASES

BASIC CHARACTER DECREASES →

All alkali metal hydroxides are strong bases.

The hydroxides of alkaline earth metals are less basic than those of alkali metals of the corresponding periods. The lesser basic strength of hydroxides of alkaline earth metals is due to their

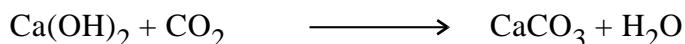
- (i) High ionisation energies
- (ii) Small ionic sizes and
- (iii) Dipositive charge on the ions.

As a result, the M-O bond in these hydroxides is relatively stronger than that of corresponding alkali metals and therefore, does not break. Therefore, they are less basic than corresponding alkali metals.

The hydroxides of alkaline earth metals are less soluble than alkali metal hydroxides. However, the solubility of hydroxides in water increases with increase in size of the metal. Be(OH)₂ and Mg(OH)₂ are almost insoluble. Ca(OH)₂ is sparingly soluble while Sr(OH)₂ is fairly soluble. The trend is due to increase in size of the cation on moving down the group so that their lattice energies decrease. Due to decrease in lattice energies, the solubility of hydroxide in water increases.

4. Formation of Carbonates :

The carbonates of alkaline earth metals can be prepared by passing carbon dioxide in limited supply through the solution of their hydroxides.



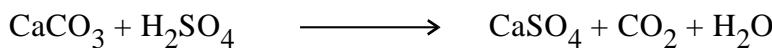
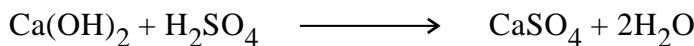
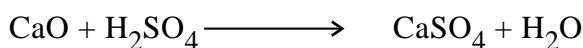
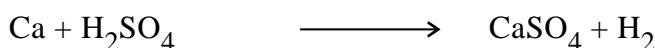
All carbonates decompose on heating to give carbon dioxide and metal oxide.



However, the stability of these carbonates increases down the group. For example, BeCO_3 is least stable while BaCO_3 is most stable. The solubilities of the metal carbonates in water decrease down the family. For example, BeCO_3 is slightly soluble in water while BaCO_3 is completely insoluble.

5. Formation of Sulphates :

These can be formed by the action of dil. H_2SO_4 on metals, metal oxides, metal hydroxides and metal carbonates.



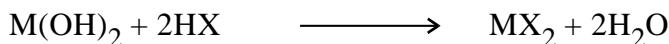
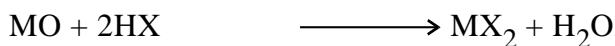
The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. Their solubilities decrease on going down the group. This is due to higher lattice energies of alkaline earth metal sulphates than alkali metal sulphates (as already explained). On moving down the group, the hydration energy decreases with increase in size of the metal ion and consequently their solubilities decrease.

6. Formation of Halides :

All the alkaline earth metals combine with halogens at higher temperatures forming their halides.

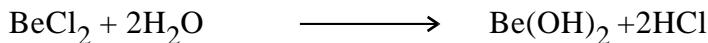


The metal halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.



- i) Beryllium halides are covalent while all other halides are ionic and are readily soluble in water.
- ii) BeCl_2 is relatively low melting solid and volatile while others have high melting points. BaCl_2 has very high melting point.
- iii) Being covalent, BeCl_2 is soluble in organic solvents.
- iv) The anhydrous halides of alkaline earth metals are hygroscopic i.e. they absorb

water molecules and form hydrates such as $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. BeCl_2 gets hydrolysed by moisture and therefore gives fumes of hydrochloric acid.

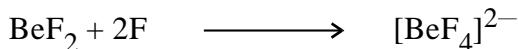


- v) Except BeCl_2 and MgCl_2 , the chlorides of the other members impart characteristic flame colours.

CaCl_2	SrCl_2	BaCl_2
Brick red	Crimson	Grassy green (Pea green)

7. Tendency to form complexes:

The Group 2 elements have tendency to form some stable complexes. Among these, beryllium and magnesium have maximum tendency to form complexes. This is due to their small size and higher charge density. For example, Beryllium forms complexes of the type $(\text{BeF}_4)^{2-}$



Chlorophyll is an important complex of magnesium.

Difference between Beryllium and Magnesium

Beryllium differs from other alkaline earth metals due to the following reasons.

- (i) Beryllium has extremely small size.
- (ii) It has comparatively high electronegativity and ionisation potential than magnesium and other members of the family.
- (iii) It has no vacant d-orbital in the valence shell.

A comparative account of the difference between beryllium and magnesium is given below.

<u>Property</u>	<u>Beryllium</u>	<u>Magnesium</u>
1. Hardness	Hard	Soft
2. M.P & B.P	High	Low
3. Compounds	Covalent	Mainly ionic
4. Action of water	No action	Forms MgO & H_2 with boiling water.
5. Oxides & Hydroxides	Amphoteric	Basic
6. Nature of carbides	Forms methane	Forms acetylene
	$(\text{Be}_2\text{C} + 4\text{H}_2\text{O} \rightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4)$	$(\text{MgC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{C}_2\text{H}_2)$
7. Action of acid	No action	Forms H_2
8. Complex formation	Forms complexes	Does not form complexes.

13.4 SOME IMPORTANT COMPOUNDS OF CALCIUM :

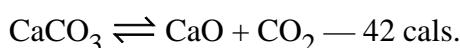
(i) Calcium oxide, CaO (Quick lime)

Lime is a very important commodity of chemical industry. It is also known as **quick lime**.

Manufacture :

Quick lime is obtained when lime stone is heated in a lime kiln. The modern lime kiln is a long cylindrical tower (Fig.13.2) fitted system. The lumps of lime stone and coal are fed from the top. Producer gas is introduced from the inlet near the base. The temperature near the middle of the tower is about 800°C .

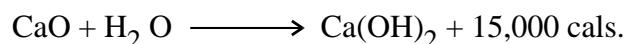
(a) Lime stone decomposes to give quick lime.



Carbon dioxide gas so formed is at once taken out otherwise back reaction may also start. The gas is taken out of the kiln by an upward draught. The product quick lime is drawn out from the bottom through the discharge door.

Properties :

1. Pure calcium oxide is a white amorphous powder.
2. It melts at 2600°C and is extremely stable.
3. It reacts vigorously with water forming calcium hydroxide and releasing tremendous amount of heat.



The process is called *slaking* and the product is also known as **slaked lime**.

4. It reacts with acids forming corresponding salts.

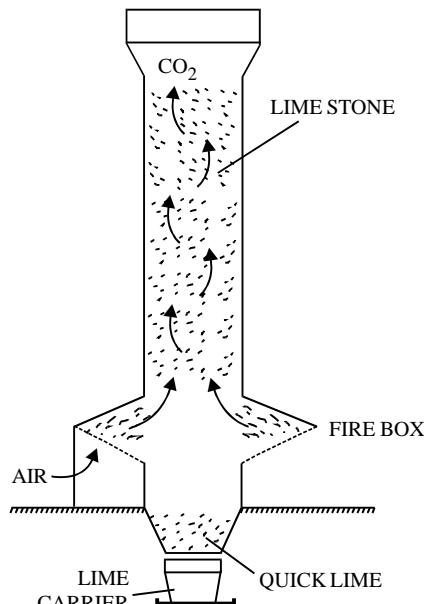
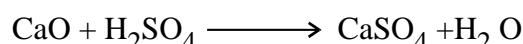
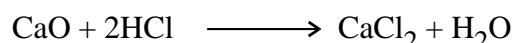
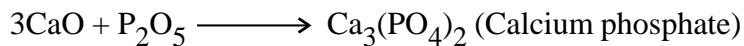


Fig. 13.2 A lime kiln

5. Being a basic oxide it reacts with acidic oxides to form salts.



Uses : It is used

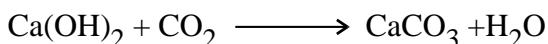
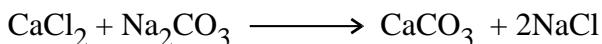
1. in the laboratory as a drying agent.
2. for the preparation of slaked lime.
3. for the preparation of bleaching powder.

(ii) Calcium carbonate, CaCO_3

Calcium carbonate occurs in large quantities in nature as *chalk*, *marble* and *lime stone*.

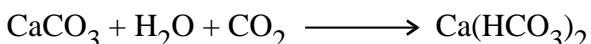
Preparation :

It is obtained in the laboratory by the action of a soluble carbonate on a calcium salt or by passing CO_2 through lime water.



Properties :

1. Calcium carbonate is a white fluffy powder.
2. It is almost insoluble in water.
3. It is soluble in water containing carbon dioxide forming calcium bicarbonate



Uses : It is used

1. For the manufacture of lime.
2. As a flux in the smelting of ores.
3. In the preparation of tooth pastes and face powder.

13.5 **BIOLOGICAL IMPORTANCE OF MAGNESIUM AND CALCIUM :**

Mg^{+2} and Ca^{+2} ions are found to be essential for human body, which contains about 25g of Mg and 1200g of Ca.

Functions :

- (i) Chlorophyll, the green pigments of the plant, contains magnesium, which makes photosynthesis possible.
- (ii) All enzymes, undergoing phosphate transfer by using ATP, need magnesium as the cofactor.
- (iii) While Mg^{+2} ions are found to be concentrated in animal cells, Ca^{+2} ions are concentrated in the body fluid outside the cell.
- (iv) While most of the body calcium is present in bones and teeth, Ca^{+2} ions are required to maintain the regular beating of the heart.
- (v) Calcium plays important role in clotting of blood and stabilisation of protein structure.
- (vi) Calcium finds its use in the functioning of neuro-muscular and interneuronal systems.

CHAPTER (13) AT A GLANCE

- 1. Quick lime - Its chemical composition is CaO
- 2. Slaked lime - Its chemical composition is $Ca(OH)_2$
- 3. The green pigment of the plant, chlorophyll contains magnesium.
- 4. Calcium and magnesium are essential for human body.

QUESTIONS

A. Very short answer type : (1 mark each)

1. Name the following compounds.
 CaO , $\text{Ca}(\text{HCO}_3)_2$
2. Why magnesium is less electropositive than calcium ?
3. What oxidation state is shown by alkaline earth elements in their compounds ?
4. Which element has the least atomic radius among the alkaline earth elements ?
5. Write the electronic configuration of Group 2 element.
6. Write the electronic configuration of calcium.
7. Why is ionisation energy of Mg greater than Al?
8. Which is bigger in size between Na^+ and Mg^{2+} ?

B. Short answer type : (2 marks each)

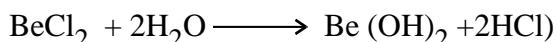
1. An element has atomic number 12. Find out its electronic structure. Name the element and quantum number of its valence shell electrons.
2. Magnesium metal burns in air to give a white ash. When this ash is treated with water the odour of ammonia can be detected. Suggest the explanation for this observation.
Hint : $[3\text{Mg} + \text{N}_2 \xrightarrow{\Delta} \text{Mg}_3\text{N}_2; \text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \longrightarrow 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3]$
3. State with equation what happens when carbon dioxide gas is passed in excess through clear lime water.
4. Name the alkaline earth metals and write their electronic configurations.
5. Name some of the important properties of the alkaline earth metals which make them similar.
6. Account for the fact that alkaline earth metals exhibit only +2 oxidation state.
7. Discuss the gradation in properties of group 2 elements with reference to
i) Atomic radii ii) Action as reducing agent iii) Ionisation energies iv) Electropositive character v) Metallic character.
8. Mention the properties in which Beryllium differs from other members of the family.
9. Compare the properties of Beryllium with that of aluminium.

C. Short answer type : (3 marks each)

1. Mention some important uses of magnesium and calcium.
2. How will you detect magnesium and calcium in separate salts by qualitative analysis ?
3. Why calcium can not be extracted from calcium oxide by carbon reduction process ?
4. Give two biological importance of Ca^{2+} and Mg^{2+}
5. State with equation what happens when excess carbon dioxide gas is passed through lime water.

6. Why do beryllium halides fume in air ?

(Hint : Due to formation of halogen acids by hydrolysis as



D. Long answer type questions. (7 marks each)

1. Account for the following :
 - (i) Energy required to remove the first electron in alkaline earth metals is higher than that in alkali metals.
 - (ii) Alkaline earth metals are less electropositive than alkali metals.
 - (iii) Alkaline earth metals are denser, harder and have higher melting points than alkali metals.
2. Compare the chemical properties of alkaline earth metals with those of alkali metals with reference to
 - i) Action with water ii) Action with oxygen iii) Action with dilute H_2SO_4 (iv) Strength of hydroxides v) Solubility of carbonates vi) Solubility of sulphates.
3. Give one method for the preparation and one important application of each of the following:
 - a) Quick lime b) Lime stone c) Slaked lime
4. Give formula of two sets of magnesium and calcium compounds and their properties which resemble each other and that of one set of compounds whose properties differ.
5. (a) The barium ion is poisonous. Why then can barium sulphate be used safely in making X-ray photographs of the digestive tract ?

 (b) Explain the following phenomenon by means of balanced equations.
 - (i) When exhaling is made through a tube passing into a solution of lime water, solution becomes turbid.
 - (ii) The turbidity of the solution (i) eventually disappears when continued exhaling is made through it.
 - (iii) When solution obtained in (ii) is heated, turbidity reappears.
 - (iv) Why are alkaline earth metals good reducing agents ?
 - (v) Why is anhydrous CaSO_4 used as a drying agent ? Why not Plaster of Paris ?
6. Discuss the chemistry of alkaline earth metals. Why sodium metal is soft, though metals are hard generally ?
7. Write the general trends in properties of Group 2 elements (alkaline earth metals), What is Epsom salt ? Mention one of its uses.
8. Discuss the chemistry of alkaline earth metals. Why sodium metal is soft, though metals are hard generally ?
9. Discuss about two characteristic properties of alkaline earth metals. What is quick lime ? Give one method of its preparation and one of its uses.



UNIT - XI

THE P-BLOCK ELEMENTS

CHAPTER - 14 (GROUP 13 ELEMENTS)

INTRODUCTION :

Elements in which the last electron enters the outermost p-orbital are called p-block elements. As there are three number of p-orbitals six electrons can be accommodated in a set of p-orbitals. Consequently there are six groups of p-block elements in the periodic table numbering from 13 to 18. Boron, Carbon, Nitrogen, Oxygen, Fluorine and Neon are the first member of these groups respectively.

14.1 **GROUP 13 ELEMENTS : THE BORON FAMILY :**

Group 13, collectively called Boron family or Boron group elements consists of five elements namely Boron (B), Aluminium(Al), Gallium(Ga), Indium(In) and Thallium(Tl). Boron is a nonmetal whereas other members of the group are silvery-white metals.

14.2 **GENERAL CHARACTERISTICS OF P-BLOCK ELEMENTS :**

(a) Electronic configuration : The p-Block elements have general valence shell electronic configuration ns^2np^{1-6} (except for He). But they may differ in their inner core electronic configuration, which in turn influences their physical properties. The presence of vacant *d*-orbitals in valence shell of heavier elements (starting from the 3rd period onwards) also influence the chemical properties.

(b) Oxidation state : The p-Block elements show a common oxidation state, also known as group oxidation state which is in general equal to number of *s*- and *p*-electrons in the valence shell. This oxidation state is the maximum value shown by elements of a particular group. In addition to this value p-Block elements may show other oxidation states which normally but not necessarily differ from the total number of valence electrons by unit of two. This trend becomes prominent as we move down the group which is commonly attributed to the ‘Inert Pair Effect’. Table 14.1 shows a list of the important oxidation states exhibited by p-Block elements.

Table 14.1 General electronic configuration and oxidation states of p-Block elements

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
First members of the group	B	C	N	O	F	He
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1 	+2, -4 	+3 -3 	+4 +2 -2 	+5 +3 +1 	+6 +4 +2

(c) Metallic character : The p-Block of the periodic table accommodates non-metals, metalloids as well as the metals. As we go down a particular group the non-metallic character decreases and metallic character increases. The trend down the group is non-metal-metalloid-metal. Thus the heaviest elements of each group is metallic in nature. The change from non-metallic to metallic character is also illustrated by the change in their oxides from acidic behaviour to basic behaviour down a group.

(d) Covalency : The non-metals present at the top of each group have higher electronegativities and higher ionisation enthalpies suitable for the formation of covalent bond. The second period elements of p-Groups starting from Boron are restricted to a maximum covalence of four (one 2s and three 2p orbitals). But the presence of d-orbitals in the valence shell of heavier elements enable them to expand their covalence above four. For example, Boron forms only $[BF_4]^-$ whereas Aluminium gives $[AlF_6]^{3-}$ ion. The first member of a group differs from heavier members in its ability to form $p\pi-p\pi$ multiple bonds (e.g., $C=C$, $C \equiv C$, $N \equiv N$, $C=O$, $C \equiv N$, $N=O$). The heavier elements form $d\pi-p\pi$ or $d\pi-d\pi$ bonds.

14.3 OCCURRENCE :

Boron occurs in two isotopic forms, $^{10}_5B$ (19%) and $^{11}_5B$ (81%). Its abundance in Earth's crust is only 0.0001% by mass. It mainly occurs as

- (1) Borax ($Na_2B_4O_7 \cdot 10H_2O$)
- (2) Kernite ($Na_2B_4O_7 \cdot 4H_2O$)
- (3) Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$)

Aluminium is the third most abundant element (8.3%) found in the earth's crust after oxygen (45.5%) and silicon (27.7%).

The important ores of aluminium are :

1. *Oxide* : **Bauxite** ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, Hydrated aluminium oxide), **Diaspore** ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) **Corundum** (Al_2O_3), Ruby (Al_2O_3), Sapphire (Al_2O_3).
2. *Fluoride* : **Cryolite** (Na_3AlF_6 or $\text{AlF}_3 \cdot 3\text{NaF}$)
3. *Silicates*: **Porcelain** and **China clay** or **Kaoline** ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), **Felspar** KAlSi_3O_8
4. *Aluminates* : **Chrysoberyl** ($\text{BeO} \cdot \text{Al}_2\text{O}_3$), **Spinel** ($\text{MgO} \cdot \text{Al}_2\text{O}_3$)
5. *Sulphate*: **Alunite** $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al(OH)}_3$

Gallium, indium and thallium are less abundant than aluminium.

Gallium (0.1 – 1%) is found in the rare mineral Germanite.

Traces of indium are found in the sulphide ores of zinc while that of thallium are found in the sulphide ore of lead.

14.4 GENERAL CHARACTERISTICS OF THE ELEMENTS

The atomic numbers and some of the important physical properties of the elements are given below.

Table 14.2 Physical properties of the elements of Group 13

Element	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Atomic Mass	10.81	26.98	69.72	114.8	204.4
Electronic configuration	$[\text{He}]2\text{s}^22\text{p}^1$	$[\text{Ne}]3\text{s}^23\text{p}^1$	$[\text{Ar}]3\text{d}^{10}4\text{s}^24\text{p}^1$	$[\text{Kr}]4\text{d}^{10}5\text{s}^25\text{p}^1$	$[\text{Ar}]4\text{f}^{14}5\text{d}^{10}6\text{s}^26\text{p}^1$
I.E.(E ₁), kJ mol ⁻¹	780	578	578	557	589
I.E.(E ₂), kJ mol ⁻¹	2428	1817	1980	1821	1972
I.E.(E ₃), kJ mol ⁻¹	3659	2747	2964	2704	2876
Electronegativity	2.0	1.5	1.6	1.7	1.8
Atomic radius, (A ⁰)	0.80	1.25	1.24	1.50	1.55
Ionic radius(M ³⁺), (A ⁰)	—	0.45	0.60	0.81	0.95
Density(g/cm ³)	2.30	2.70	5.90	7.31	11.85
Melting point(K)	2300	932	312	429	577
Boiling point(K)	4000	2700	2500	2300	1740

1. Electronic Configuration

The electronic configuration of these elements (Table 14.2) shows the presence of three electrons ($ns^2 np^1$) in their outer-most shell, two in ns and one in np orbitals.

On the basis of the electronic configuration of the penultimate shell (second last), these elements are categorised into two groups. B and Al are of one type and Ga, In and Tl, of other type. The first type, B and Al have inert gas type configuration (s^2 or $s^2 p^6$) in the penultimate shell. The second type Ga, In and Tl have $s^2 p^1 d^{10}$ type configuration in the penultimate shell. This difference in electronic configuration is responsible for the difference in properties of the elements B and Al with the rest of the elements (Ga, In, Tl).

2. Oxidation states

All these elements form compounds in their +3 oxidation state due to the presence of 3 electrons in their valence shells. Oxidation states shown by the elements of this group are $B=+3$, $Al=+3$, $Ga=+3, +1$, $In=+3, +1$, and $Tl=+3, +1$. B and Al show +3 oxidation states. Heavier elements of this group Ga, In and Tl show +1 oxidation state as well as +3 oxidation state. +1 Oxidation state becomes more and more stable as we move down the group ($Ga^+ < In^+ < Tl^+$). This is due to *inert pair effect*. Therefore Tl, the last element of the group prefers to exist in lower oxidation state that is +1 than to exist in higher oxidation state of +3, Thallium forms stable monovalent ion Tl^+ .

Boron, due to its small size and high ionisation energy cannot lose three valence electrons to form B^{3+} ion and therefore forms covalent compounds. Al also has tendency to form covalent compounds. Example : $AlCl_3$.

3. Atomic and ionic radii

As usual the atomic radii of these elements are expected to increase down the group due the successive addition of new orbits. But moving from Al to Ga the atomic radius, instead of increasing slightly decreases ($Al = 1.25 \text{ \AA}^0$, $Ga=1.24\text{\AA}^0$). The outer-shell configurations of Al and Ga are $3s^2$, $3p^1$ and $3d^{10}, 4s^2, 4p^1$ respectively. Since the $3d$ orbitals present in Ga are larger in size and poorly screen the nucleus of Ga, the effective nuclear charge in Ga becomes slightly more than that in Al. Therefore, the atomic radius of Ga becomes slightly less than that of Al. In and Tl show the expected increasing trend in atomic radii. The ionic radii of M^{3+} and M^+ cations ($M=Al, Ga, In, Tl$) increase down the group as expected.

Atomic radii of the elements of boron family are comparatively smaller than atomic radii of corresponding members of Group 1 and Group 2. This is because, the boron family elements have higher value of nuclear charge.

4. Ionisation energies

The ionisation energies of the elements show a fluctuation with the increase in the atomic number. The I.E. of Al is less than B as expected. This is due to an appreciable increase in atomic radius and effective shielding of the nuclear charge in case of Al. The trend reverses while going from Al to Ga. I.E. of Al is less than Ga. In gallium the *d*-subshell is being filled. These intervening *d*-electrons do not screen the nuclear charge effectively and the effective nuclear charge becomes greater than screening effect in Ga than Al. Similarly, the fluctuating tendencies of I.E. can be explained in case of Ga to Tl on the basis of effective nuclear charge and screening effect.

The first ionisation energies of these elements are less in comparison to the corresponding values of Group 2 elements. In case of these elements an electron is removed from *p*-orbital and less energy is required to remove a *p*-electron than removing from *s*-orbital.

The second and third ionisation energies of these elements are considerably higher since the successive electrons are removed from the *s*-orbital.

5. Electropositive or Metallic Character

Boron is less metallic than aluminium since the ionisation energy of B is more than that of Al. B is regarded as a semi-metal or *metalloid*. It has more properties of a non-metal. It has high ionisation energy. It is crystalline, hard and also a poor conductor of electricity. Al and the other remaining elements are metallic in nature. Their metallic character is more or less the same, since their ionisation energy values are slightly different from each other.

The elements of this group have less electropositive or metallic character than the elements of Groups 1 and 2. This is due to the smaller size and higher ionisation energies of these elements as compared to the elements of Groups 1 and 2.

6. Electronegativity

On moving down the group from B to Al, the electronegativity values first decreases and then increases marginally (Table 14.2). This is because of the discrepancies in the atomic size of the elements.

7. Density

Densities of the elements of this group increase regularly on moving down the group from B to Tl. Boron and aluminium have relatively very low densities whereas other members of the group have high densities.

8. Melting point and Boiling point.

The melting points decrease from B to Ga and then increase from Ga to Tl. This irregular trend in melting points may be attributed to structural changes. Boron atoms are firmly bound to one another and thus it has a very high melting point. The low value of melting point of Ga is due to the fact that its structure consists of Ga_2 molecules. The boiling points decrease regularly down the group from B to Al. Gallium has unusual low melting point (303K). It exists in liquid state in summer. Its high B.P. (2676K) makes it a useful material for measuring high temperature.

Chemical properties :

All the elements of the group form M^{3+} compounds. With the increase of the size of to M^{3+} to Tl^{3+} , the tendency of these ions to form covalent compounds decreases. The nature of compounds of M^{3+} ions is decided by Fajan's rule (the smaller the cation, the greater is its tendency to form covalent compounds). Therefore the compounds of B^{3+} are predominantly covalent while Al^{3+} , Ga^{3+} and Tl^{3+} give ionic compounds. Boron does not form B^+ ion. Ga^+ , In^+ and Tl^+ ions exist. Tl^+ ion is quite stable.

General trend in chemical properties

- Hydrides :** The elements of group IIIA do not react directly with hydrogen. Their hydrides are prepared by indirect way. Boron forms a large number of stable covalent hydrides which are called *boranes*. Boranes are of two types.

- a) Boranes of B_nH_{n+4} type : B_2H_6 , B_5H_9 , B_6H_{10} etc.
- b) Boranes of B_nH_{n+6} type : B_4H_{10} , B_5H_{11} , B_6H_{12} etc.

B_2H_6 is the most important borane. It is used for preparing high energy fuels and for welding torches. It is used to prepare organic boron compounds. It is also used as a reducing agent and as a catalyst in polymerisation reactions. Boranes are electron deficient compounds. Al, Ga and In give high molecular mass polymeric hydrides, such as $(AlH_3)_2$, $(GaH_3)_2$, $(InH_3)_2$ respectively. Tl does not form a hydride. B, Al and Ga form complex hydrides which contain $[AH_4]^-$ ion (A=B, Al, Ga).

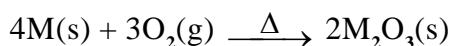
Example : $NaBH_4$, sodium borohydride, $LiAlH_4$, lithium aluminium hydride etc.

The hydrides of the elements of this group are electron-deficient and hence act as lewis acids.

2. Oxides and Hydroxides

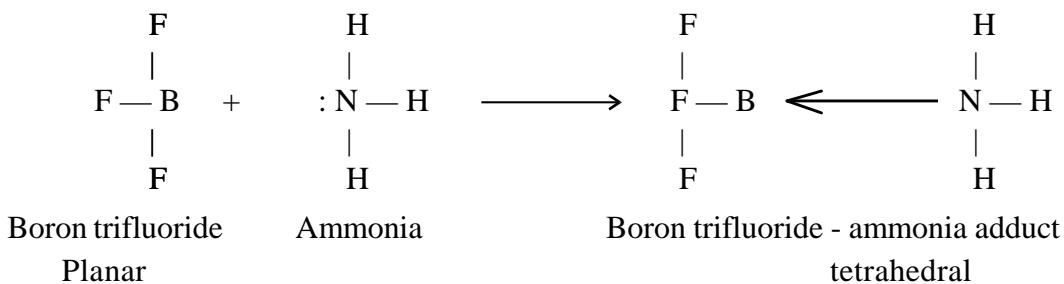
All the elements of this group form sesquioxides of general formula M_2O_3 . These elements form trihydroxides of $M(OH)_3$ type. On moving down the group, there is gradual change from acidic to amphoteric and then to basic character of the oxides and hydroxides.

B_2O_3 (acidic), Al_2O_3 (amphoteric) Ga_2O_3 (amphoteric), In_2O_3 (basic) and Tl_2O_3 (strongly basic).



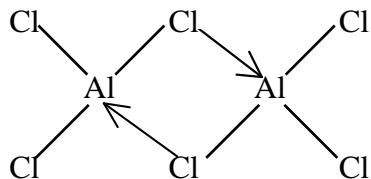
3. Halides

All the elements of this group except thallium react with halogens to form trihalides MX_3 . BF_3 , BCl_3 and BBr_3 are covalent compounds. These compounds are called Lewis acids since they accept lone pair of electrons from groups containing donor atoms like S, O, N etc.



Aluminium halides except AlF_3 are covalent in nature. However, aluminium chloride hydrolyses in water to give Al^{3+} (aq) ion.

In the trivalent state, most of the compounds being covalent are hydrolysed by water to form either tetrahedral species, $[M(OH)_4]^-$ in which the central element is sp^3 - hybridized or octahedral species, $[M(H_2O)_6]^{3+}$ in which the central element is sp^3d_2 - hybridized. For example, BCl_3 on hydrolysis forms tetrahedral $[B(OH)_4]^-$ species, as Boron can not expand its covalency beyond four (due to absence of d -orbitals) whereas, Al_2Cl_6 on hydrolysis gives octahedral $[Al(H_2O)_6]^{3+}$ species, where the Al^{3+} is sp^3d^2 hybridized.



Tetrahedral

Boron trihalides exist as monomers whereas trihalides of Al, Ga and In exist as dimers, e.g. Al_2Cl_6 in the vapour state.

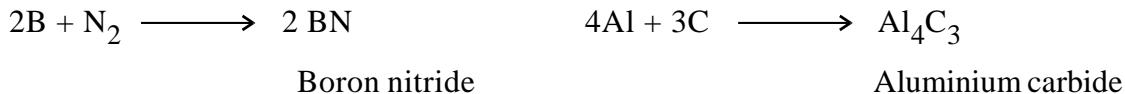
Boron being small in size cannot coordinate with four large halide ions whereas aluminium atom due to its size is capable of coordinating with four halide ions.

Al, Ga and In form unstable monohalides. Thallium monohalides, Tl^+X^- are stable ionic compounds.

The bonding characteristics of halides change from covalent character to ionic character as we go down the group from boron to thallium.

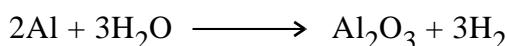
4. Nitrides and Carbides

All the elements of this group combine with nonmetals like nitrogen and carbon forming nitrides and carbides respectively.



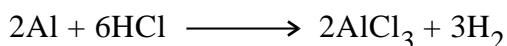
5. Reaction with water

All the members of Group III A except boron decompose water when heated at high temperature.

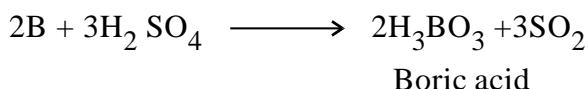


6. Reaction with acids

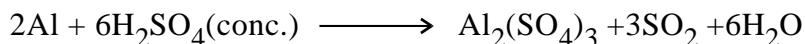
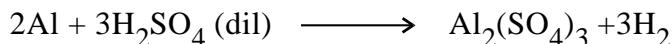
With HCl : Boron does not react with hydrochloric acid. Aluminium readily dissolves in dilute as well as concentrated hydrochloric acid liberating hydrogen.



With H_2SO_4 : Boron reacts with hot concentrated sulphuric acid and is oxidised to boric acid.



Aluminium does not react with dilute sulphuric acid at ordinary temperature. Hot dilute H_2SO_4 reacts slowly liberating hydrogen. Sulphur dioxide is evolved when conc. H_2SO_4 acts on aluminium metal.



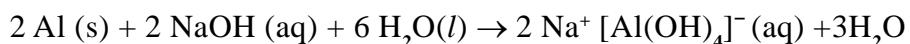
With HNO₃: Hot concentrated nitric acid oxidises boron to boric acid



Aluminium becomes passive when reacts with concentrated HNO₃. This is because a thin layer of its oxide gets coated on the metal which prevents further action of nitric acid. Gallium has similar behaviour towards acids as that of aluminium. Indium reacts with all acids. Thallium does not react with HCl. However, the metal reacts with sulphuric acid and nitric acid.

7. Reaction with alkalies :

Boron does not react with alkalies even at moderate temperature. Aluminium being amphoteric in nature reacts with aqueous alkali liberating hydrogen gas.



Tetrahydroxoaluminate (III)

Behaviour of Boron

Anomalous properties : Boron differs from others of its group members in many properties. because of its small atomic size and absence of orbitals.

Table 14.3: Differences between boron and other members of the Group 13

Property	B	Al, Ga, In and Ti
1. Nature of compounds	Boron has small atomic radius, small size, high charge and hence high charge density for which all its compounds are covalent. B ³⁺ ion does not exist.	Form covalent as well as ionic compounds
2. Maximum covalency	Boron shows a maximum covalency of four, due to absence of d-orbitals.	Show covalency of six or more, as the d-orbitals are available.
3. Electron accepting power of compounds	Boron has less than four valence electrons for which it has a great tendency to accept electrons. Therefore, its compounds behave as strong Lewis acids and form large number of complex compounds.	Less tendency to accept electrons.
4. Inert pair effect	Does not exhibit inert pair effect	Exhibit inert pair effect.

Difference between Boron and Aluminium

The difference in the properties between boron and aluminium is due to the large difference in their size and ionisation potential.

Table 14.4: Differences in properties between Boron and Aluminium

Property	Boron	Aluminium
1. Nature	Non-metal	Metal
2. Hardness	Its crystalline form is very hard	It is sufficiently soft
3. Melting point	2300K	932K
4. Electrical conductivity	Bad conductor	Good conductor
5. Nature of compounds	Forms covalent compounds only	Forms both covalent and electrovalent compounds
6. Nature of hydrides	Forms number of stable covalent hydrides	Does not form stable hydrides.
7. Nature of hydroxide	$\text{B}(\text{OH})_3$ or H_3BO_3 is weakly acidic.	$\text{Al}(\text{OH})_3$ is amphoteric
8. Action on steam	Does not decompose water or steam.	Decomposes steam to liberate hydrogen.
9. Action with acids	Does not react with dilute acids	$2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2 \uparrow$ Reacts with dilute acids to form hydrogen.
10. Combination with metals.	Combines with metals to form borides $3\text{Mg} + 2\text{B} \rightarrow \text{Mg}_3\text{B}_2$ (Magnesium boride)	$2\text{Al} + \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2 \uparrow$ Combines with metals to form alloys.

Similarities in properties of Boron and Aluminium

In Group 13 of the periodic table aluminium is lying just below boron and exhibit many properties similar to those of boron.

Following are the properties in which boron resembles aluminium:

- Both have similar electronic configurations having three electrons in their outer most orbits. $\text{B}(5) = 1s^2, 2s^2, 2p^1$; $\text{Al}(13) = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
- Both elements are trivalent. Since the penultimate shell of both elements are complete and stable, they do not show variable valencies. The common oxidation state of these elements is +3. Boron however shows -3 oxidation state in the metal borides.

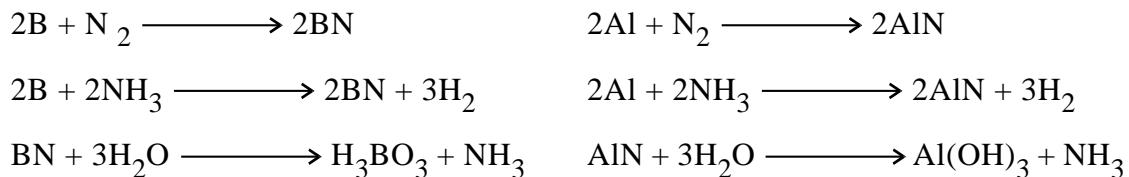
3. Both form amphoteric oxides when heated with oxygen at high temperature.



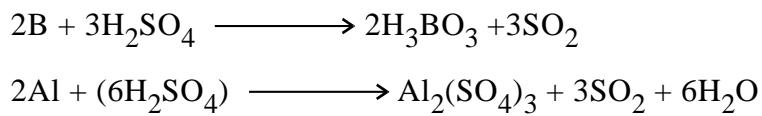
4. Both form covalent trichlorides when heated with chlorine.



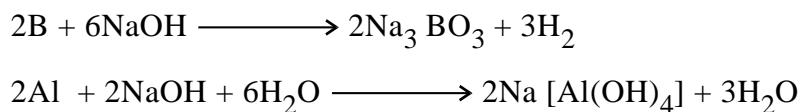
5. Both, when heated with nitrogen or ammonia form nitrides. These nitrides are decomposed by steam to form ammonia.



6. Both react with conc. H_2SO_4 to form SO_2 .



7. Both react with alkalis to form H_2



Position of Boron in the periodic table

We know that boron is present as 1st element in Group 13 and Silicon as 2nd element in Group 14 of the periodic table.

13 14 The element silicon is diagonally related to boron in its properties.

B C Both the elements have almost the same electronegativity values.

Al Si ($\text{B}=2.0$. $\text{Si}=1.8$) and they have identical values of ionic potentials

Ga Ge ($= \frac{\text{charge}}{\text{radius}}$), $\text{B}^{+3} = 0.073$ and $\text{Si}^{+4} = 0.074$.

According to diagonal relationship, the elements of the 2nd period of the periodic table show similarities in properties with the elements which are lying diagonally opposite right in 3rd period. Thus, B-Si pair is called diagonal pair and these two elements show many similar properties.

Similarities in properties of Boron and Silicon:

The following similarities in properties justify the diagonal relationship between B and Si.

1. Both of the elements are non-metals and hence bad conductors of heat and electricity.
2. Both the elements exist in two allotropic forms viz. amorphous and crystalline. Their crystalline forms are hard.
3. Both elements have almost the same electronegativity, ionisation potential and density. Their boiling points are very high and close to each other. Both have high melting points.
4. Most of the compounds of these elements are covalent in nature.
5. Both with hydrogen form gaseous hydrides; B_2H_6 and SiH_4
6. Both elements form stable oxides B_2O_3 and SiO_2 respectively. These oxides are weakly acidic in nature, since in water they give weak acids.



Boric Acid

Metasilicic acid

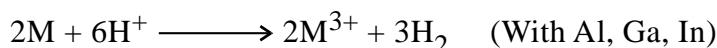
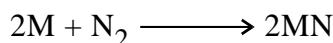
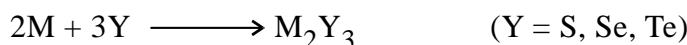
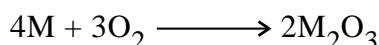
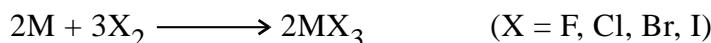
7. The halides of both the elements are covalent in nature and have many similar properties. BCl_3 and $SiCl_4$ both are liquids and get hydrolysed by water to form H_3BO_3 and H_2SiO_3 .



8. Both the elements can be prepared by reducing their oxides with magnesium metal.



Some important common chemical characteristics of Group 13 elements



Gallium, Indium and Thallium

Gallium is one of the rarest elements. It is silvery - white, hard and low melting metal. Next to mercury it has the lowest melting point of all the metals. This property makes it useful as a thermometric liquid for high temperature thermometers.

The chemistry of gallium is similar to that of aluminium. Gallium is a good reducing agent like aluminium. Ga^{3+} ion exists exclusively in solution. Aqueous solutions of its salts undergo hydrolysis like solutions of aluminium salts.

Uses:

1. Just as mercury, gallium is used in arc lamps employed for spectroscopic analysis.
2. Liquid gallium, like mercury does not wet the glass or quartz and it is used in quartz thermostats for measuring high temperatures.

Indium

Indium is a rare metal. In aqueous solutions In^{3+} is hydrolysed to a lesser extent than Al^{3+} and Ga^{3+} ions. In addition to +3 oxidation state indium exists in +1 oxidation state. Its compounds like InCl , InBr , InI and In_2O are known.

Thallium

Thallium is a soft grey metal and differs from other metals in Group III A, that the +1 state is quite stable in addition to +3 state. The behaviour of Tl^+ salts are similar to those of alkali metal salts. However, TlCl is insoluble in water.

Uses

Though thallium as a metal does not have any worthwhile application, its salts are very useful.

1. Thallium salts are used as germicide, fungicide and for rat poison.
2. Thallium salts have high refractive index for which these are used in the making of optical glasses like Crooke's glasses.
3. Its salts are used in ointments for the treatment of ringworms.

14.5 BORON

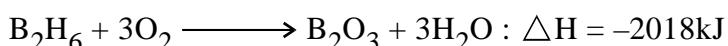
Boron is an important non-metal. Its electrical conductivity is very low and increases with the increase in temperature like a typical semiconductor. Boron is used in making boron–steels which are very hard and are used as control rods in atomic reactors. Boron compounds have numerous industrial applications. Boron and boric acid are industrially important. Metal borides are used in nuclear industry as protective shields and control rods since boron-10(B^{10}) isotope has high ability to absorb neutrons.

Some important compounds of boron:

Boranes:

Boron forms covalent hydrides like carbon. These are called **boranes**. Two series of boranes are known having molecular formulae B_nH_{n+4} (B_2H_6 , B_5H_9 , B_6H_{10} etc) and B_nH_{n+6} (B_4H_{10} , B_5H_{11} , B_6H_{12} , etc). All boranes are electron deficient compounds like diborane (B_2H_6) and therefore, have hydrogen-bridge structures.

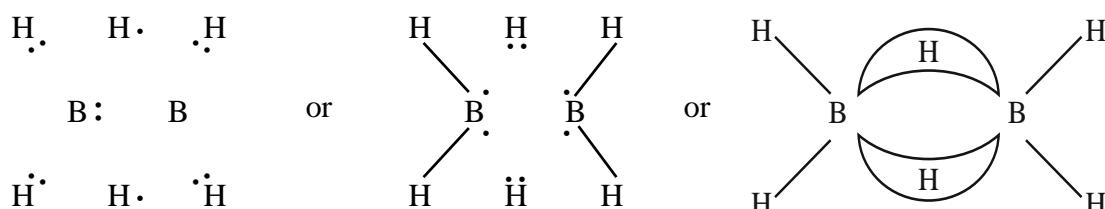
Boranes are inflammable and liberate considerable amount of energy during combustion.



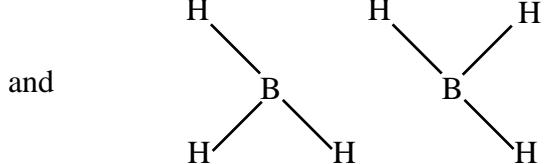
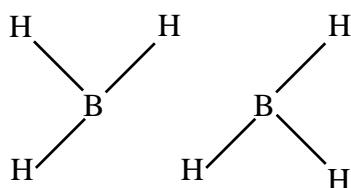
There is a considerable interest in boranes today as possible rocket fuels.

Structure of Diborane :

Diborane, B_2H_6 : Diborane is the simplest of boranes and analogous in molecular formula to ethane (C_2H_6). Each B atom is sp^3 hybridized. Boron atoms and the four of the six hydrogen atoms lie in one plane with the remaining two hydrogen atoms lie outside it and occupy 'bridge' positions between the boron atoms. The four terminal B–H bonds are regular two centre-two electron bonds while the two bridge (B–H–B) bonds are three centre-two electron bonds referred as **banana bonds**. The electron-dot structure of diborane can be written as:



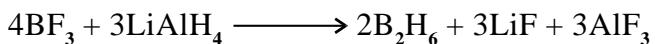
Thus, we find there are one electron bonds between boron and the bridging hydrogen atoms. This arises as a result of resonance between the structures given below.



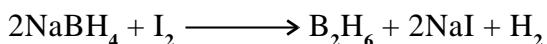
In 1976, **William Discount** was awarded Nobel Prize for elucidating the structures of boranes.

Preparation of Diborane :

1. It is prepared by treating boron trifluoride with LiAlH_4 in diethyl ether.



2. It is prepared in the laboratory by the oxidation of sodium borohydride with iodine.



3. It is produced in the industry by the reaction of BF_3 with sodium hydride.

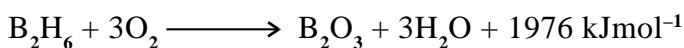


Properties :

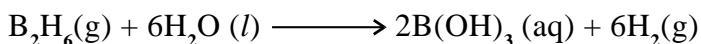
1. **Physical :** Diborane is a colourless, highly toxic gas with a B.P. of 180K.

Chemical : (1) Reaction with Oxygen :

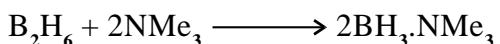
On exposure to air Diborane catches fire spontaneously releasing an enormous amount of energy.



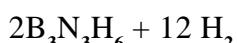
2. **Hydrolysis :** Diborane gets readily hydrolysed by water to give boric acid.



3. Reaction with Lewis bases : With Lewis bases they give borane adducts.

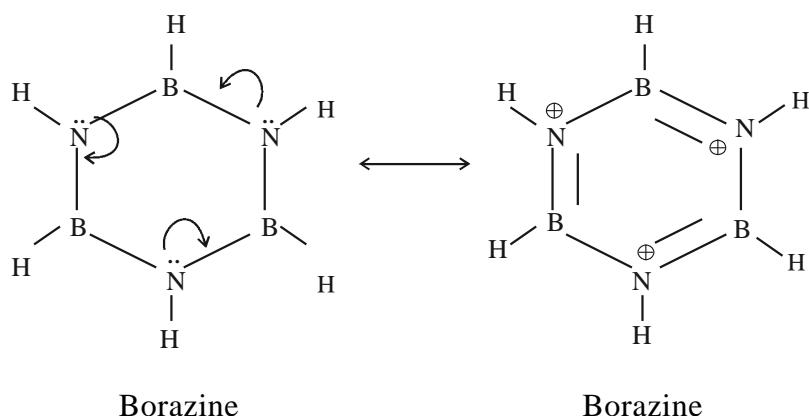


4. **Reaction with Ammonia :** Diborane combines with ammonia to give an addition product $B_2H_6 \cdot 2NH_3$, which when heated at 473K decomposes to give a volatile compound called ‘borazine’.

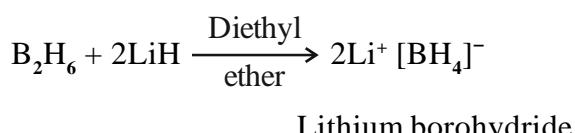
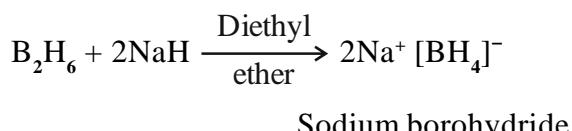


Borazine

Borazine is isoelectronic with benzene. Its ring structure is like that of benzene with alternate 'BH' and 'NH' groups, therefore known as 'inorganic benzene'.



5. **Formation of complex borohydrides :** Diborane reacts with metal hydrides in diethylether to form tetrahydridoborates, commonly known as borohydrides.

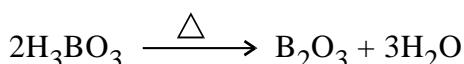


Sodium borohydride and lithium borohydride are used as reducing agents in organic synthesis. They are also starting materials for many other borohydrides.

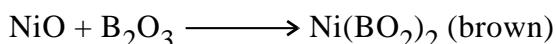
Boric oxide (B_2O_3)

It is nonvolatile and an extremely stable compound, acidic in nature and dissolves in alkalis to give borates. It is so stable that it cannot be even reduced by carbon at high temperature.

It is prepared by heating boric acid to red heat.



It reacts with metal oxides to form transparent metaborates.



These reactions are used to detect the presence of metals in qualitative analysis.

14.6 BORAX ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, SODIUM TETRABORATE DECAHYDRATE)

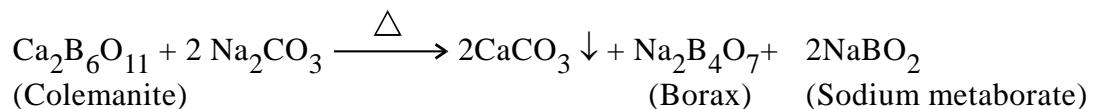
Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is the most important compound amongst borates.

It is sodium salt of tetraboric acid ($\text{H}_2\text{B}_4\text{O}_7$)

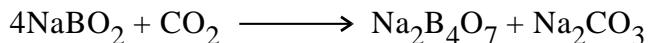
Occurrence and preparation :

In India it is obtained in the name **Tincal** from dried up lakes in eastern Kashmir valley. Borax is also found in Tibet and California (U.S.A). Tincal is the crude form of borax and contains many impurities. The finely powdered Tincal mineral is digested in hot water which dissolves borax leaving the impurities undissolved. The borax solution is collected as filtrate, concentrated and cooled to obtain the crystals of borax.

Borax can also be prepared from the mineral **colemanite**. The mineral is boiled with sodium carbonate when the following reaction takes place.

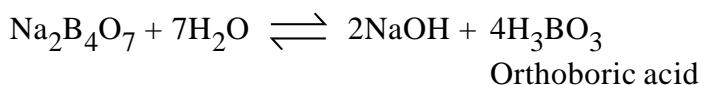


Calcium carbonate precipitates. The mother liquor contains borax and sodium metaborate. Sodium metaborate is also converted to borax by passing carbon dioxide through the mother liquor.



Properties:

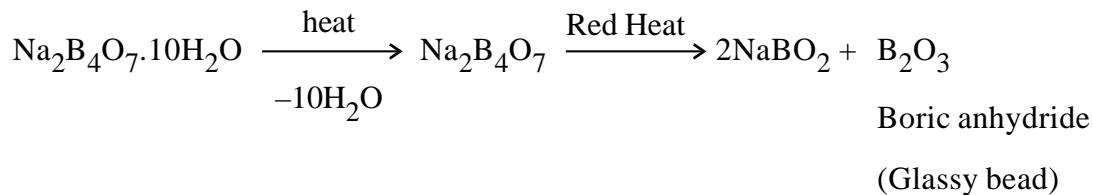
Borax is a white crystalline solid, sparingly soluble in cold water and fairly soluble in hot water. It contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and correct formula therefore is $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$. In water it gets hydrolysed and results $NaOH$ and H_3BO_3 (orthoboric acid).



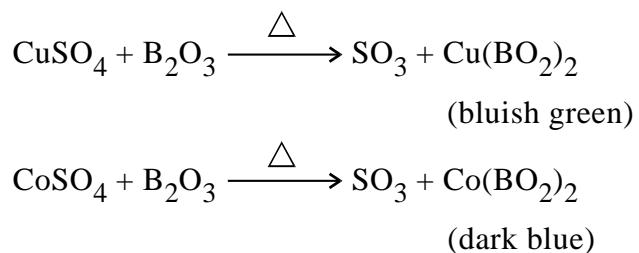
Borax Bead Test :

Borax when heated finally gives a colourless glassy bead, ($\text{NaBO}_2 + \text{B}_2\text{O}_3$). This bead further acquires a characteristic colour when heated along with a coloured salt.

Borax bead test is used for the detection of cations of coloured salts. In this test, borax is heated on a platinum loop when a glassy bead is obtained.

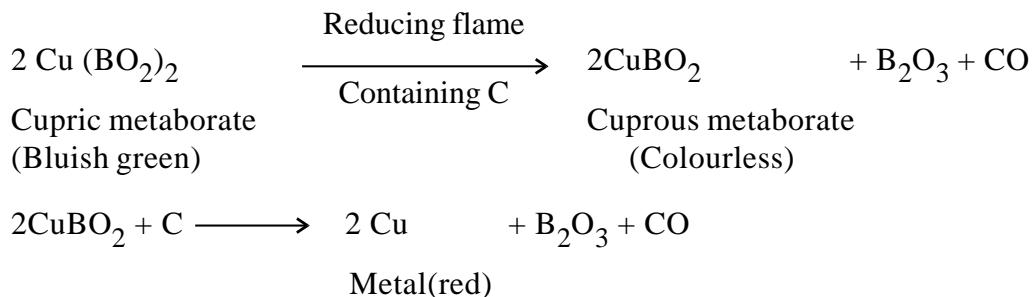


This colourless glassy bead when brought in contact with coloured salt (to be identified) and heated again in the oxidising flame, the bead acquires a characteristic colour due to the formation of metaborate.



Similarly, for Cr³⁺ and Ni²⁺ ions, Cr(BO₂)₃ (green) and Ni(BO₂)₂ (reddish brown) beads are respectively obtained.

When the coloured bead is heated in reducing flame the colour of the bead changes.



Uses : Borax is used

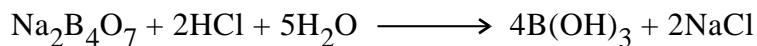
1. As a flux in soldering, welding and certain metallurgical operations.
2. In enamelling and in making glazes for pottery and tiles.
3. In leather industry for cleaning hides and skins and in leather-dyeing.
4. In making optical glasses and borosilicate glass (pyrex glass) which is resistant to heat and shock.
5. As a good cleansing agent, since it hydrolyses to form mildly alkaline solution.
As a water-softening agent.
6. In borax bead test to detect cations of coloured salts.
7. For impregnating match sticks to prevent after-glow.
8. As a mild antiseptic.

14.7 **BORIC ACID (H_3BO_3 , ORTHOBORIC ACID)**

Orthoboric acid, commonly known as boric acid is an important oxy-acid of boron. It is found in the volcanic regions of Italy.

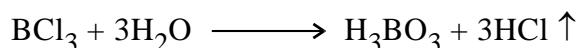
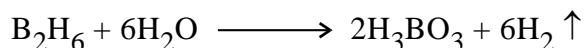
Preparation:

1. Orthoboric acid is prepared by acidifying an aqueous solution of borax with dil.HCl or dil. H_2SO_4 .



Orthoboric acid crystallises out by cooling the resulting solution.

2. Orthoboric acid is also obtained by the hydrolysis (reacting with water or dilute acids) of boron compounds such as hydrides, halides etc.



Properties:

It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in Fig. 14.1.

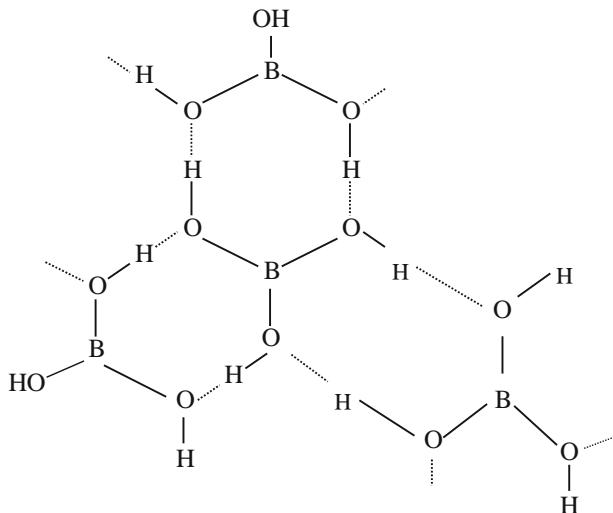


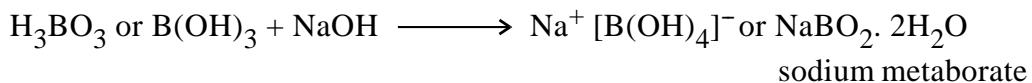
Fig. 14.1 Structure of Orthoboric Acid

1. It forms soft pearly-white, needle like crystals with a greasy feel.
2. It is moderately soluble in water and completely soluble in hot water.
3. H_3BO_3 is a very weak acid and ionises as a monobasic acid. Although it is not a proton donor, it behaves as a Lewis acid by accepting an electron pair.

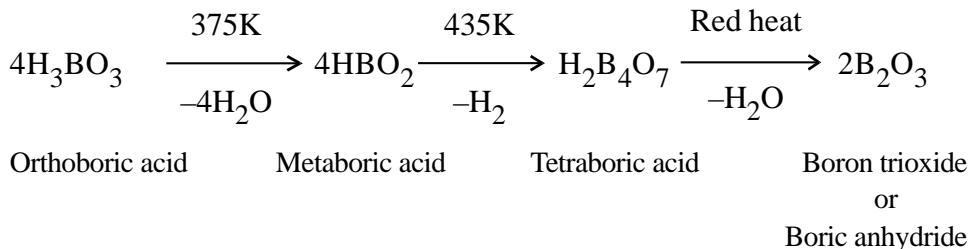


Here H_3BO_3 accepts an electron pair from OH^- (that is obtained from the ionisation of H_2O).

4. It reacts with sodium hydroxide forming sodium metaborate,



5. Orthoboric acid on heating slowly loses water molecules and finally forms boron trioxide B_2O_3 .



Uses: Boric acid is used

1. As an antiseptic and as an eye-wash (eye lotion) in medicine. A solution of boric acid in water is commonly used as a mild antiseptic.
2. As a food preservative, a preservative for milk and other food.
3. In making enamels and borate glazes in pottery.
4. In candle industry to stiffen wicks and in tanning industry.

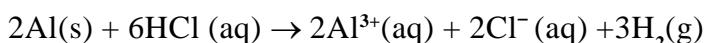
14.8 ALUMINIUM

Aluminium is a very important and strategic metal. It is one of the most common metals in use.

Reaction of Aluminium with Acids and Alkalies :

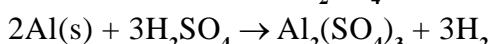
- (1) With dil. HCl:

Aluminium dissolves in dil. HCl and liberates dihydrogen.



- (2) With dil. H_2SO_4 :

Alumunium with dil. H_2SO_4 also liberates hydrogen gas.



- (3) With conc. H_2SO_4 :

Aluminium with conc. H_2SO_4 liberates SO_2 gas.

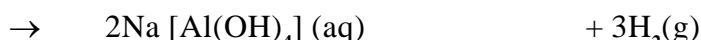


- (4) With conc. HNO_3 :

With conc HNO_3 acid, the metal gets coated with oxide and becomes passive.

- (5) With NaOH :

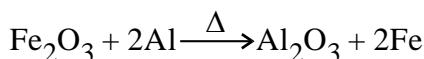
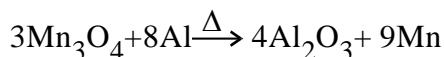
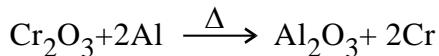
Aluminium reacts with alkalis liberating hydrogen gas.



Sodium tetrahydroxo aluminate (III)

Uses :

- Being light and cheap, aluminium and its alloys are extensively used for the construction of aircraft, railway coach, bus bodies, household utensils etc.
- With the increasing cost of copper in India, aluminium wires are progressively used in transmission cables.
- Aluminium foils are used as wrappers for food materials, tobacco etc. Its powder is used to give shining paints to metallic structures.
- The reducing property of the metal is used in **thermite welding** (Fig.14.2) and for the extraction of metals like chromium, manganese etc. This is also called **alumino-thermic process**. The following reactions are involved in the process.



5. It is used in making house-hold utensils, for winding moving coils for dynamos and motors.

6. Many salts of aluminium like aluminium chloride, alums etc. are useful in various ways. A mixture of aluminium powder and aluminium nitrate is used in bomb making.

Alloys of aluminium

Aluminium alloys are useful because they, in general, possess high tensile strength and resistance towards corrosion.

Table 14.5. Some important alloys of aluminium

Name	Composition	Uses
Magnalium	Al 98%, Mg 2%	Being tough can be used in lathes, used for construction of balance beams etc.
Duralumin	Al 95%, Cu 4% Mn 0.5% Mg 0.5%	Used to make bodies of airships.
Aluminium bronze	Al 90%, Cu 10%	Used for making coins, picture frames, trays etc.
Y-alloy	Al 92.5%, Cu 4%, Mg 1.5%, Mn 2%	Used for making some aeroplane parts.

14.9 ALUM

Alums are double salts having the general formula,

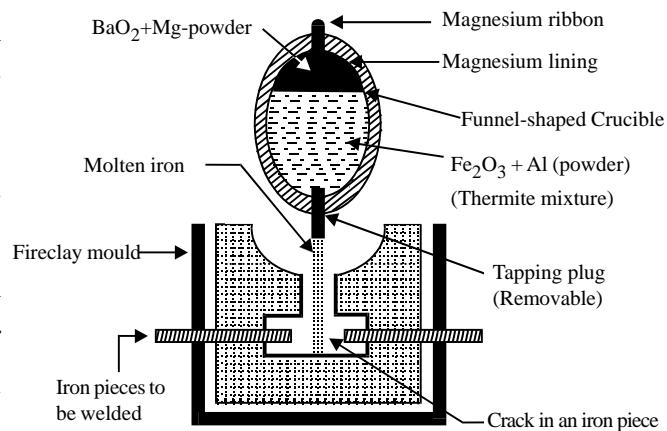
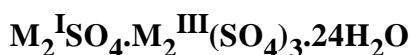
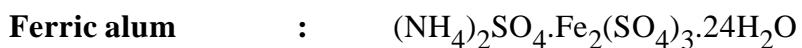


Fig.14.2. Thermite welding process

(where M is a monovalent ion like Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Tl^+ etc, and M^{III} is a trivalent ion like Al^{3+} , Fe^{3+} , Cr^{3+} , Ga^{3+} , Co^{3+} etc.). An alum is prepared by dissolving equimolar quantities of $\text{M}_2\text{I}\text{SO}_4$ and $\text{M}_2\text{III}(\text{SO}_4)_3$ salts in water and crystallising. Potash, ferric, chrome and sodium alums are the most commonly used alums.

Potash alum : $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is prepared by dissolving alunite ore in dil. H_2SO_4 or bauxite in dil. H_2SO_4 and adding K_2SO_4 to the solution. It is a colourless crystal, soluble in water and acidic in nature.



Uses:

- i) Alums are used as mordants in dyeing and calicoprinting
- ii) For purification of drinking water.
- iii) In tanning of leather, sizing paper and making water proof clothes.

CHAPTER (14) AT A GLANCE

1. Group 13 or Boron family or Boron group elements consist of boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl).
2. Boron family elements have three electrons in their outermost shell ($ns^2 np^1$)
3. The oxidation states shown by the elements of boron group are $B=+3$, $Al=+3$, $Ga = +3, +1$, $In = +3, +1$ and $Tl = +3, +1$.
4. Boron is a semimetal or metalloid. It has more properties of non-metal. Boron forms covalent compounds due to its small size and high ionisation energy. Al and other elements of Group IIIA are metallic in nature.
5. The atomic radii and ionic radii of elements of Boron group increase down the group particularly in case of Al, Ga, In and Tl, from Al to Ga atomic radius slightly decreases.
6. The ionisation energies of these elements show fluctuation with the increase in the atomic number down the group.
7. On moving down the group from B to Tl, the electronegativity values do not show the expected decrease. Group 13 or Boron group elements are more electronegative as compared to those of Group 12 elements.
8. Densities of the elements of Boron group increase regularly on moving down the group.
9. The melting points decrease from B to Al and then increase from Ga to Tl. The boiling points decrease regularly down the group from B to Al.
10. All the elements of the Boron group form M^{3+} compounds. The tendency of M^{3+} ions to form covalent compounds decreases. Boron does not form B^+ ion.
11. Boron forms a large number of stable covalent hydrides called **boranes**. Boranes of B_nH_{n+4} type are B_2H_6 , B_5H_9 , B_6H_{10} etc. Boranes of B_nH_{n+6} type are B_4H_{10} , B_5H_{11} , B_6H_{12} etc.
12. Trihalides of boron are electron deficient compounds and are Lewis acids, since they accept lone pair of electrons from donor atoms.
13. All these elements form oxides of the type M_2O_3 and hydroxides of the type $M(OH)_3$. The basic character of oxides and hydroxides increases from B to Tl.
14. Boron differs from other members of the Group 13 elements. All compounds of boron are covalent. B^+ ion does not exist. It has greater tendency to accept electrons in comparison to other elements of the group. Boron does not exhibit inert pair effect.
15. Boron, the first element of Group 13 has many similar properties with those of silicon, the second element of group 14. This is due to the *diagonal relationship* between B and Si.

16. Some important common chemical properties of Group 13 elements are as follows.
(M = element of Group 13)
- $2M + 3X_2 \longrightarrow 2MX_3$ (X=F, Cl, Br, I)
 - $4M + 3O_2 \longrightarrow 2M_2O_3$
 - $2M + 3Y \longrightarrow M_2Y_3$ (Y=S, Se, Te)
 - $2M + N_2 \longrightarrow 2MN$
 - $2M + 6H^+ \longrightarrow 2M^{3+} + 3H_2$ (With Al, Ga, In)
17. Gallium is one of the rarest elements and used as a thermometric liquid for high temperature thermometers.
18. Since thallium salts have high refractive index these are used in the making of optical glasses like Crookes glass.
19. Boron is an important semimetal and its electrical conductivity is very low and increases with increase in temperature. Boron steels are used as control rods in atomic reactors. Metal borides are also used as control rods since they absorb neutrons.
20. Boron mainly occurs as **borax** ($Na_2B_4O_7 \cdot 10H_2O$)
21. **Boranes** are covalent hydrides of boron. Since boranes are inflammable and liberate considerable amount of energy during combustion, these are considered as possible rocket fuels.
22. **Borax**, $Na_2B_4O_7 \cdot 10H_2O$ is the most important compound of boron. It is sodium tetraborate decahydrate. It is a white crystalline solid, gets hydrolysed to give boric acid H_3BO_3 . Borax has numerous uses in metallurgical operations, making optical glasses and pyrex glass, leather industry, medicine etc.. Borax is also used in borax bead test to detect basic part (cations) of coloured salts.
23. **Boric acid or Orthoboric acid**, H_3BO_3 is an important compound of boron. It is soft pearly-white needle like crystals prepared from borax. It is used in medicine as an antiseptic and eye-wash. It is used in food preservation, pottery and pigment.
24. Some important ores of aluminium are **Bauxite**, $Al_2O_3 \cdot 2H_2O$, **Corundum**, Al_2O_3 , **Cryolite**, Na_3AlF_6 and **Alunite**, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$.
25. Aluminium and its alloys are extensively used in construction of aircraft, railway coach, bus bodies, utensils etc. Also aluminium wires are used in transmission cables.
26. Aluminium metal is used to prepare metals like Cr, Mn etc. by reducing their oxides in the process called **thermite welding (Alumino-thermic process)**.
27. **Potash alum** is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.
32. Alums are used as mordant in dyeing and calico printing. It is used for purifying drinking water and tanning leather.

QUESTIONS

A. Very short answer type. (1 mark each)

1. Write the formula of orthoboric acid.
2. What is borax ? Give one use of borax.
3. Name one important ore of aluminium and its composition.
4. Name any two elements of group 13.
5. Write the formula of cryolite.
6. Complete the equation: $\text{Al}_2\text{O}_3 + \text{NaOH} \longrightarrow \dots + \text{H}_2\text{O}$
7. Between boron and aluminium, which metal has a higher value of atomic radius ?
8. What is borax bead test ?
9. Aluminium oxide is _____
(neutral oxide, acid oxide, basic oxide, amphoteric oxide)
10. Which one of the following is an ore of aluminium ?
(i) Haematite (ii) Bauxite (iii) Dolomite (iv) Cuprite
11. What happens when orthoboric acid is heated ?
12. Write the formula of orthoboric acid.

B. Short answer type. (2 marks each)

1. How is orthoboric acid prepared ?
2. What happens when orthoboric acid is heated ?
3. What is borax ? Write two uses of borax.
4. Write the preparation of orthoboric acid from borax.
5. To which block of the periodic table B and Al belong ? Explain why.
6. What happens when aluminium hydroxide is treated with sodium hydroxide solution ?
7. Name two ores of aluminium.
8. Complete the equation $\text{NaAlO}_2 + 2\text{H}_2\text{O} \longrightarrow$
9. Write the balanced chemical equation for the following:
On heating, borax first swells forming anhydrous borax and then changes to metaborates and boron trioxide.
10. Which of the cations Mg^{2+} and Al^{3+} is smaller ? Give reason.
11. Write a note on orthoboric acid.
12. What happens when borax is heated ?
13. Give reactions to show that aluminium is an amphoteric element.
14. Why boron trifluoride is called electron deficient compound ? Explain

C. Short answer type : (3 marks each)

1. Why boron halides do not exist as dimers while AlCl_3 exists as Al_2Cl_6 ?
2. BCl_3 is trigonal planar while AlCl_3 is tetrahedral in dimeric state. Explain.
3. Why BBr_3 is a stronger Lewis acid as compared to BF_3 though fluorine is more electronegative than bromine.

(Hint : In BBr_3 , the size of $4p$ -orbital of Br containing the lone pair of electrons is much bigger than the empty $2p$ -orbitals of B and hence donation of lone pair of electrons of Br to B does not occur to any significant extent. So electron deficiency of B in BBr_3 is much higher than that of BF_3 . Hence it is a stronger Lewis acid.)

D. Long answer type : (7 marks each)

1. Write general trends in properties of the group IIIA elements (Boron family). How borax is prepared ? Mention one of its uses.
2. Write notes on (3.5 marks)
 - (i) Aluminothermic process
3. Discuss the similarities and dissimilarities between boron and aluminium.

E. Explain the following:

1. Boron has high m.p and b.p.
2. Boron does not form B^{3+} ion.
3. AlCl_3 forms a dimer but BCl_3 does not form dimer.
4. Boron and aluminium halides behave as Lewis acids.
5. Aluminium is stable in air and water.
6. No visible reaction occurs when aluminium is left in contact with concentrated nitric acid.
7. Aluminium containers can be used to store conc. HNO_3 .
8. Aluminium vessels should not be cleaned with cleaning agent containing washing soda.
9. Aluminium metal is frequently used as reducing agent for the extraction of metals such as Cr, Mn, Fe etc.
10. The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other.
11. Aluminium hydroxide is amphoteric. Why ?
12. Why aluminium chloride is not ionic ?
13. AlCl_3 is a Lewis acid, explain.

MULTIPLE CHOICE TYPE

F. Select the correct answer :

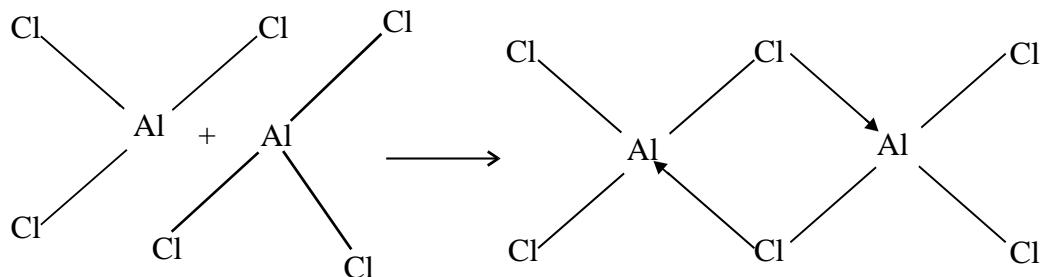
1. Which of the following is a p-block element ?
 - a) Magnesium
 - b) Aluminium
 - c) Sodium
 - d) Neon
2. Borax on heating with cobalt oxide forms a bead of
 - a) $\text{Co}(\text{BO}_2)_2$
 - b) CoBO_2
 - c) $\text{Co}_3(\text{BO}_3)_2$
 - d) No reaction
3. The product formed in the reaction, $\text{BCl}_3 + \text{H}_2\text{O} \longrightarrow$ is
 - a) $\text{H}_3\text{BO}_3 + \text{HCl}$
 - b) $\text{BO}_3 + \text{HOCl}$
 - c) $\text{B}_2\text{H}_6 + \text{HCl}$
 - d) No reaction
4. Which of the following is not an ionic trihalide ?
 - a) AlF_3
 - b) BF_3
 - c) InF_3
 - d) GaF_3
5. In which of the following, +1 oxidation state is stabler than +3 ?
 - a) Ga
 - b) Al
 - c) Tl
 - d) B
6. Boron carbide, B_4C is widely used in _____.
 - a) Making plaster of paris
 - b) Making boric acid
 - c) As a hardest substance after diamond
 - d) Making acetylene
7. One that marks the paper like lead is _____.
 - a) Ga
 - b) B
 - c) Ti
 - d) Tl
8. Which is used in high temperature thermometry ?
 - a) Na
 - b) Tl
 - c) Hg
 - d) Ga
9. The two type of bonds present in BH are covalent bond and _____.
 - a) Hydrogen bridge bond
 - b) Co-ordinate bond
 - c) Ionic bond
 - d) None.
10. Borax bead test is responded by
 - a) divalent metals
 - b) metals which form coloured metaborates
 - c) light metals
 - d) heavy metals
11. Alumina is
 - a) Acidic
 - b) Basic
 - c) Amphoteric
 - d) Neutral

(CHSE, 1988S)
12. Which metal is protected by layer of its own oxide ?
 - a) Al
 - b) Ag
 - c) Au
 - d) Fe
13. Aluminium forms
 - a) Electrovalent compounds only
 - b) Covalent compounds only
 - c) Electrovalent and covalent compounds both
 - d) Coordinate compounds only.

14. Which of the following metals burns in air at high temperature with the evolution of much heat ?
a) Cu b) Hg c) Pb d) Al
15. Which metal is powdered, suspended in oil and used as a paint for mirrors ?
a) Fe b) Sn c) Ag d) Al
16. Aluminium deposited as vapour on glass forms a good mirror, essentially because :
a) Coating is much smoother b) It does not tarnish in air
c) It has better shine than silver d) It does not scratch
17. The most covalent aluminium halide is
a) Aluminium fluoride b) Aluminium chloride
c) Aluminium bromide d) Aluminium iodide
18. Which of the following compounds can make cloth fire proof ?
a) Ferrous sulphate b) Aluminium sulphate
c) Cuprous sulphate d) Magnesium sulphate
19. Aqueous solution of borax is
a) neutral b) faintly acidic c) alkaline d) strongly acidic
20. The blue coloured minerals '**Lapis Lazuli**' which is used as a semi precious stone is a mineral of the following class.
a) Sodium aluminium silicate b) Boron trioxide
c) Zinc cobaltite d) Basic copper carbonate
21. Which of the following is an ore of aluminium:
a) Haematite b) Bauxite c) Dolomite d) Cuprite
22. The structure of diborane (B_2H_6) contains
(a) four 2c–2e bonds and two 3c–2e bonds.
(b) two 2c–2e bonds and four 3c–2e bonds.
(c) two 2c–2e bonds and two 3c–2e bonds.
(d) four 2c–2e bonds and four 3c–2e bonds.
23. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively
(a) sp^2 and sp^2 (b) sp^3 and sp^3
(c) sp^3 and sp^2 (d) sp^2 and sp^3
24. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in
(a) exhibiting maximum covalency in compound.
(b) exhibiting amphoteric nature in their oxides
(c) forming covalent halides.
(d) forming polymeric hydrides.

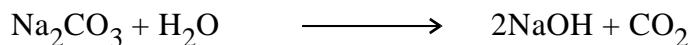
ANSWERS

- A. 1) H_3BO_3
 2) Sodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. Borax is used in making optical glasses and borosilicate (pyrex) glass which is resistant to heat and shock.
 3) Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.
 4) Boron and aluminium.
 5) Na_3AlF_6 or $\text{AlF}_3 \cdot 3\text{NaF}$
 6) $\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$
 7) Aluminium
 8) Refer Text.
 9) amphoteric oxide
 10) Bauxite
 11) B_2O_3
 12) H_3BO_3
- D. 1. Boron has very high mp. and b.p. because it exists as a giant covalent, polymeric structure both in solid as well as in liquid state.
 2. Boron has small size and high ionisation energy for which it is very difficult to remove three electrons to form B^{3+} ion.
 3. AlCl_3 forms dimer by completing octet of Al accepting electron pairs.



4. Both boron and aluminium atoms in their halides are electron deficient.
 5. Aluminium reacts readily in air and water at ordinary temperature to form protective layer of its oxide which protects it from further action.
 6. Aluminium becomes passive due to coating of Al_2O_3 when comes in contact with conc. HNO_3 and becomes inert for further action.
 7. Aluminium in contact with conc. HNO_3 becomes passive due to the coating of Al_2O_3 on it. Therefore aluminium containers can be used to store conc. HNO_3 .

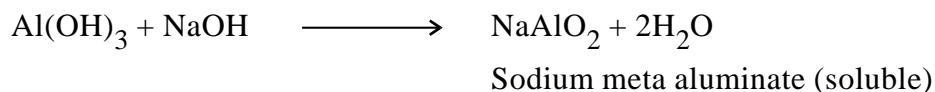
8. Washing soda, Na_2CO_3 reacts with water to form NaOH and aluminium dissolves in sodium hydroxide.



9. Al has greater affinity for oxygen and thus it reduces a large number of less electropositive metal oxides to metals.



10. Al(OH)_3 gets dissolved in sodium hydroxide whereas Fe(OH)_3 is insoluble in NaOH.



11. Al(OH)_3 reacts with acid as well as base to give corresponding salts.

12. Refer text.

13. Refer text.

E.	1) b	2) a	3) a	4) b	5) c	6) c
	7) d	8) d	9) a	10) b	11) c	12) a
	13) c	14) d	15) d	16) b	17) d	18) b
	19) c	20) a	21) b	22) a	23) d	24) a



CHAPTER - 15

THE CARBON FAMILY

(GROUP 14 ELEMENTS)

The carbon family comprises of the elements Carbon, Silicon, Germanium, Tin and Lead. These elements belong to group 14 of the periodic table. Carbon and silicon are non-metals. Germanium is a metalloid since it shows both nonmetallic and metallic properties. Tin and Lead are well known metals.

15.1 ELECTRONIC CONFIGURATIONS :

The atomic numbers and electronic configurations of the elements are given below :

Table 15.1 Electronic configurations of the elements of carbon family

Element	Symbol	Atomic number	Electronic Configuration	Oxidation states
Carbon	C	6	[He] 2s ² p ²	4
Silicon	Si	14	[Ne] 3s ² 3p ²	4
Germanium	Ge	32	[Ar] 4s ² 4p ²	2 4
Tin	Sn	50	[Kr] 4d ¹⁰ 5s ² 5p ²	2 4
Lead	Pb	82	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	2 4

15.2 OCCURRENCE :

Carbon occurs in nature in free state as diamond, graphite and coal. Coal and graphite are mined in large quantities. Diamond is mined in extremely small quantities. In combined state carbon occurs in large quantities in crude oil and metal carbonates such as lime stone CaCO_3 , magnesite MgCO_3 and dolomite $\text{MgCO}_3 \cdot \text{CaCO}_3$. Carbon dioxide occurs in small amounts in the atmosphere and plays the vital role in the carbon cycle in photosynthesis and respiration. Again, we know that carbon is the most essential constituent of all organic compounds.

Silicon is the second most abundant element by weight in earth's crust. Silicon occurs very widely as silica SiO_2 in the form of sand and quartz. Silicon is also present in large varieties in silicate minerals and clays. Germanium is available in traces in some silver and zinc ores and in some types of coal.

Tin is present in its important ore tinstone or cassiterite SnO_2 . Lead occurs in its ore galena (PbS).

15.3 GENERAL CHARACTERISTICS OF THE ELEMENTS :

Physical properties :

Some of the important physical properties of the elements are given in Table 15.2 below.

Table 15.2 Physical properties of the elements of group 14

Element	Atomic mass	Atomic radius	Density gm/cc	M.P K	B.P K	Ionisation energy KJ/mol	Electronegativity
C	12	0.77	2.22	853	5100	1086	2.5
Si	28	1.15	2.33	1673	2950	787	1.74
Ge	72.6	1.22	5.32	1210	3103	460	2.00
Sn	118.7	1.41	5.75	505	2960	707	1.70
Pb	207.2	1.47	11.35	600	1990	715	1.55

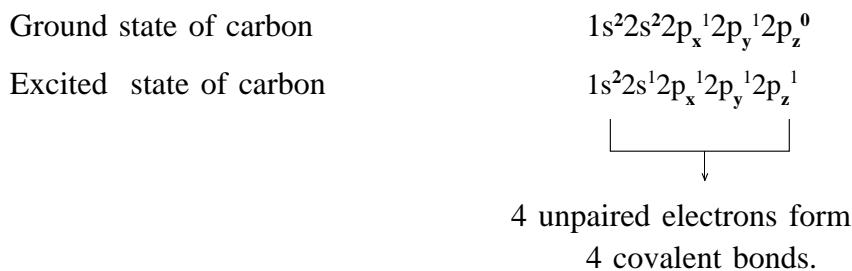
- Atomic radius:** Atomic radii of elements increase with increase in atomic number as expected. This is due to successive addition of new orbits.
- Density :** The density of elements gradually increases with increase in atomic number.
- Melting and Boiling points :** The melting point as well as boiling point of carbon, the first element are exceedingly high. However, within the group the value gradually decreases with increase in atomic number. The melting points of Sn and Pb are relatively low.
- Ionisation energy :** All these elements have high ionisation energies. Ionisation energy of carbon is very high due to its small size. In case of carbon the valence electrons are strongly held by nucleus and more energy is required to remove a valence electron. Again there is a sharp decrease in ionisation energy from carbon to next element silicon. That is due to an appreciable increase in size of silicon atom. There is however, a very small decrease in ionisation energy as we move from Si to Sn. In case of Ge and Sn, there are the presence of 'd' electrons in the inner configuration which shield the nuclear charge less effectively than is done by 's' and 'p' electrons for silicon atom. In case of Pb there are 'f' electrons in the inner configuration and shield the nuclear charge less effectively than 'd' electrons. And hence the ionisation energy of Pb, instead of decreasing, shows marginal increase.
- Electronegativity :** Carbon is the most electronegative element of this group. The electronegativity values decrease from carbon to silicon and thereafter no regularity is observed. This appears to be due to the filling of d - orbitals in the case of germanium and tin and also f- orbitals in the case of lead.

- 6. Metallic and nonmetallic characters :** Since the ionisation energy decreases on descending the group, the metallic character increases. Carbon and silicon are nonmetals. Germanium exhibits both nonmetallic as well as metallic character and hence it is a semimetal. Tin and lead are metals. The metallic behaviour of these elements are reflected in their chemical properties also. The increased tendency to form M^{2+} ion and decrease in acidic character or increase in basic character of their oxides and hydroxides explains their metallic character.

15.4 **OXIDATION STATES :**

All these elements belong to p Block having ns^2np^2 general electronic configuration in the outermost shells of their atoms. Due to the presence of four electrons (two s electrons and two p electrons) in their valence shells, they all exhibit valency four corresponding to +4 oxidation state. Besides, the elements show +2 oxidation state for the presence of two electrons in their outermost 'p' orbital. Silicon exhibits unstable +2 oxidation state. Germanium and tin have well characterised +2 oxidation states. Lead shows stable +2 oxidation state.

Chemical properties : Majority of the compounds of group 14 elements are tetravalent. In this case all four outermost electrons participate in bonding. Promotion of electrons from the ground state to an excited state is followed by sp^3 hybridisation resulting in a tetrahedral structure.



From the ground state one 's' electron is promoted to the 'p' orbital and then the four unpaired electrons in the excited state occupy four sp^3 hybrid orbitals resulting in four equivalent bonds tetrahedrally directed.

The high values of their ionisation potential do not favour M^{4+} oxidation state. The elements do not also form M^{4+} ion for their low electronegativity. However, germanium, tin and lead show M^{4+} and M^{2+} oxidation states. On descending the group, the +2 oxidation state is more stable than the +4 oxidation state. The stability of M^{2+} ion is more than that of M^{4+} ion and this is due to **inert pair effect**. The inert pair effect is more prominent in the heavier elements. In such cases only the two outermost unpaired p electrons take part in bonding and the outermost paired s electrons do not. The tendency of non-participation of the paired s electrons in bond formation is known as **inert pair effect**. The last three elements Ge, Sn and Pb have a tendency to form M^{2+} ions as well as M^{4+} ions. However, they prefer to form M^{2+} ions. Thus, Sn^{2+} and Pb^{2+} exist as stable ions and are more common than Sn^{4+} and Pb^{4+} ions.

Again, Sn (IV) and Pb (IV) compounds are more covalent than ionic in nature as expected from **Fajan's rule**. According to Fajan's rule, the smaller the ions, the greater is its

tendency towards covalency. Sn^{4+} and Pb^{4+} ions have much smaller radii than Sn^{2+} and Pb^{2+} and thus they tend to form covalent compounds.

15.5 GENERAL TRENDS IN THE CHEMICAL PROPERTIES OF THE ELEMENTS :

Hydrides : All the elements form volatile covalent hydrides with hydrogen. The formation of number of hydrides and their stability decrease from carbon to lead. Carbon with hydrogen forms a series of aliphatic hydrocarbons alkane. C_nH_{2n+2} , alkene C_nH_{2n} and alkyne C_nH_{2n-2} . It also forms aromatic hydrocarbons, for example benzene C_6H_6 and its derivatives. Carbon forms alkane C_nH_{2n+2} i.e. CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} etc. The number of hydrides is less for silicon and they are silanes, SiH_4 , Si_2H_6 etc, the germanium hydrides or germesanes are similar to silicon hydrides. Stannane SnH_4 and Plumbane PbH_4 are only hydrides of tin and lead and they are difficult to prepare.

Oxides : All the elements form two types of oxides. They are monoxides and dioxides. The **monoxides** are CO, SiO, GeO SnO and PbO.

All these elements form **dioxides** of the general formula MO_2 . The acidic properties of their dioxides decrease down the group. Carbon dioxide CO_2 and silica SiO_2 are acidic. Germanium dioxide GeO_2 is less acidic than SiO_2 . Tin dioxide SnO_2 and lead dioxide PbO_2 are amphoteric having both acidic and basic characters.

Halides : All elements of this group form tetrahalides of the type MX_4 which are covalent and tetrahedral. The stability of tetrahalides decreases on moving down the group from carbon to lead. The tetrahalides of all these elements except carbon are hydrolysed by water.

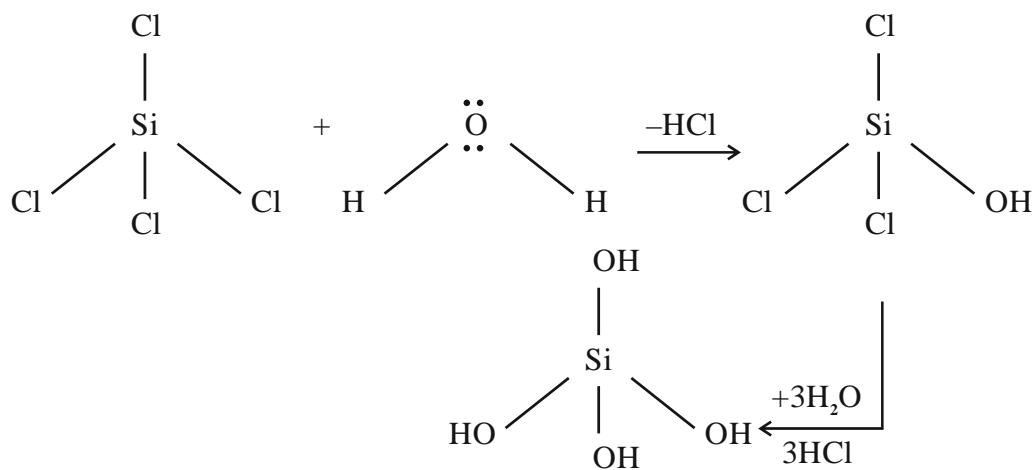
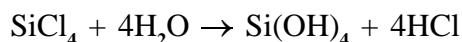


Fig. 15.1 : Structure of Silicic Acid

In the presence of excess acids, the halides of all elements except carbon form complexes. Carbon halides do not form complexes because of absence of vacant d - orbitals in carbon. Complex formation with other halides take place due to the presence of vacant d - orbitals of the group elements.

Ex : SiF_6^{2-} , $[\text{GeCl}_6]^{2-}$, $[\text{Sn}(\text{OH})_6]^{2-}$ etc. Here central atom is sp^3d^2 hybridised.

All these elements are known to form dihalides of the type MX_2 . The stability of halides increase down the group. Carbon dihalides are highly unstable whereas SnCl_2 and PbCl_2 are quite stable.

15.6 ANOMALOUS CHARACTER OF CARBON :

Carbon differs considerably from other members of the group due to its small size, high ionisation energy and maximum electronegativity.

- (i) It is the hardest element and has highest melting and boiling points.
- (ii) Carbon exhibits maximum covalency of four, whereas other members of the group can extend their covalency beyond four by using their vacant d - orbitals.
- (iii) Carbon does not form complex compounds due to the absence of the vacant d - orbitals.
- (iv) It has unique ability to form multiple bonds such as
 $\text{C} = \text{C}$, $\text{C} \equiv \text{C}$, $\text{C} = \text{O}$, $\text{C} = \text{S}$ and $\text{C} \equiv \text{N}$.

15.7 CARBON : CATENATION

Carbon has marked tendency to form long chains. This property is called **catenation** or self-linkage. Catenation is the tendency of an element to form long chains of identical atoms. Among the group 14 elements carbon has maximum tendency for catenation. The tendency for catenation decreases down the group. Sn and Pb hardly have this tendency. Carbon having this remarkable property forms thousands of organic compounds in which carbon atoms are bonded to each other.

Comparison of carbon and silicon : Carbon and silicon, the typical elements of Group 14 are very much similar in properties and compounds. These two elements have some points of similarity in occurrence, electronic configuration and tetracovalency, nonmetallic character, tendency for catenation and formation of similar compounds.

There are marked similarities between compounds of carbon and silicon as shown below.

Table 15.3 Formation of similar compounds.

Compounds	Carbon	Silicon.
Dioxides	CO_2 is acidic, formed by burning C with oxygen.	SiO_2 is acidic, formed by burning Si with oxygen.
Acids	Carbonic acid, H_2CO_3	Metasilicic acid H_2SiO_3
Hydrides	Methane CH_4 , Ethane C_2H_6	Silicomethane SiH_4 , Silico ethane Si_2H_6
Halides	Carbon tetrachloride CCl_4	Silicontetrachloride SiCl_4
Other compounds	Chloroform CHCl_3	Silico-chloroform SiHCl_3

These two elements also differ from each other in many respects as given below. (table - 15.4)

Table.15.4 Difference between carbon and silicon.

Property	Carbon	Silicon.
Valency	Shows maximum covalency of 4. Therefore, forms more stable compounds.	Shows maximum covalency of six and thus silicon compounds are comparatively unstable.
Conductivity	Some varieties of carbon are good conductors of electricity	Bad conductors of electricity.
Melting point	Does not melt at all. M.P. is very high 3773 K.	Comparatively low M.P. 1673 K
Nature of hydrides	Hydrocarbons e.g. CH_4 and C_2H_6 . These are very stable	SiH_4 comparatively less stable
Action with O_2	CO and CO_2 are gases	SiO_2 is a solid
Action with alkalis	No action with alkalis.	Liberates hydrogen when reacts $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2$
Nature of hydrolysis of halides	Carbon tetrachloride and chloroform are stable liquids and are not hydrolysed easily by water	SiCl_4 is easily hydrolysed by water $\text{SiCl}_4 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_3 + 4 \text{ HCl}$

15.8 ALLOTROPES OF CARBON :

Different structural forms of the same element show allotropy .

The allotropic forms or allotropes have same chemical properties but different physical properties.

Carbon exists in different allotropic forms. There are three allotropic forms of carbon.

- (1) Diamond (2) Graphite (3) Amorphous carbon.

Diamond and graphite belong to crystalline variety. Amorphous type of carbon includes charcoal, coke, lamp black, gas carbon etc. Again charcoals are of many types. These are wood charcoal, sugar charcoal and animal charcoal. Blood charcoal and bone charcoal belong to the category of animal charcoal.

Table 15.5 Comparison of physical properties among allotropic forms of carbon.

Property	Diamond	Graphite	Amorphous carbon
Colour	Colourless	Dark grey	Black
Appearance	Transparent	Lustrous	Opaque
Specific gravity	Cystalline	Soapy touch	
Purity	3.5	2.5	1 to 1.5
Hardest	100%	95 –99%	60 – 90%
Electrical conductivity	Hardest	Soft and marks paper	Hard (Lamp black is soft)
	Bad conductor	Good conductor	Bad conductor
			(Gas carbon is a good conductor)

15.8.1 Diamond Structure :

Ocurrence : Diamond occurs native in nature. In India it is mined from Golconda mines. It is mined from Kimberley mines in South Africa. South Africa supplies about 90% of the world production of diamond. Australia and South America have also diamond mines.

Natural diamond varies in size, colour and lustre. The cost of diamond depends upon its lustre, colour and size. The weight of diamond is measured in carats. One carat weighs 0.2054 gram. Cullinan, the largest diamond, weighs about 3026 carats. The following are some well known varieties of diamond.

Diamond	Weight in Carat
Cullinan	3026
Excelsier	97.2
Hope	44.6
Kohinoor	11.6

Preparation of artificial diamond :

In 1896, Moissan first prepared diamond by heating iron with sugar charcoal (carbon) in a graphite crucible in an electric furnace at a temperature of about 3300 K. At this condition molten iron dissolved most of the carbon. The crucible was then taken out and dipped into molten lead at 600K. During the process the outer layer of iron solidified due to such sudden cooling and expanded. Iron, on expansion, exerted a great pressure on the interior liquid mixture and converted it to solid. The carbon at such high pressure was converted to diamond crystals and emerged out of the solution mixture. The diamond crystals and graphite were washed with hydrochloric acid to dissolve iron. Finally diamond was separated from graphite.

Structure : Diamond is a three - dimensional polymer consisting of a large number of carbon atoms tetrahedrally arranged. The structure of diamond was established by X - ray diffraction studies. In diamond each carbon atom lies at the centre of a regular tetrahedron and is linked to four surrounding carbon atoms lying at the corners of the tetrahedron. The carbon atoms are bound to each other by sp^3 hybridised covalent bonds. Since all the carbon atoms are joined tetrahedrally the resulting structure becomes a giant **hexagonal structure** containing a series of interlocking hexagons.

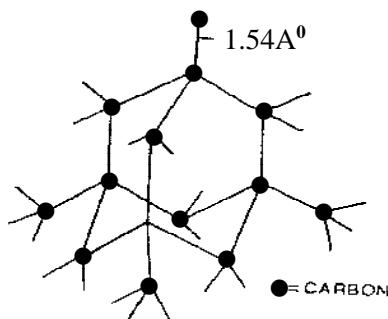


Fig 15.2 : Structure of diamond

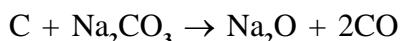
In diamond the C - C bond distance is 1.54 \AA^0 , each bond angle is $109^{\circ}28'$. Due to short bond distance a large amount of energy is required to break the bonds. Therefore diamond is very hard and melts at about 3800 K. During the formation of four equivalent sp^3 hybridised bonds around each carbon atom, all the four outermost valence electrons of carbon are utilised. There are neither free electrons nor any vacant orbital present for the migration of electrons and therefore diamond is a non-conductor of heat and electricity.

Chemical properties : Diamond is chemically inert, does not react under ordinary condition. Due to its compact structure, it is less prone to chemical attack.

1. When heated in presence of oxygen at 1180 K, diamond forms CO_2 without leaving any residue which shows that it is 100% carbon . $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
2. It is oxidised to carbon dioxide when heated with potassium dichromate and concentrated



3. When fused with Na_2CO_3 diamond is converted to carbon monoxide



Uses :

1. Diamond is used as a valuable decorative gem since it has a high refractive index 2.45 and reflects any amount of light that falls on it. This property attributes to the bright lusture of diamond. It is measured in carats (1 carat = 200 mg)
2. Black diamonds such as **Carbonado** and **Bort** are used for cutting glass, marble stones and other gems. It is also used for cutting, grinding and polishing hard materials.
3. Diamond is used in making rock drills and diamond dust is used as an abrasive in polishing colourless stones.
4. Diamond dies are used to draw wires of tungsten filaments for electric lamps.

15.8.2 Graphite :

Graphite, also called Black lead or Plumbago is found widely distributed in nature. It occurs as a soft grey or black mineral in countries like USA, Canada, India, Cylone, Italy and Siberia.

Manufacture of artificial graphite (Acheson Process)

Graphite is obtained from coke or anthracite by heating with sand in heat resistant electric furnace fitted with two carbon electrodes connected by thin carbon rods. The charge is covered with a mixture of carbon and sand. On passing alternating current through the carbon rods a temperature of 3775 K is produced. The temperature is maintained for 30 hours.

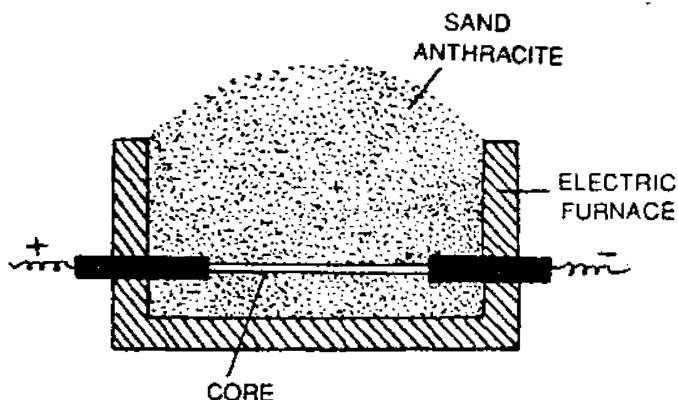
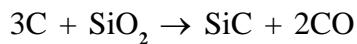
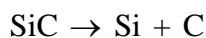


Fig 15.3 Manufacture of artificial graphite.

During the process silicon carbide is formed first, but it decomposes at high temperature of the arc into graphite and silicon.



Coke



Structure : Graphite forms a two dimensional sheet like polymeric structure.

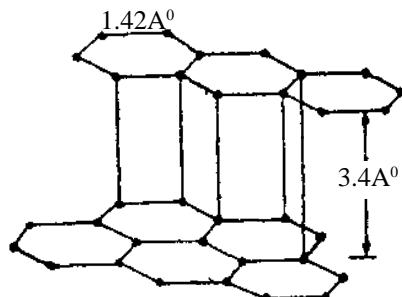


Fig 15.4 Structure of graphite.

Chemical properties :

1. Graphite is chemically inactive and is not affected by dilute acids and alkalies.
2. It burns in oxygen to form CO_2 .
3. It is slowly oxidised to CO_2 by chromic acid.
4. It is oxidised by concentrated HNO_3 to give insoluble yellowish green graphitic acid, $\text{C}_{11}\text{H}_4\text{O}_5$.
5. When fused with Na_2CO_3 it forms CO.
6. Fluorine attacks graphite forming $(\text{CF})_n$

In graphite each carbon atom is bonded to three other neighbouring carbon atoms through sp^2 hybridised sigma(σ) covalent bonds. The fourth unhybridised orbital of each carbon atom containing one electron may laterally overlap on the similar orbital of each neighbouring carbon atom to form pi (π) bond. These π electrons are delocalised and are free to move under the influence of heat and electricity. Thus, **graphite is a good conductor of heat and electricity.**

The carbon atoms in graphite are arranged in a number of layers composed of hexagonal planar rings. The C - C bond distance 1.42 \AA^0 being short indicates strong bonding. Each layer may be regarded as a fused system of benzene rings. These account for the stability of graphite, with each layer of carbon atoms being firmly bonded by strong covalent bonds. Therefore the melting point of graphite is quite high, 3775 K .

The different layers in graphite are held together by relatively weak van der Waals forces and are about 3.4 \AA^0 apart (in comparison to short C - C bond distance) for which one layer slides over the other. And therefore graphite is quite soft, cleaves easily between the layers and exhibits lubricating properties.

Graphite is chemically inert. It is slightly more reactive than diamond. Due to its more open structure it is more prone to chemical attack as compared to diamond.

Uses : Graphite is used in :

1. Making lead pencils. Here powdered graphite and clay are pressed into sticks.
2. Making electrodes for electric furnace and refractory crucible.
3. As a good lubricant for machine parts subjected to high temperature.
4. Electrotyping i.e making type.
5. As a pigment in paint.
6. Nuclear reactors make use of graphite rods as moderators to slow down the high energy neutrons.
7. Making synthetic diamond when heated at 1880 K by a pressure of $50,000 - 60,000$ atmospheres.

15.8.3 Recently discovered allotrope of carbon : Fullerenes :

Smalley and Curl of U.S.A and Kroto of U.K. discovered a third crystalline allotrope of carbon in 1985 and named it as Fullerene in honour of Dr. R. Buckminster Fuller, an American Engineer who invented the famous 'Geodesic dome', because this molecule resembles the structure of the geodesic dome-a soccer ball-like structure. Fullerene does not mean a separate molecule or cluster, rather all the members of a special class of carbon clusters. So, it is better to call them together as Fullerenes and term the individual molecules as C_{60} fullerene, C_{70} fullerene etc. depending upon the number of carbon atoms present in each molecule. The most abundant fullerene C_{60} is also called 'bucky ball' because of its football like structure.

Preparation : C_{60} and C_{70} fullerenes were first prepared in 1985 by Smalley, Curl and Kroto. Carbon was vapourised by directing an intense laser beam on graphite surface and allowed to cool in an inert atmosphere of helium. The carbon cluster, thus formed, was analysed and found to contain two clusters – a dominant cluster with 60 carbon atoms and another with 70 carbon atoms.

In 1991, physicists Kratschmer and Huffmann were able to produce isolable quantities of C_{60} and C_{70} fullerenes by heating graphite rods in an electric arc in a low pressure helium atmosphere and extracting the soot in an organic solvent.

Structure : Among the members of the fullerene family, C_{60} is the stable one and hence abundant due to its perfect symmetrical structure, the relative position of each and every carbon being identical to that of other 59 carbon atoms. The structures of all the members are made up of combination of pentagons and hexagons. For example, in C_{60} fullerene 12 pentagons and 20 hexagons have combined to give rise to a perfect football-like structure. (Fig. 15.5)

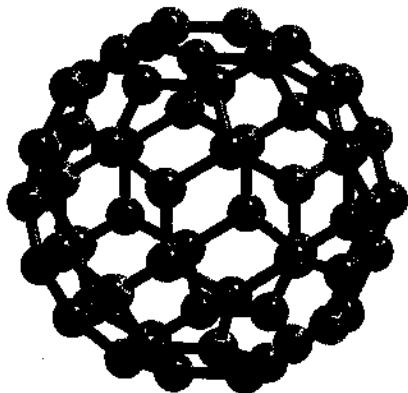


Fig. 15.5 Bucky ball

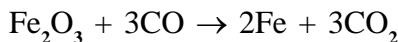
Properties : After diamond and graphite, the 'bucky ball' is deemed to be the third crystalline allotrope of carbon. Unlike diamond and graphite, which are actually infinite network solids, the fullerenes are finite with no free bond existing in them. Bucky ball is considered to be the **purest form of carbon**. In the pure state it is an insulator, but can be suitably converted to semiconductors and even superconductors. Fullerene compounds (fullerides or buckides) can be used for the betterment of mankind and therefore fullerene research has got tremendous potentialities.

- Uses:**
1. Fullerides or buckides can be used as semiconductors and superconductors.
 2. Buckyball's ability to trap different atoms or molecules has successful application in medical and biomedical fields. Radioactive isotope encapsulated C_{60} can be used in cancer therapy and AIDS therapy.
 3. Fullerenes can improve antiwear, antiseize, antifriction properties of lubricating oil.
 4. Catalytic amounts of fullerene can be used in petrochemical refining industries.

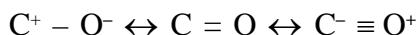
15.9 SOME IMPORTANT COMPOUNDS OF CARBON

15.9.1. Carbon monoxide CO is a poisonous gas, sparingly soluble in water and neutral in character. It is formed when carbon is burnt in a limited supply of air. **Water gas** is an equimolar mixture of CO and H₂. **Producer gas** is a mixture of CO and N₂. Coal gas is a mixture of CO, H₂, CH₄ and CO₂. All these gaseous mixtures are important industrial fuels.

Carbon monoxide is a good reducing agent and can reduce many metal oxides to the metal



Structure : The structure of carbon monoxide is represented by electron dot formula and resonance hybrid structures.

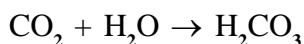


Carbon monoxide is found to be an important ligand that can donate lone pair of electron to form co-ordinate bond with many transition metals. And as a result many carbonyl complex compounds are formed, M ← C ≡ O. The highly poisonous nature of CO arises because of its ability to form a complex with haemoglobin which is about 300 times more stable than the oxy-haemoglobin complex and destroys the oxygen - carrying property of it resulting in death.

While explaining the structure of such carbonyl complexes, the electronic structure of CO has been debated. However, carbon monoxide may be represented as :



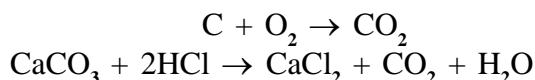
15.9.2. Carbon dioxide CO₂ is acidic in nature and dissolves in water forming carbonic acid H₂CO₃. Carbon dioxide is also called the anhydride of carbonic acid.



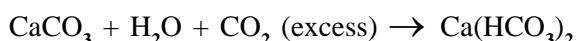
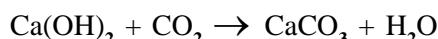
Carbonic acid is unstable but gives rise to carbonate and bicarbonate salts.

Carbon dioxide is present in the atmospheric air about 0.03 % by volume. It is also present in volcanic gases and in supersaturated solution in certain spring waters.

Carbon dioxide is obtained by burning carbon in excess of air or by the action of dilute acids on carbonate salts.



The gas when passed through lime water Ca(OH)₂ or baryta water Ba(OH)₂, white precipitate of CaCO₃ or BaCO₃ is formed. By passing excess of carbon dioxide through such solutions the corresponding soluble bicarbonates are formed.

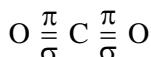


Solid carbon dioxide is known as **dry ice**. Carbon dioxide gas when solidifies under pressure, dry ice is formed. Dry ice sublimes without melting. It is used as a **refrigerant**. A mixture of dry ice and chloroform or ether can be used to maintain a very low temperature of about 196K.

Structure of carbon dioxide It is a linear molecule with zero dipole moment.

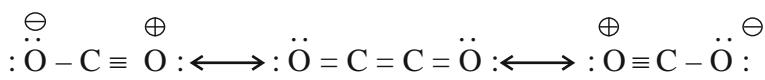
C	$\frac{\uparrow}{2(sp)}$	$\frac{\uparrow}{2(sp)}$	$\frac{\uparrow}{2p}$	$\frac{\uparrow}{2p}$
O	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow\downarrow}{2p}$	$\frac{\uparrow}{2p}$	$\frac{\uparrow}{2p}$
O	$\frac{\uparrow\downarrow}{2s}$	$\frac{\uparrow\downarrow}{2p}$	$\frac{\uparrow}{2p}$	$\frac{\uparrow}{2p}$

There are two oxygen atoms on either side of the carbon atom bound by double bonds.



Carbon has two *sp* hybrid orbitals and two unhybridised *p*-orbitals. Each of the *sp* orbitals of carbon overlaps with one *p* orbital of each oxygen atom resulting in two sigma σ bonds each disposed on each side of the carbon atom. Further, one unhybrid orbital *p* overlaps with *p* orbital of one oxygen. The other *p* orbital of carbon overlaps with the *p* orbital of the second oxygen atom. So in addition to two σ bonds, two π bonds are formed between C and two 'O' atoms ($p_{\pi} - p_{\pi}$) type.

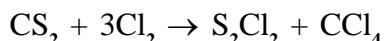
In order to explain the carbon - oxygen bond length 1.15 \AA^0 in carbon dioxide the resonance hybrid structures are also proposed. Resonance structure of CO_2 :



15.9.3. Carbon tetrachloride : It is the most important halide of carbon. Since carbon and chlorine do not combine directly, it is prepared by reacting carbon disulphide with chlorine. Carbon combines with sulphur directly at high temperature to form carbon disulphide.



Carbon disulphide liquid is treated with chlorine gas forming carbon tetrachloride.



Carbon tetrachloride is then distilled from sulphur monochloride.

Carbon tetrachloride is a colourless, non-inflammable liquid which is an important industrial solvent. It is used as a fire extinguisher and in dry washing of clothes.

Carbon tetrachloride is also used to prepare **Freons**.



Freons are mixed chlorofluoro hydrocarbons such as CFCl_3 , CF_2Cl_2 , and CF_3Cl . These are unreactive and are widely used as refrigeration fluids.

15.9.4. Carbides

Carbides are compounds of carbon with another less electronegative element than itself.

Carbides have been broadly classified into three groups depending on the nature of bonding and the consequent properties.

(i) Ionic or salt like carbides : These are carbides of strongly electropositive elements. Their structures are comparable to those of ionic compounds. Some ionic carbides are CaC_2 , Al_4C_3 , etc.

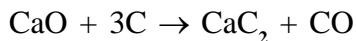
(ii) Covalent carbides : In these carbides carbon is covalently bound with an electronegative element of close electronegativity ; Examples : CH_4 , CO_2 , CCl_4 , CS_2 , SiC etc. CH_4 , CO_2 , CCl_4 , CS_2 are small molecules and have low melting and low boiling points, whereas SiC contains giant molecules with very high melting point.

(iii) Transition metal carbides or Interstitial carbides : These compounds are formed by transition elements with carbon at high temperature. Often they do not have normal composition. Small carbon atoms penetrate the crystal lattice of the metal. Examples : TiC , ZrC , WC , Mo_2C , etc. These carbides have a wide range of stoichiometries.

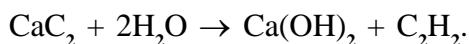
Carbides are usually obtained by heating the element or its oxide with carbon at very high temperature.

Carbides find numerous applications in industry.

Calcium carbide CaC_2 : Calcium carbide is prepared by heating lime, CaO with coke in an electric furnace.



Calcium carbide reacts with water at room temperature to produce the important gas, acetylene, C_2H_2 .



Acetylene is a very important starting material in the manufacture of a large number of organic chemicals. Acetylene is also a valuable fuel in oxy - acetylene torches.

15.10 COMPOUNDS OF SILICON

15.10.1. Silicon dioxide : Silicon dioxide is a high melting polymeric solid. It is commonly called silica and exists in three different crystalline forms : Quartz, Tridymite and Cristobalite. In nature silica occurs mostly in crystalline quartz form. Though each of these forms has a different structure basically in all these forms each silicon is bonded tetrahedrally to four oxygen atoms and each oxygen atom is common to two tetrahedra. The difference between these structures is the arrangement of the tetrahedral SiO_4 units.

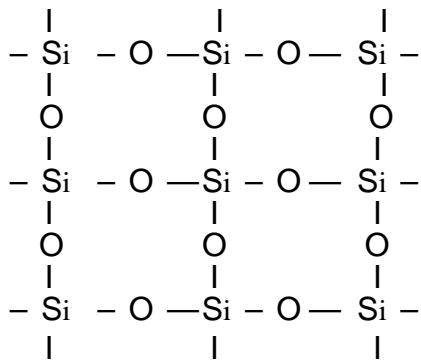
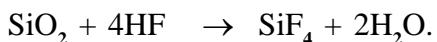


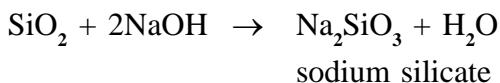
Fig. 15.6 The nature of bonding in silica.

The π bond formation in CO_2 is possible because of small size of carbon atom (9.77 \AA^0). The p -orbitals of carbon atom can approach quite closely the p -orbitals of oxygen for an effective overlap to form π bonds. Thus, carbon dioxide is a linear molecule existing in gaseous form. Such a case does not arise in SiO_2 because Si atom cannot form double bonds with oxygen due to its large size. Silicon satisfies its tetravalency by forming a three dimensional net work in which each silicon atom is bound to four oxygen atoms in a tetrahedral arrangement and therefore SiO_2 remains in solid form.

Silicon dioxide is one of the most abundant natural compounds. Molten SiO_2 when cooled does not crystallise but slowly solidifies to a glass that becomes a rigid solid with random arrangement of its atoms. This substance is the basic ingredient in manufacture of different types of glasses. Different oxides are added to SiO_2 to make varieties of glasses. Glass is amorphous in its structure. SiO_2 and glasses are not attacked by acids except hydrofluoric acid.



However, basic substances may react with silica at high temperature to form silicates.



15.10.2. Silicates and Zeolites : A large number of silicate minerals and aluminosilicate clays occur in earth's crust. These are often extremely complicated in structural pattern. Some simpler types of silicates are :

- (a) **Orthosilicates** containing SiO_4^{4-} units, tetrahedral and monomeric, example : Mg_2SiO_4 .
- (b) **Pyrosilicates** containing $\text{Si}_2\text{O}_7^{6-}$ units formed by linking two tetrahedra SiO_4^{4-} units through a common oxygen atom, example : $\text{Se}_2\text{Si}_2\text{O}_7$.
- (c) **Cyclic silicates** containing $\text{Si}_3\text{O}_9^{6-}$ units in which three SiO_4^{4-} tetrahedra are linked through three common oxygen bridges, example : $\text{BaTiSi}_3\text{O}_9$.
- (d) **Chain silicates** containing $\text{Si}_6\text{O}_{18}^{12-}$ units in which six SiO_4^{4-} tetrahedra are linked with each other through six bridging oxygen atoms, example is beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$.

Besides these above silicates, we have **sheet silicates** and **three dimensional silicates**. Sheet silicates are two dimensional in structure. Three dimensional silicates are **quartz** or Rock crystal, **Zeolite** and **Ultramarines**. Quartz is a transparent colourless crystal, electrically neutral used for making optical and chemical apparatus. Some quartz are opaque or milky. Quartz has framework structure with silicon and oxygen only, having graphite like structure. Zeolites are aluminosilicates with three dimensional structures. Zeolites like NaAlSiO_4 , $\text{NaAlSi}_2\text{O}_6$ and $\text{NaAlSi}_3\text{O}_8$ are known. These are complicated silicates which have ion exchange properties. These find use as water softening materials. Zeolites have **honeycomb** like structure that absorbs or loses certain molecules and acts as **molecular sieves**. Sodium zeolites can exchange their sodium ions for calcium ions present in hard water. Thus, they act as cation exchangers when used for softening hard water.

Sodium silicate :

Sodium metasilicate commonly known as **sodium silicate** Na_2SiO_3 is a glass. It dissolves in water and hence it is often called **water glass**. Sodium silicate with excess of sand is used to manufacture water glass for commercial uses. It is used in soaps, cleansers, in fireproofing, as an adhesive and in preserving eggs. Silicates such as asbestos or mica and silicates containing aluminium are heated with lime stone to make portland cement .

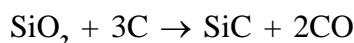
When soluble silicates are dissolved in dilute acid solutions, a hard jelly is formed. The jelly is then dehydrated to obtain a porous variety of silica known as **silica gel**.

Silica gel is used as dehumidifying agent in commercial air conditioning units and as a dehydrating agent in desiccators. It is used to recover industrial vapours since it is able to absorb gases. It is also used in the chemical industry as a catalyst.

15.10.3. Silicon Carbide, SiC

Silicon carbide SiC is among the hardest known substances. In industry it is widely used as an abrasive material under the name **carborundum**.

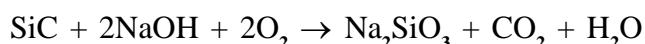
It is prepared by heating to about 3000K, a mixture of five parts silica and three parts powdered coke along with some saw dust. The saw dust keeps the mixture porous. The heating is done in an electric arc furnace between two carbon electrodes.



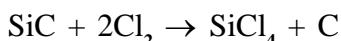
After completion of the reaction, the carborundum is washed with H_2SO_4 and then with NaOH.

Pure samples of silicon carbide are pale yellow to colourless. Sometimes it is often dark, dark purple or dark green due to traces of iron and other impurities. It is very hard, as hard as diamond and infusible.

Silicon carbide is chemically unreactive. It is unaffected by acids. However it reacts with sodium hydroxide in presence of air.



It reacts also with chlorine at about 300 K to form silicon tetrachloride.



Uses :

1. Due to its extreme hardness silicon carbide is used as an abrasive for grinding surfaces and sharpening metallic tools.
2. Used as a refractory material.
3. It is often used as semi-conductor in transistor.
4. It finds application as a container for fuel elements used in atomic reactors.

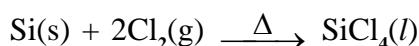
Structure :

Silicon carbide has a three dimensional structure of Si and C atoms. Each atom is tetrahedrally surrounded by four of the other kind. Its structure is similar to that of diamond.

15.10.4. Silicon Tetrachloride (SiCl_4) :

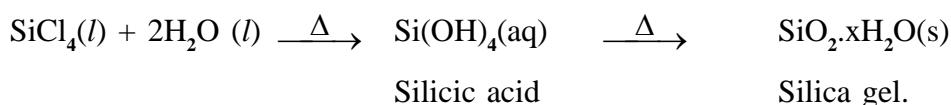
Preparation :

By heating silicon or silicon carbide with chlorine silicon tetrachloride is formed.



Properties and Uses :

It is a volatile liquid with boiling point 330.57K. Hydrolysis of SiCl_4 gives silicic acid, Si(OH)_4 which on further heating gives silica gel.



Silica gel is used as a catalyst in petroleum industry and as an adsorbent in column chromatography.

Reduction of SiCl_4 with dihydrogen gives ultrapure form of silicon which is useful for making transistors, computer chips and solar cells.



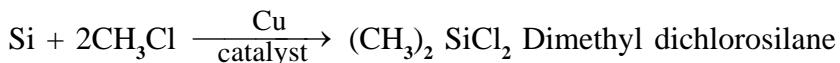
15.10.5. Silicones

Silicones are long chain organosilicon polymers.

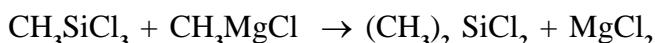
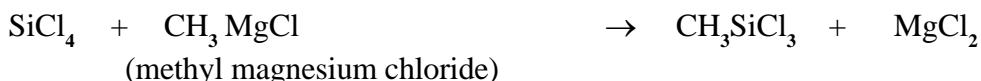
Preparation :

The preparation of silicones involves three steps. (i) Preparation of alkyl chlorosilanes (ii) Hydrolysis of alkyl chlorosilane to form alkyl hydroxy silane (iii) condensation of alkyl hydroxy silane to get long chain polymers of silicones.

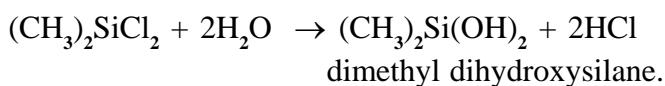
- (i) **Preparation of alkyl chlorosilane :** When silicon reacts directly with chlorinated hydrocarbons in presence of a metal catalyst alkyl chlorosilanes are prepared. For example, silicon reacts with chloromethane (methyl chloride) in presence copper catalyst to yield dimethyl dichlorosilane.



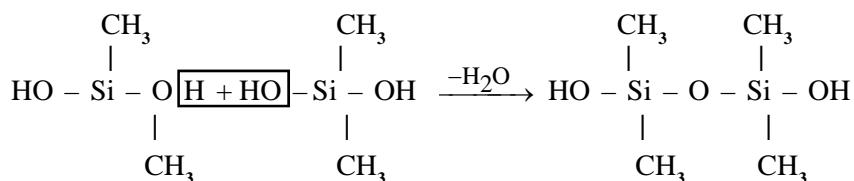
Alkyl chlorosilanes are also prepared by a Grignard's reaction.



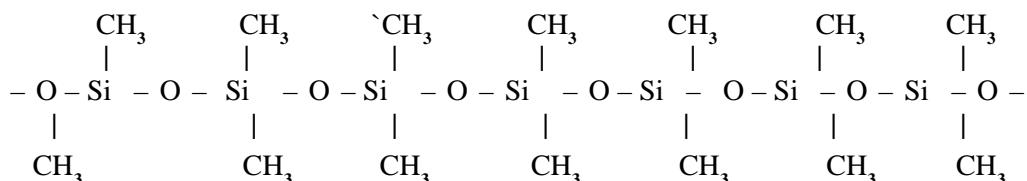
- (ii) Hydrolysis of dimethyldichlorosilane results in dimethyl dihydroxysilane



- (iii) Two molecules of dimethyl dihydroxysilane undergo condensation with elimination of one water molecule resulting in a unit containing Si – O – Si linkage.



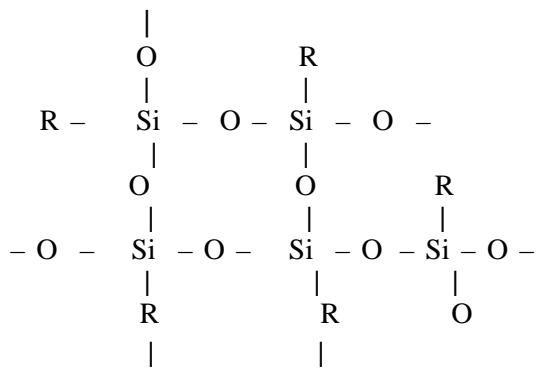
The condensation reaction can be continued to get silicone polymer.



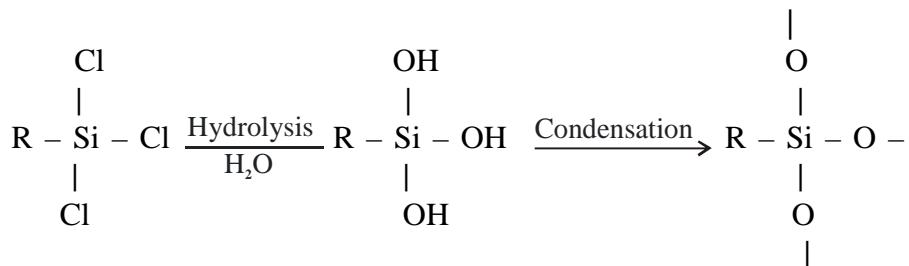
A silicone polymer.

Different types of alkyl or aryl substituted chlorosilanes can be used as starting materials to prepare varieties of silicone polymers.

The hydrolysis of alkyl trichlorosilane RSiCl_3 results in a complex crossed link polymer.



In the above structure we notice that from $RSiCl_3$ on hydrolysis we obtain three oxygen links that are bonded to other three Si atoms.

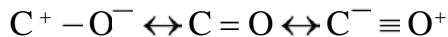


Uses

1. Straight chain silicone polymers are used as silicone oils and rubbers. Viscous polymers are obtained with increased chain length. Silicone rubbers for its elasticity are used as good electrical insulators. Silicone oils are used as greases, varnishes and resins.
2. Silicones are water-repellants and are good insulators. They are, therefore, used for water proofing and electrical condensers.
3. These polymers are used in waterproofing textiles, in glassware, as lubricants, as polish and antifoaming agents.
4. Branched chain silicone polymers are used in paints, varnishes and used as water repellants for treating masonry.

CHAPTER (15) AT A GLANCE

1. Group 14 comprises of elements like Carbon, Silicon, Germanium, Tin and Lead.
2. Electronic configuration of the outermost shell of these elements is nS^2np^2 .
3. All elements exhibit +4 oxidation state. Besides +4 oxdn. state, +2 oxidation state is also exhibited by germanium, tin and lead.
4. The stability of M^{2+} ion is more than M^{4+} ion. This is due to inert pair effect. The tendency of nonparticipation of the paired s-electrons in bond formation is known as Inert Pair effect.
5. Carbon differs from other members of the group due to its small size, high ionisation energy and high electronegativity. Carbon has the tendency to combine with other carbon atom thereby forming a long chain. This self-linking property is known as catenation.
6. CO_2 is a gas whereas SiO_2 is a solid. CCl_4 can be easily hydrolysed.
7. When different structural forms of the same element have same chemical properties but different physical properties, the phenomenon is known as Allotropy and the different forms are Allotropes. Diamond, graphite, charcoal, lamp black, coke etc. are the different allotropes of carbon. Buckyball or Fullerene (C_{60}) is a recently discovered crystalline allotrope of carbon.
8. Diamond is the hardest naturally occurring allotrope of carbon. The carbon atoms are sp^3 hybridised, therefore joined tetrahedrally forming a giant hexagonal structure. C–C bond distance is 1.54 \AA and bond angle is $109^\circ 28'$. It is bad conductor of heat and electricity.
9. Graphite (Black lead) is another crystalline allotrope of carbon. It forms a two dimensional sheet like polymeric structure. Carbon atom is sp^2 hybridised, arranged in a number of layers composed of hexagonal planar rings. C–C bond distance is 1.42 \AA . Different layers are held by weak van der Waal's force and are about 3.4 \AA apart. One layer slides over the other. Graphite is quite soft and exhibits lubricating property. It is good conductor of heat and electricity.
10. Structure of CO : $\ddot{:}C\ddot{:}\ddot{\cdot}O\ddot{:}$ or $C \equiv O$



Resonating structures

11. Solid CO_2 is known as dry ice. It is used as a refrigerant.
12. Besides ortho, cyclic and chain silicates there are sheet silicates and three dimensional silicates. Sheet silicates are two dimensional. Three dimensional silicates include quartz or rock crystal, zeolite and ultramarines. Quartz is a transparent colourless crystal, electrically neutral used for making optical and chemical apparatus.
13. Sodium silicate dissolves in water and hence is called waterglass .
14. Freons are mixed chlorofluoro carbons, such as $CFCl_3$, CF_2Cl_2 , CF_3Cl . and used as refrigeration fluids.
15. Silicones are long chain organosilicon polymers. These are water repellants and are good insulators. These are used for water proofing and electrical condensers .

QUESTIONS**A. Very short answer type questions. (1 mark each)**

1. How many elements constitute 14 Group of periodic table ? Name them.
2. What is the characteristic electronic configuration 14 Group of periodic table ?
3. Is diamond an element or compound ?
4. What is dry ice ?
5. What is carborundum ?
6. Which non metal conducts electricity ?
7. What are silanes ?
8. Name the element of group 14 which is a metalloid.
9. What is the arrangement of atoms in graphite ?
10. Which allotrope of Carbon is used as a moderator in atomic reactors.
11. What is the hybridisation of carbon in carbondioxide ?
12. Whether carbon dioxide is a Lewis acid or base ?
13. What is the most recently discovered allotrope of carbon ?
14. What is the commercial name of SiC ?

B. Point out the true or false statements (1 mark each)

1. Flint is a natural variety of silica
2. Silicon is the second most abundant element by weight in earth's crust
3. Carbon dioxide is an amphoteric oxide
4. Germanium metal finds extensive applications as semiconductor.
5. Silanes are strong reducing agents
6. Opal is an amorphous variety of silica
7. Carbon dioxide is less acidic than SiO_2
8. Carbon monoxide is a neutral oxide
9. Fluoro carbons, known as Freon are used as refrigerant.
10. Zeolites are cationic exchangers.
11. Chief constituent of water glass is sodium silicate
12. Chief constituent of water gas is sodium silicate
13. A mixture of CO_2 and 5% to 10% any gas is called carbogen used in artificial respiration.
14. Silicon carbide is used in the construction of atomic reactors.
15. Coke is an amorphous type of carbon.

C. Very short answer objective type questions. (1 mark each)

1. Diamond and graphites are (a) isotopes (b) allotropes (c) isomers (d) polymers
2. Variety of carbon used as lubricant under trade name oil drag is (a) coke (b) oil carbon (c) graphite (d) diamond
3. Lead pencil contains (a) lead (b) PbS (c) an alloy of lead (d) graphite
4. Which of the following gases has the highest percentage in coal gas.
(a) CO_2 (b) CO (c) N_2 (d) H_2
5. Glass is best described as (a) solid (b) a liquid (c) occluded solid (d) a super cooled liquid
6. Solid carbon dioxide is called dry ice because (a) it does not wet hands easily (b) it looks like ice (c) it sublimes and releases no trace of water (d) all the above
7. When SiCl_4 is hydrolysed, we get (a) SiO_2 (b) $\text{Si}(\text{OH})_4$ (C) H_2SiO_2 (d) H_2SiO
8. Water gas is a mixture of (a) CO and H_2 (b) CO_2 and H_2O (C) C_2H_2 and H_2O (d)CO and H_2O
9. Which allotrope of carbon is used as a moderator in atomic reactors ?

D. Short answer type questions. (2 marks each)

1. Explain : Carbon shows tetravalency but does not show divalency.
2. Describe the structure of diamond. Why diamond is an insulator ?
3. What is catenation ?
4. Define allotropy
5. What is animal charcoal ?
6. Write the symbols, atomic numbers and electronic configuration of group IV elements
7. Explain why SiO_2 is hard solid but CO_2 is a gas.
8. Explain on the basis of structure the conducting and lubricating properties of graphite
9. Why the melting point of diamond is very high ?
10. What is sugar charcoal ?
11. State Fajan's rule.
12. Explain why diamond is an insulator and graphite is a conductor
13. What is inert pair effect ?
14. Explain why SnCl_2 is a solid while SnCl_4 is a liquid ?
15. What happens when carbon dioxide passed through lime water ?
16. Give the allotropic forms of carbon
17. What happens when magnesium wire burns in carbon dioxide ?
18. Justify the position of carbon and lead in the periodic table on the basis of electronic configuration

19. Why dryice does not wet the cloth in which it is placed.
20. Explain why diamond is hard while graphite is soft.
21. Mention the hybrid state of carbon in diamond and graphite.
22. What is allotropy ?
23. What is water gas ? How is it prepared ?

E. Long type questions.

1. Give a comparative account of Group 14 elements (Carbon family) of the periodic table.
2. What are silicones ? How silicones are prepared ? Mention the important uses of silicones.

ANSWERS

- A. 1. Five Carbon, Silicon, Germanium, Tin and Lead.
 2. ns^2np^2
 3. Element Crystalline form of carbon
 4. Solidified carbon dioxide
 5. Silicon carbide
 6. graphite carbon
 7. Silicon hydrides
 8. Germanium.
 9. Carbon atoms are arranged in a number of layers composed of hexagonal planar rings.
 10. Graphite
 11. sp^2
 12. Lewis acid
 13. Fullerene
 14. Carborundum
- B. 1. True 2. True 3. False 4. True 5. True 6. True
 7. False 8. True 9. True 10. True 11. True 12. True
 13. True 14. True 15. True
- C. 1. b 2. c 3. d 4. d 5. d
 6. d 7. b 8. a

MULTIPLE CHOICE TYPE QUESTIONS

1. The general electronic configuration of Group 14 elements is
 - (a) ns^2np^2
 - (b) ns^2
 - (c) ns^2np^6
 - (d) None
2. Which of the following occurs in free state ?
 - (a) C
 - (b) Si
 - (c) Ge
 - (d) Sn
3. Diamond and graphite are
 - (a) isomers
 - (b) allotropes
 - (c) isotopes
 - (d) polymers
4. A gas which burns with blue flame is
 - (a) CO
 - (b) CO_2
 - (c) O_2
 - (d) N_2
5. Poisonous gas present in the exhaust fumes of a car is
 - (a) CH_4
 - (b) C_2H_6
 - (c) CO_2
 - (d) CO
6. Sugar of lead is
 - (a) $PbSO_4$
 - (b) $(CH_3COO)_2Pb$
 - (c) $PbCl_2$
 - (d) $PbCO_3$
7. Which of the following can attack glass ?
 - (a) H_2SO_4
 - (b) HI
 - (c) HCl
 - (d) HF
8. Silicon is an important constituent of
 - (a) Chlorophyll
 - (b) Haemoglobin
 - (c) Rocks
 - (d) Amalgams
9. Which of the following compounds has peroxide linkage ?
 - (a) Pb_2O_3
 - (b) CO_2
 - (c) PbO_2
 - (d) SiO_2
10. Graphite is a good conductor because
 - (a) It is crystalline
 - (b) It has free atoms
 - (c) It has free electrons
 - (d) It has sp^2 hybridisation
11. Property of catenation is strongest in
 - (a) C
 - (b) Si
 - (c) N
 - (d) O
12. Which of the following is an insulator ?
 - (a) Diamond
 - (b) Graphite
 - (c) Aluminium
 - (d) Silicon

ANSWERS TO MULTIPLE TYPE QUESTIONS

- | | | | | |
|-------|-------|-------|-------|-------|
| 1. a | 2. a | 3. b | 4. a | 5. d |
| 6. b | 7. d | 8. c | 9. c | 10. c |
| 11. a | 12. d | 13. a | 14. b | 15. c |
| 16. a | 17. c | 18. d | 19. d | 20. d |
| 21. b | | | | |



UNIT - XII

ORGANIC CHEMISTRY

CHAPTER - 16

SOME BASIC PRINCIPLES AND TECHNIQUES

16.1 GENERAL INTRODUCTION

The term *organic chemistry* was coined in 18th century for those compound which were obtained from plants or animals i.e. from living organisms. It was **Lavoisier** who first proved that all the compounds of plant origin are composed of carbon, hydrogen and oxygen. So also the compounds of animal origin contain the same elements along with nitrogen or sulphur or phosphorus.

Since it was assumed that organic compounds could be produced only by living organisms, Swedish chemist **Berzelius** (1779-1846) put forth vital force theory with the assumption that a vital force (life force) was responsible for the production of organic compounds. Synthesis of these compounds in the laboratory was impossible due to the absence of this vital force.

Vital force theory remained unchallenged till 1828 when a German chemist **Friedrich Wohler** reported that lead cyanate on treatment with ammonium hydroxide produced urea, a well known organic compound already isolated from human urine by Roulle in 1780.



Synthesis of urea by Wohler followed by synthesis of acetic acid by **Kolbe** in 1845 and synthesis of methane by Berthelot by 1856 discarded the baseless Vital force theory.

The synthesis of urea marked the beginning of a new era in organic chemistry with a new definition which is not restricted only to the carbon compounds of living system but also includes the synthetic organic compounds under one roof.

Organic chemistry is defined as the study of carbon compounds where carbon is covalently bonded to carbon, hydrogen, oxygen, halogens, nitrogen and sulphur. Compounds of carbon containing only carbon and oxygen like carbon dioxide, carbonates, carbon monoxide etc. and compounds containing only carbon and nitrogen are not considered as organic compounds.

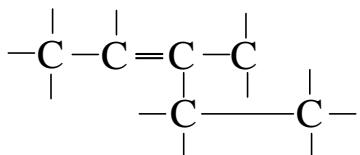
Organic compounds made up of only carbon and hydrogen atoms are called hydrocarbons and all other organic compounds may be considered as the derivatives of hydrocarbons by the replacement of one or more of their hydrogen atoms by other atoms or groups. Thus organic chemistry may be defined more precisely as the chemistry of hydrocarbons and their derivatives.

16.2 BASIC CONCEPTS OF ORGANIC COMPOUNDS

Organic compounds are studied separately because of the following characteristic features of such compounds.

1. Vast number :

The number of organic compounds is very large compared to inorganic compounds. At present, the number is more than million and it is steadily increasing since new compounds are being synthesised in different laboratories of the world everyday. The vastness of organic compounds is due to the special nature of the carbon atom, a property of the carbon atom to combine with itself through covalent bonds forming long chains or rings of different sizes and shapes. This self-linking property is known as **catenation**.



2. Complex nature :

Organic compounds are large and complex. For example, cane sugar has the molecular formula $C_{12}H_{22}O_{11}$ and fat has the formula $C_{57}H_{110}O_6$. Fats and proteins have high molecular masses ranging from several thousands to over a million.

3. Non-ionic and reversible nature of organic reactions :

Organic reactions are mostly non-ionic in nature and involve cleavage and formation of covalent bonds. They are very slow and reversible.

4. Isomerism :

Organic compounds having the same molecular formula but different physical and chemical properties are called **isomers** or **isomerides** while the phenomenon is known as **isomerism**. This is very common in organic compounds. For example, molecular formula C_2H_6O represents both ethyl alcohol (CH_3CH_2OH) and dimethyl ether (CH_3-O-CH_3) which have entirely different physical and chemical properties.

5. Homologous series :

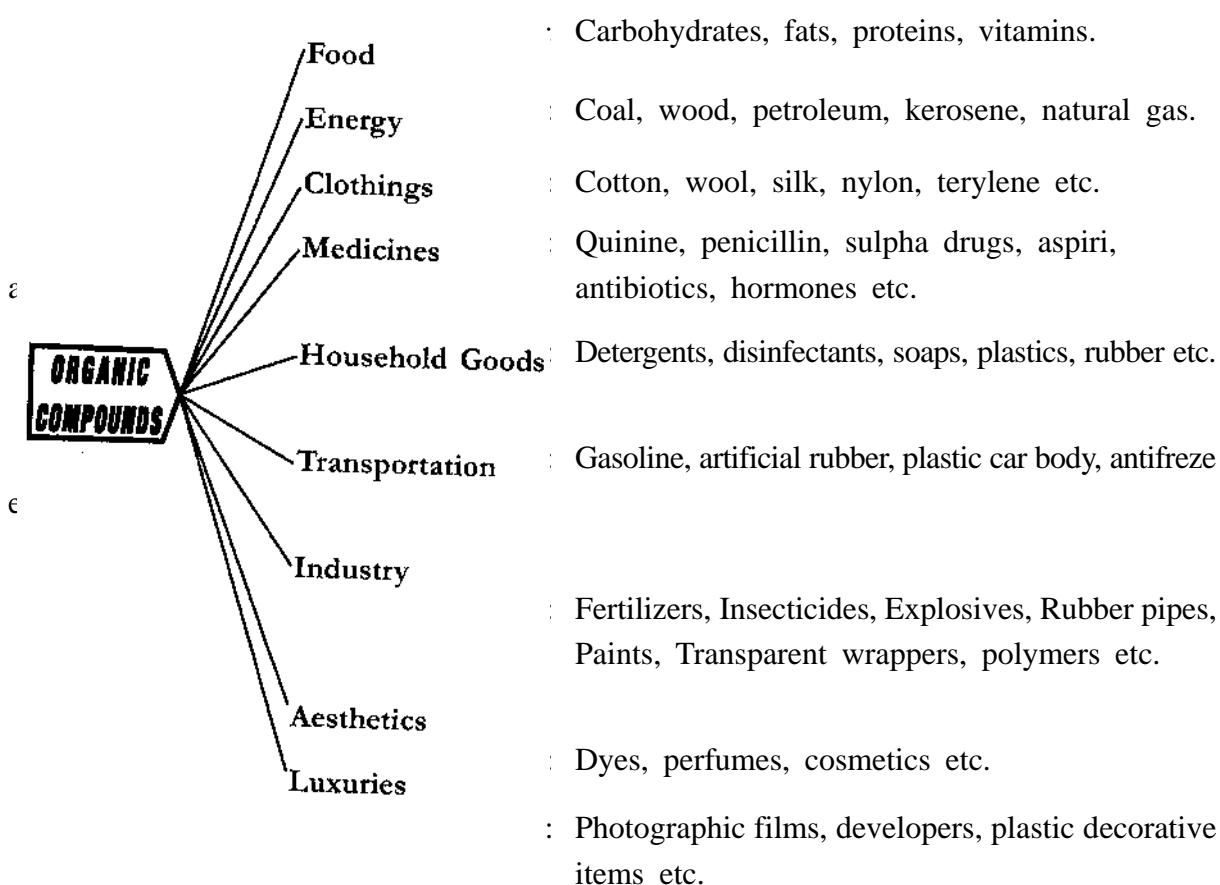
Although the number of organic compounds is very large, they can be classified into different groups or families known as **homologous series**. Different members belonging to a homologous series (**homologues**) are characterised by the presence of a characteristic group, called **functional group** and can be represented by one general formula having similar methods of preparation and chemical properties. One member of a particular homologous series differs from the consecutive member by a $-\text{CH}_2-$ group (molecular mass 14).

6. Solubility :

Organic compounds mostly dissolve in organic solvents like alcohol, ether, benzene etc. in which inorganic compounds do not dissolve.

7. Vast application :

Organic compounds play a very vital role in our daily life. All our requirements of life are mostly organic in nature. Our body is made up of tissues which are organic compounds. The following illustration gives an idea about the vast application of organic compounds.



16.3 CHARACTERISTICS OF CARBON ATOM

The essential constituent of all organic compounds is carbon. The structure, formation and nature of the organic compounds can be very well understood by studying the characteristics of carbon atom.

1. Tetracovalency of Carbon atom :

Carbon is placed in the Group-IV of the periodic table. Its high ionisation potential, moderate electronegativity and electron affinity do not permit it to lose or gain electrons. Since it has four electrons in the outermost shell, it can complete its octet by sharing four electrons with other atoms including other carbon atoms and exhibits tetracovalency. **Le Bel** and **van't Hoff** proved that in carbon atom the four valencies are directed towards the four corners of a regular tetrahedron making an angle of $109^{\circ}28'$ or 109.5° between any two bonds. All saturated compounds retain the tetrahedral configuration and hence stable. Thus, methane is represented as shown in Fig. 16.1

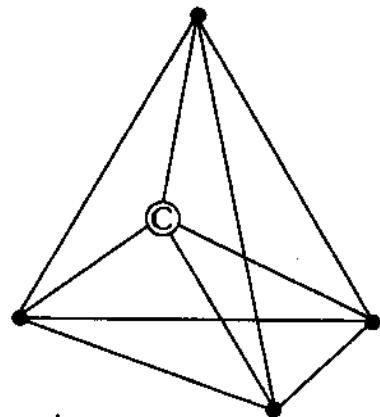
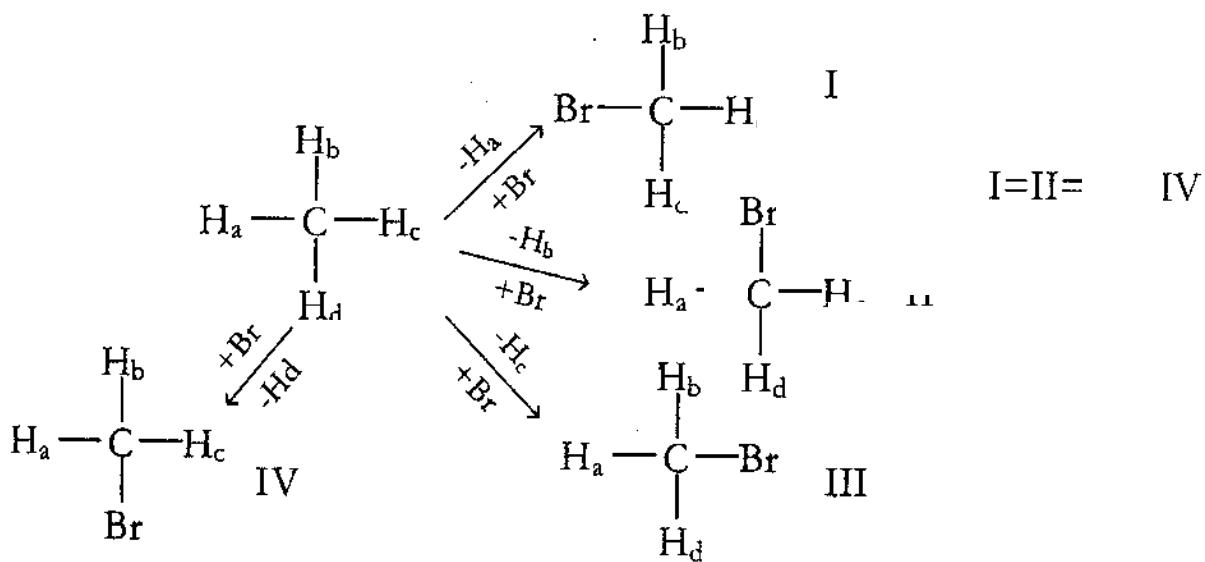


Fig 16.1 Tetrahedral carbon atom

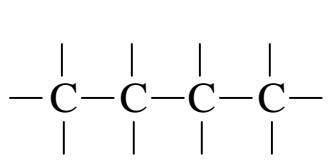
2. Equivalence of four valencies in Carbon atom :

In organic compounds of type CH_4 (methane), all the four valencies of carbon are equivalent. Thus, if a hydrogen atom is replaced by a bromine atom, one at a time, then the same methyl bromide will be obtained.

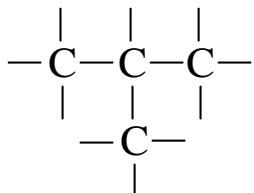


3. Catenation :

Carbon has the unique tendency to combine with other carbon atoms repeatedly to form carbon chains or rings. This self-linking property is called **catenation** and this occurs due to the formation of covalent bonds between carbon atoms. Thus, carbon atoms can form linear chain, branched chain or cyclic structure as shown below.



(Straight chain)



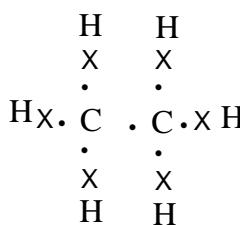
(Branched chain)

(cyclic)

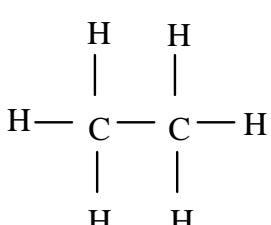
4. Type of bonds :

Three types of bonds are formed in carbon compounds : (a) single (b) double (c) triple

(a) *Single bond* : It is formed when two carbon atoms or a carbon atom and an atom of another element share a pair of electrons e.g. ethane or methyl chloride. The bond is a sigma (σ) bond, which is quite strong and does not easily break during chemical reaction.



Ethane
(electron-dot structure)



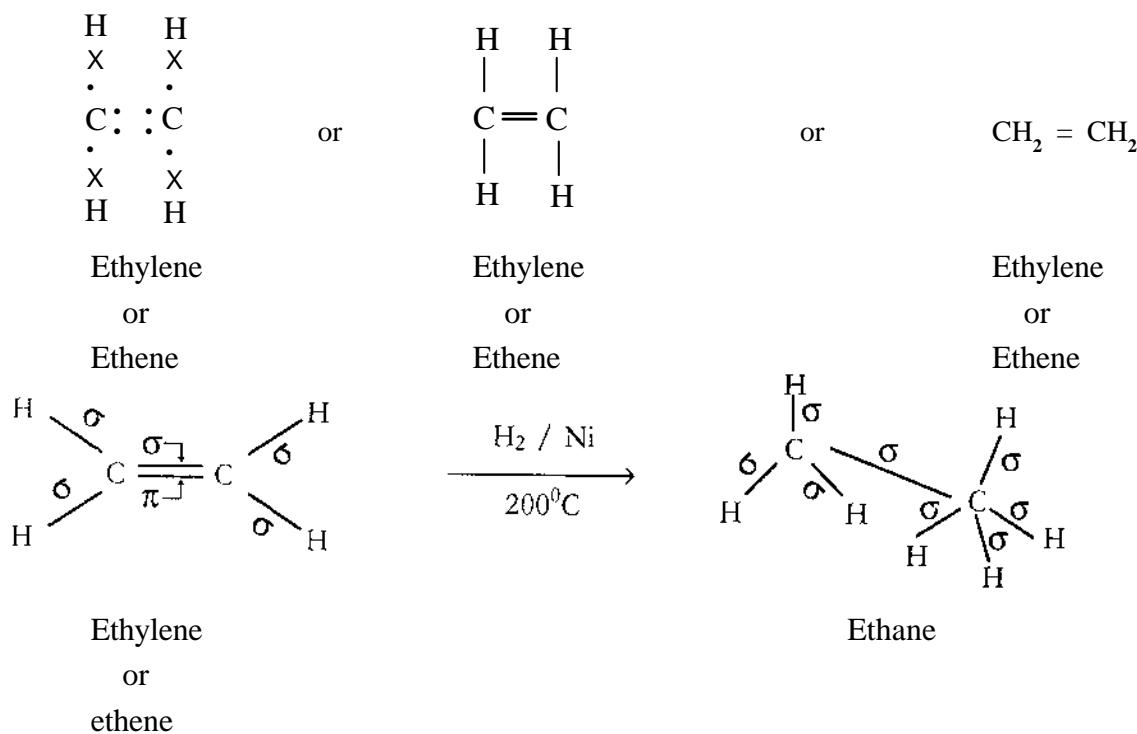
Ethane
(Graphic structure, straight
line for single bond)



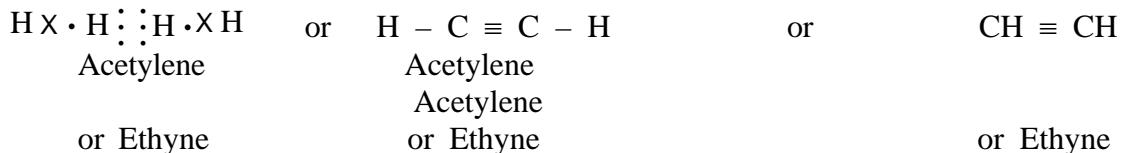
Ethane

(Condensed formula)

(b) *Double bond* : It is formed when two pairs of electrons are shared by two carbon atoms or by a carbon atom and another atom, e.g. ethylene (ethene). Out of the two bonds of a double bond, one is a strong sigma (σ) bond and the other is a weak π (π) bond. The double bonds, also known as ethylenic bonds, though stronger than a single bond, can be ruptured easily during chemical reaction. The double bonds are very reactive and always tend to undergo addition reactions whereby the π bonds are destroyed.



- (c) *Triple bond* : It is formed by sharing of three pairs of electrons between two carbon atoms or between a carbon atom and another atom. e.g. as in acetylene (ethyne) molecule.



A triple bond, also known as an acetylenic bond consists of one σ bond and two π bonds. Triple bonds, though stronger than other two types of bonds are very reactive and are easily during chemical reaction. The triple bonds being very reactive undergo addition reactions easily.



16.4 HYBRIDISATION AND TETRACOVALENCY OF CARBON

The electronic configuration of carbon atom is $1s^2, 2s^2, 2p_x^1, 2p_y^1$. Since there are two half-filled p-orbitals carbon is expected to be divalent. But carbon is tetravalent. To explain this, it is assumed that one of the 2s electrons is promoted to the vacant $2p_z$ orbital. The

electronic configuration of carbon in this excited state would be $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$ $2p_z^1$. Now, the four half-filled orbitals would explain the tetracovalency of carbon. However, the energy of $2s$ orbital is less than $2p$ orbitals, so one of the bonds of carbon should be different from the other three. But it has been established that all the four bonds of methane are equivalent.

To explain this discrepancy, the concept of hybridisation was introduced. According to this concept, the atomic orbitals of an atom having equal or nearly equal energies mix and redistribute their energies to form an equal number of equivalent or hybrid orbitals. Three different types of hybrid orbitals – sp^3 , sp^2 and sp may be formed by the mixing of s and p orbitals. The hybrid orbitals are similar to atomic orbitals except that

- (i) they do not overlap laterally
- (ii) they have directional character

Because of the directional character of the hybrid orbitals, the compounds formed by the electrons of such orbitals have a definite geometrical shape.

sp^3 -hybridisation :

In this case, *one* $2s$ orbital and *three* $2p$ orbitals mix to form *four* equivalent sp^3 hybrid orbitals, each having 25% **s** character and 75% **p** character. They are directed towards the four corners of a regular tetrahedron, the angle being $109^\circ 28'$ between any two bonds. Each of these hybrid orbitals overlap linearly with the $1s$ orbitals of four hydrogen atoms to form four equivalent C-H σ bonds in methane (Fig. 16.2). In saturated compounds carbon is always sp^3 hybridised.

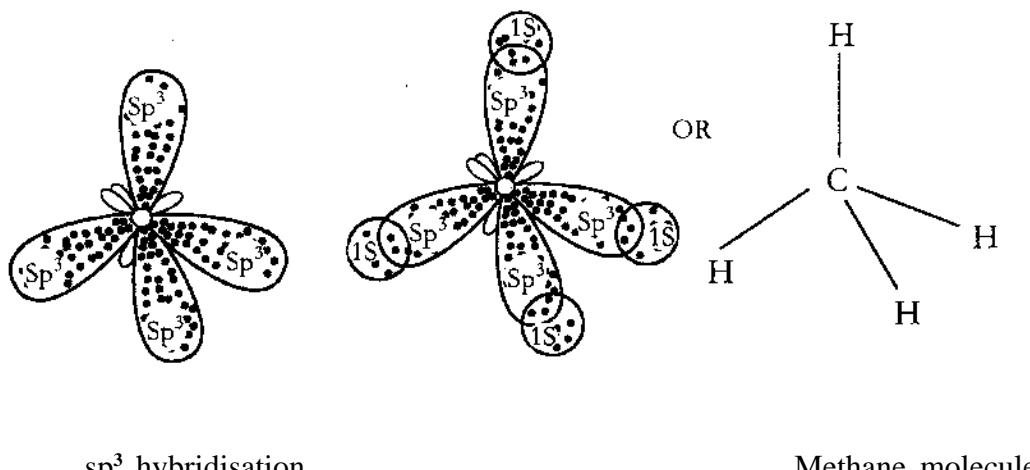


Fig.16.2 sp^3 -hybridisation in methane molecule

sp^2 -hybridisation :

This type of hybridisation occurs in compounds containing double bonds. *One* $2s$ and *two* $2p$ orbitals mix to produce three equivalent sp^2 hybrid orbitals. sp^2 hybrid orbitals are

planar making an angle 120° with each other (Fig 16.3) sp^2 hybrid orbitals have 33.33% s character and 66.66% p character. The third 2p orbital lies perpendicular to the plane containing the hybridised orbitals.

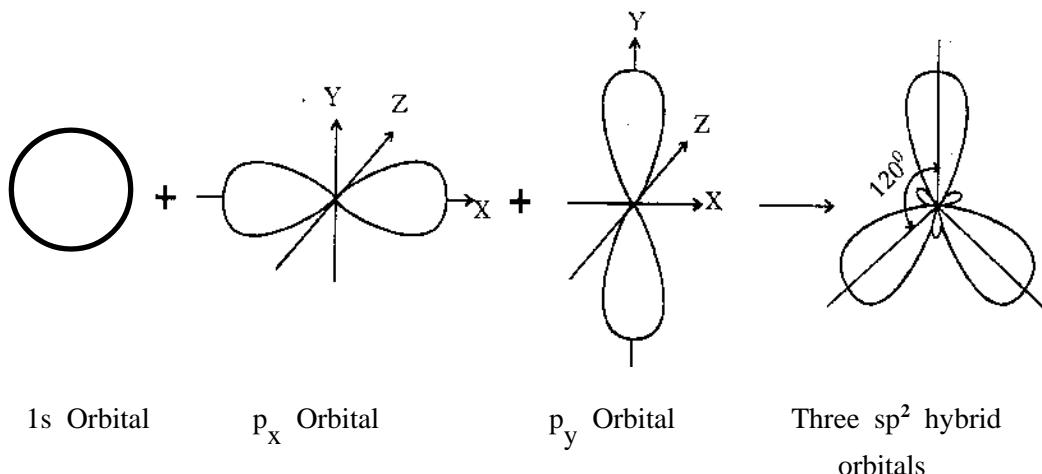


Fig 16.3 : Formation of sp^2 hybridised orbitals

In ethylene (ethene) molecule the two sp^2 hybrid orbitals of each carbon atom overlap linearly forming a C-C σ bond. The two other sp^2 hybrid orbitals of each carbon atom overlap with 1s orbital of four hydrogen atoms to form four C-H σ bonds. The unhybridised p orbitals overlap laterally, partly above and partly below the nuclear plane to form C-C π bond (Fig 16.4).

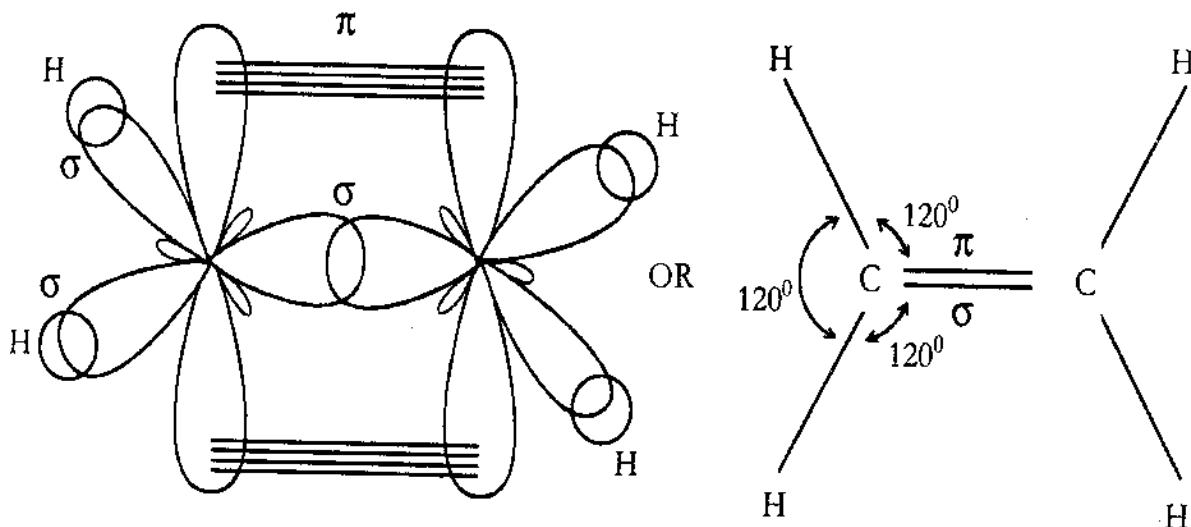


Fig 16.4 : Orbital structure of ethylene molecule

Since lateral overlapping is less significant than linear overlapping, the π bond is **weaker** than the σ bond and can be easily broken.

sp-hybridisation :

In compounds containing triple bonds, one 2s and one 2p orbital mix to form two equivalent sp hybrid orbitals. They are linear (i.e. they make 180° with each other (Fig 16.5) The sp hybrid orbitals possess 50% s and 50% p character. This hybridisation leaves two pure 2p orbital unaffected.

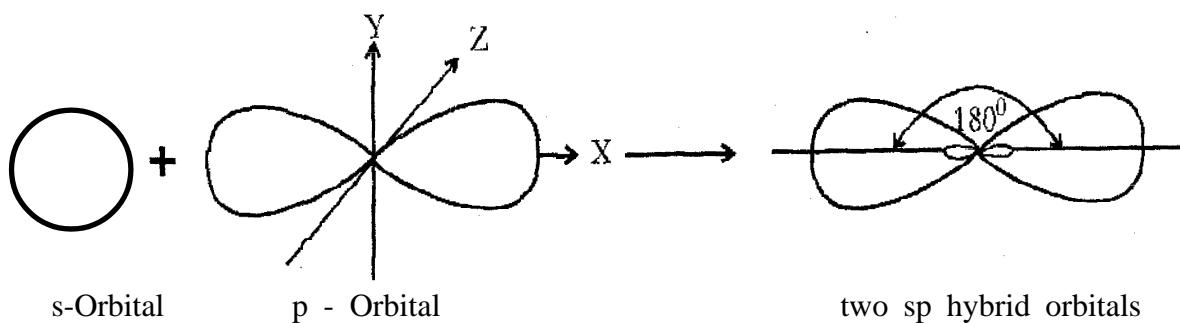


Fig 16.5 : Formation of sp hybrid orbitals

In acetylene (ethyne) molecule, sp hybrid orbital of each carbon atom overlap linearly to form C–C σ bond. The other sp hybrid orbital of each carbon atom overlaps with 1s orbitals of two hydrogen atoms to form two C–H σ bonds. The two pure p orbitals which lie perpendicular to the plane containing hybrid orbitals and with each other overlap laterally with similar p orbitals of the other carbon atom forming two C–C π bonds (Fig 16.6). Therefore, the triple bond between two carbon atoms consists of one σ bond and two π bonds.

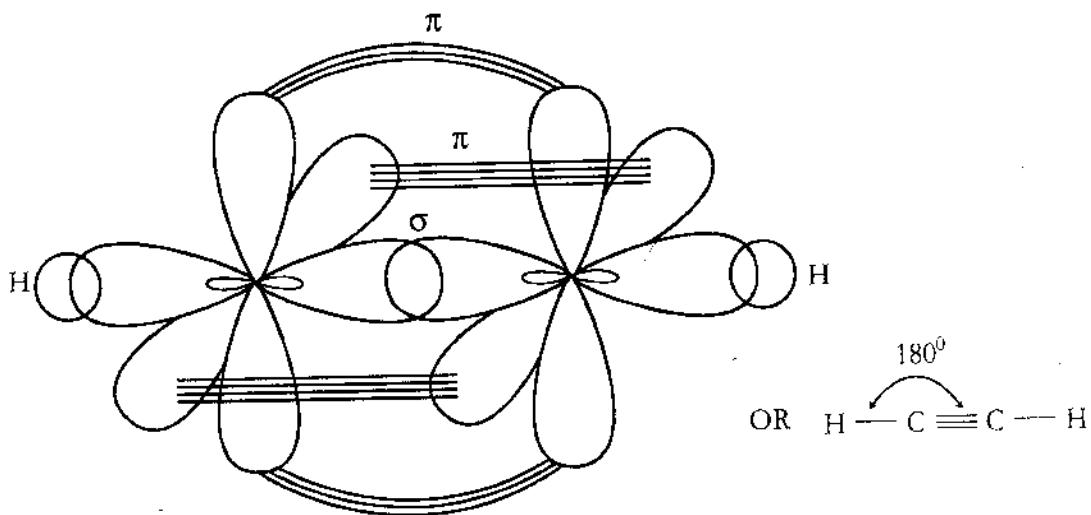


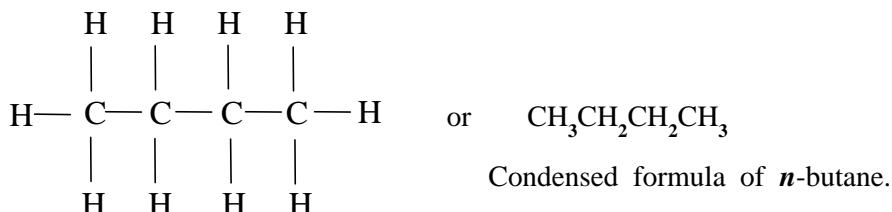
Fig 16.6 : Orbital structure of acetylene molecule

The simplest way to write the structural formula of a compound is to represent each covalent bond between the combined atom by a line (—). Thus, methane can be represented

as $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ But this does not give the idea about the spatial configuration. For

example, methane is tetrahedral and not planar.

In case of larger molecules, since the detailed structural formulae, require a lot of space, condensed structural formulae are often written without showing their bonds (except double and triple bonds). Atoms of elements other than hydrogen are written after the hydrogen atom. For example.



Structural formula of *n*-butane

It may be noted that the carbon is always tetravalent and in condensed formula when carbon atom is written near another carbon atom, it should be understood carbon is linked with carbon and hydrogen atoms are attached to the carbon atoms as shown above. Less often ethane is represented as H_3CCH_3 , rather CH_3CH_3 is more commonly used.

16.5 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Organic compounds whether extracted from a natural source or prepared in the laboratory are never found free from impurities. Various methods used for the purification of organic compound depend on

- (i) The nature of the organic compound and
- (ii) The nature of the impurity present in it.

The common techniques applied for purification are :

A. CRYSTALLISATION :

Crystallisation is the most commonly used method for purification of solid substances which is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.

The process of crystallisation involves the following steps :

(a) Choice of the solvent :

Solvent must satisfy the following characteristics

- (i) It does not dissolve the compound completely at room temperature, but appreciably soluble at higher temperature.
- (ii) It dissolves the impurities to a small extent.
- (iii) It possesses a relatively low boiling point in order to effect its easy removal from the crystals of the pure compound.
- (iv) The solvent does not react chemically with the substance.

(b) Making the solution :

The crude sample is dissolved on heating in the minimum volume of suitable solvent to get nearly a saturated solution. A pinch of animal charcoal may be added to the solution during boiling to remove colouring materials by the process of adsorption.

(c) Hot filtration :

The saturated solution is filtered hot to remove the insoluble impurities.

(d) Cooling and separation of crystals :

The hot solution is then cooled in a container surrounded by ice cold water. The pure solid separates out as crystalline precipitate which is separated by filtration (Fig 16.7)

(e) Drying :

The precipitate is then dried in a steam oven or hot air oven at a suitable temperature or by means of a vacuum desiccator (Fig 16.8)

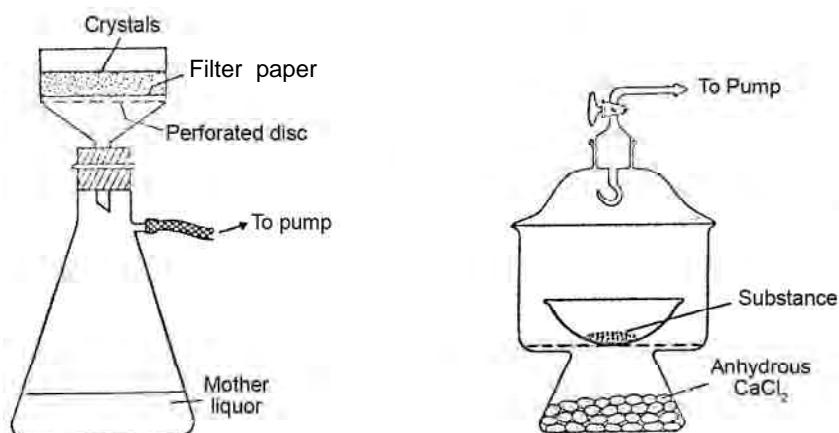
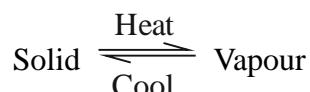


Fig. 16.7 Filtration under reduced pressure using Buchner funnel.

Fig. 16.8 Vacuum desiccator

B. SUBLIMATION :

Sublimation may be defined as the process in which solid substances when heated, pass directly from the solid to the vapour state without melting and the vapour when cooled give back the solid substances.



This process is very useful in separating volatile from non-volatile solid but is of limited application as only a few substances like naphthalene, camphor and benzoic acid can be purified by this process.

The process of sublimation can be shown in Fig. 16.9 where the impure substance is heated in a dish covered with a perforated asbestos sheet on which an inverted funnel is placed. The funnel is kept cool by wrapping it with a wet filter paper or wet cloth. Vapours of the substance rise up and condense on the cooler walls of the funnel.

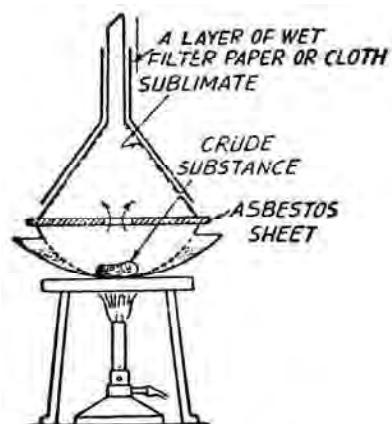


Fig. 16.9 Sublimation

C. DISTILLATION :

The operation of distillation is employed for (i) the separation of volatile liquids from non-volatile impurities and (ii) the liquids having sufficient difference in their boiling points.

Various methods employed for the purification of liquids depend on the nature of the liquid and the nature of impurities present. These are :

(a) Simple distillation :

Liquids which boil under ordinary pressure without decomposition and are associated with non-volatile impurities are generally purified by simple distillation. It is a process in which vaporization and condensation are going on side by side. The impure liquid is taken in a distillation flask fitted with a thermometer and a condenser and heated on a wire gauze. The liquid vaporizes and vapours are condensed as they pass through the air or water

condenser. The pure liquid is collected in the receiver while the non-volatile impurity is left behind as shown in Fig. 16.10. Some glass beads are generally added to the distillation flask to avoid bumping.

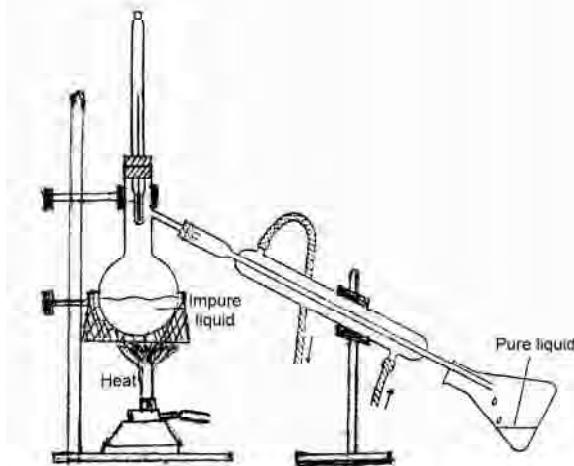


Fig. 16.10 Simple distillation apparatus

(b) Fractional distillation :

When the liquids present in the mixture have their boiling points close to each other, the separation is best effected by fitting the distillation flask with a fractionating column which in turn is connected to the condenser as shown in Fig. 16.11.

Vapour of the liquid with higher boiling point condense before the vapour of the liquid with lower boiling point and consequently the vapours rising up in the fractionating column will be richer in more volatile component. The role of fractionating column is to provide many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. So the vapour of low boiling point on reaching the top become pure and pass through the condenser and the pure liquid is collected in a receiver. When series of successive distillations are carried out, the remaining liquid in the distillation flask get enriched in high boiling component. Each successive condensation and vaporization unit in the fractionating column is called a Theoretical Plate.

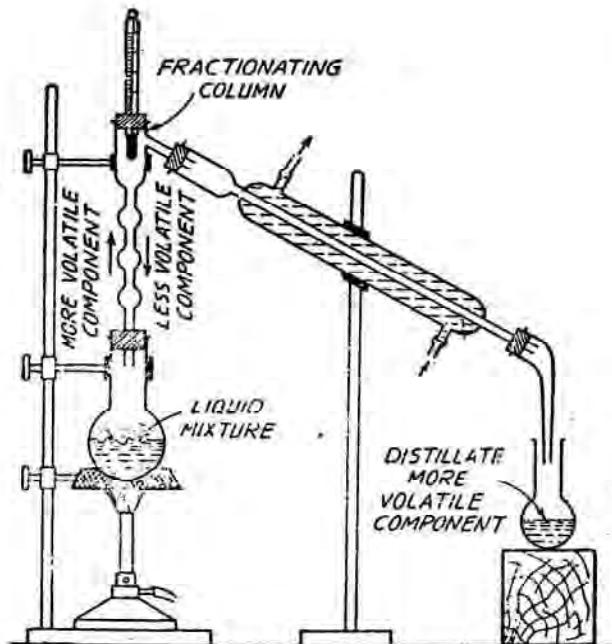


Fig. 16.11 Fractional distillation

The use of fractionating column has found a remarkable application in modern industry, especially in the distillation of petroleum, coal-tar and crude alcohol.

(c) Distillation under reduced pressure :

This method is applicable to purify liquids having very high boiling points and those, which decompose before their boiling point is reached.

A liquid boils when its vapour pressure is equal to the atmospheric pressure. When the pressure is reduced by a water pump or a vacuum pump, the liquid boils at a lower temperature and distils over undecomposed. Distillation under reduced pressure is carried out in a specially designed apparatus (Fig. 16.12). The receiver is attached to a vacuum pump to lower the pressure registered by the manometer provided and the distillation is carried out as usual.

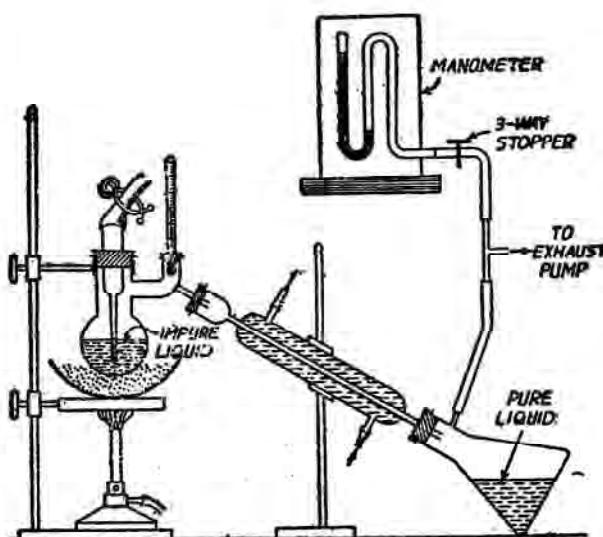


Fig. 16.12 Distillation under reduced pressure

An important application of this process is the recovery of glycerol form spent-lye in soap industry. Glycerol decomposes at its boiling point (298°C) but can be distilled unchanged at 12mm pressure when it boils at 180°C . Another application of vacuum distillation is the concentration of sugar juice under reduced pressure where it serves to economise fuel.

(d) Steam distillation :

Liquid practically immiscible with water, volatile in steam and possessing a fairly high vapour pressure are purified by steam distillation.

Steam is bubbled through the impure liquid in a flask heated on a sand bath (Fig. 16.13). On vigorous boiling the vapours of the organic substance mixed with steam rise up and condense as they pass through the water condenser. Thus the condensate is a mixture of the organic substance and water. The two, being immiscible are separated in a separating funnel.

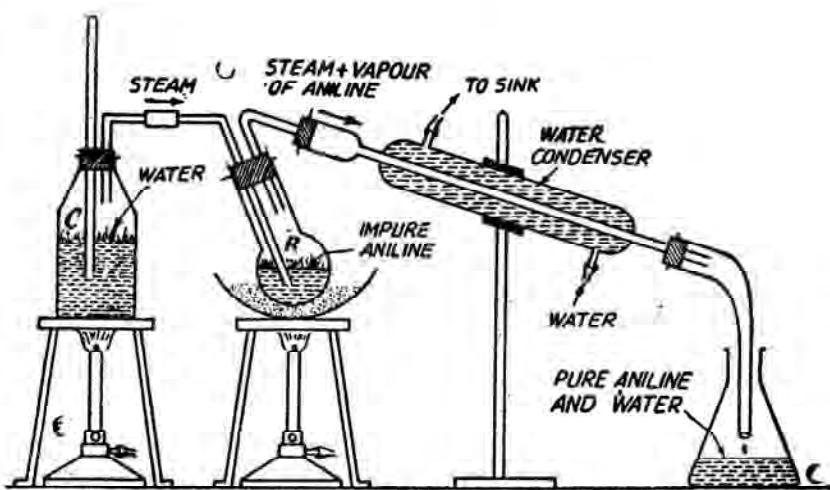


Fig. 16.13 Steam distillation

Theory of steam distillation :

Let p_1 and p_2 be the vapour pressures of water vapour and liquid at the distillation temperature. The liquid boils when their sum is equal to the atmospheric pressure P i.e.

$$p_1 + p_2 = P \text{ or } p_2 = P - p_1$$

So when a liquid boils in the presence of steam p_2 , the partial pressure of organic liquid is less than the atmospheric pressure. That implies the substance boils at a temperature lower than its boiling points.

The actual amount of the substance which distils over is given as

$$\frac{w_1}{w_2} = \frac{p_1 \times 18}{p_2 \times M}$$

where w_1 = weight of water which distils over

w_2 = weight of compound which is carried over

p_1 = vapour pressure of water

p_2 = vapour pressure of the compound

Molecular mass of water = 18

Molecular mass of the compound = M

Steam distillation is employed in industry for the recovery of various essential oils from plants and flowers. It is also used in the manufacture of aniline and turpentine oils.

D. EXTRACTION WITH A SOLVENT ;

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed *extraction*.

When an organic substance is present as solution in water, it can be recovered from the solution by the following steps :

- (i) The aqueous solution is shaken well with an immiscible organic solvent in which solute is more soluble.
- (ii) The solvent layer is separated by means of a separating funnel as shown in Fig.16.14
- (iii) The organic substance is then recovered from it by distilling off the solvent.

According to Partition Law, it is always better to extract two or three times with smaller quantities of the solvent than once with the bulk of the solvent provided.

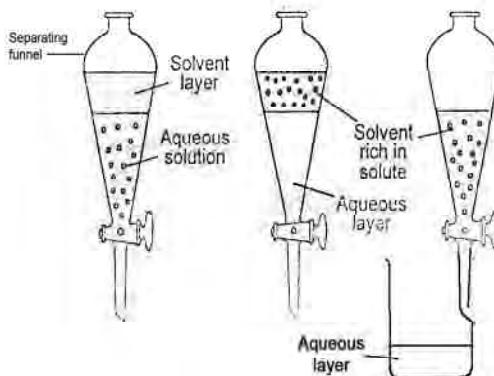


Fig. 16.14 Extraction with a solvent

E. CHROMATOGRAPHY :

Chromatography is an important modern technique for the separation, isolation, purification and identification of the components present in a mixture. The name derived from Greek words Chroma meaning colour and Graphe meaning writing, suggests that this technique was originally confined to the separation of the coloured substances like plant pigments or dyestuffs. But now this technique is equally applied to colourless substances.

(a) Principle :

Chromatography is based on the principle of selective distribution of the components of a mixture between two phases, a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is solid, the basis is **adsorption**, and when it is a liquid, the basis is **partition**.

(b) Types of Chromatography :

Basing on the principle involved, chromatography can be classified into two different types. These are :

1. Adsorption chromatography :

In this technique, the fixed phase is a solid such as alumina, silica gel, magnesium oxide where the components of a mixture are adsorbed to different degrees. When a mobile phase is allowed to move over the stationary phase (adsorbent), the components move with different mobility.

Again it can be of two types.

(i) Column chromatography : Column chromatography is named after the container of the stationary phase in which the adsorbents like alumina, silica gel etc. are packed in a glass tube fitted with a stopcock at its lower end. (Fig 16.15)

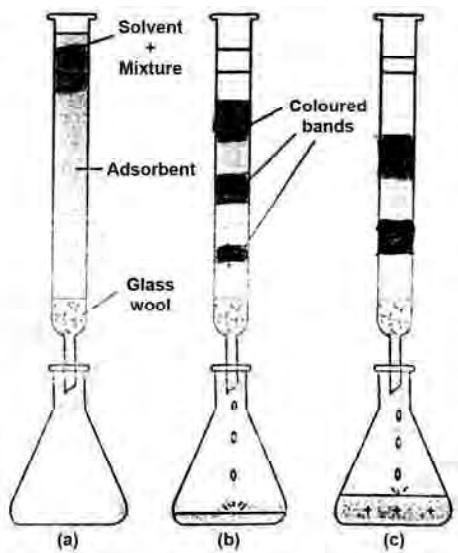


Fig. 16.15 Separation of a mixture by column chromatography (a) mixture added to top of the column; (b) appearance of bands; (c) collection of fraction.

A small amount of the concentrated solution of the sample is placed on the top of the column. A suitable solvent called *eluant* or a mixture of liquids is allowed to flow down the column slowly. As the components move down the column, their rates are determined by the distribution behaviour between the fixed adsorbent and the moving liquid. The most readily adsorbed substances are retained near the top and others come down to various distances. As the process of elution continues, the zones of enhanced concentration gradually separate and become distinct. Now each zone contains only a single component. The process of separating the components of a mixture into zones or bands of pure substances, each located at a different place on the column is called the *development* of the chromatogram and the process of removing each component from column and collecting them one by one is called *elution*.

(ii) Thin Layer Chromatography (TLC) : With thin layer chromatography, it is possible to separate even minute quantities of mixtures. A sheet of glass is coated with a thin layer of adsorbent which acts as the fixed or stationary phase. After drying the plate, a drop of the solution of the mixture is placed just above one edge, which is then dipped in a pool of solvent. The solvent is drawn up the adsorbent layer by capillary action and consequently the components of the mixture move up along with the eluent to different distances depending on their degree of adsorption and separation taking place (Fig. 16.16).

The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. R_f value given as

$$R_f = \frac{\text{Distance moved from the base line by the substance}}{\text{Distance moved from the base line by the solvent front}}$$

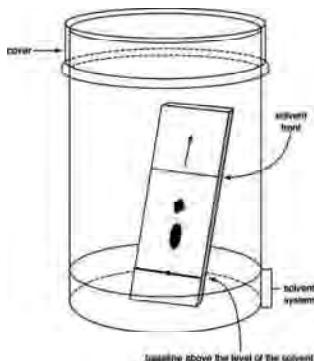


Fig. 16.16 Thin Layer Chromatography

The spots of coloured compounds are visible on TLC plate due to their original colour. But the spots of colourless compounds can be detected by spraying the plate with developing or colouring agents like ninhydrin reagent as in case of aminoacids.

2. Partition chromatography :

It operates by a mechanism analogous to counter-current distribution. The fixed phase may be a liquid strongly adsorbed on solid which acts as a support. In this case the solute gets distributed between the fixed liquid and the moving liquid (solvent).

Paper chromatography is a special type of partition chromatography in which the water trapped in the cellulose molecules of the paper acts as the stationary phase.

The paper chromatographic technique is partly partition and partly adsorption. A mixture of components to be separated is generally dissolved in water and is then placed on a strip of chromatographic paper. The second solvent (mobile phase) placed in the vessel is allowed to travel along the strip. The cellulose in the filter paper acts as a support for the stationary phase with water adsorbed on it. The mixture of the components is thus subjected to partition between the stationary phase and moving phase. Due to continuous and repeated partitioning, the rate of migration of each component in different causing the separation of the components (Fig. 16.17).

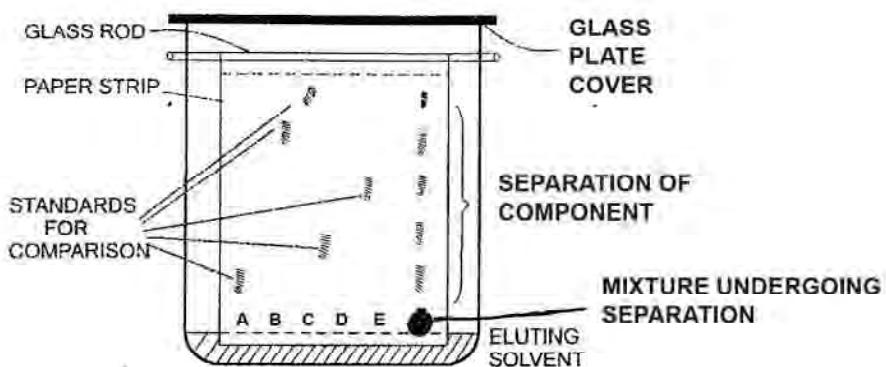


Fig. 16.17 Paper Chromatography

Rf value which is characteristic of a particular component can be determined as :

$$R_f = \frac{\text{Distance travelled by the solute from the base line}}{\text{Distance travelled by the solvent from the base line}}$$

16.6 [QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS]

For the complete diagnosis and characterisation of an organic compound, the first and foremost step is to detect the elements present in it. The principal elements present in organic compounds are : carbon, hydrogen and oxygen. In addition to these, they may contain nitrogen., sulphur, halogens and phosphorus.

(A) Detection of Carbon and Hydrogen :

A mixture of organic compound and dry copper (II) oxide is heated in a dry test tube fitted with a delivery tube provided with a bulb in middle containing anhydrous CuSO_4 . The other end of the delivery tube is dipped into lime water in another test tube.

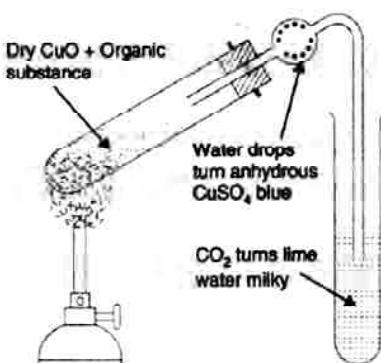
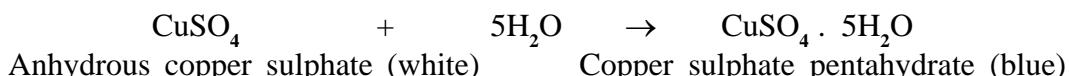


Fig. 16.18 Detection of carbon and hydrogen

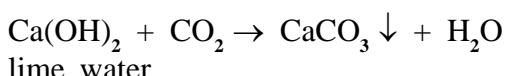
On heating the mixture, carbon and hydrogen present in the organic compound get oxidized to CO_2 and H_2O respectively.



- (i) Water formed converts anhydrous CuSO_4 (white) to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue) indicating the presence of hydrogen in the organic compound.



- (ii) CO_2 formed turns lime water milky indicating the presence of carbon in the organic compound.



(B) Detection of Oxygen :

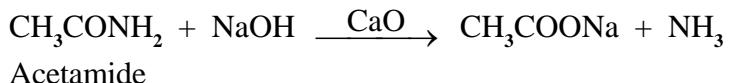
Though there is no conclusive test for oxygen, its presence in organic compounds is indicated by indirect methods.

- (i) When the substance is heated alone in a dry test tube, in an atmosphere of nitrogen, formation of droplets of water on cooler parts of the tube shows the presence of oxygen. A negative result, however, does not necessarily show the absence of oxygen.
- (ii) If any of the various oxygen containing groups like $-\text{OH}$, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$, $-\text{NO}_2$ etc is detected, the presence of oxygen is confirmed.
- (iii) The sure test for oxygen depends on the determination of the percentage of all other elements present in the compound. If the sum of these percentages falls short of hundred, the remainder gives the percentage of oxygen and thus confirms its presence.

(C) Detection of Nitrogen :

The presence of nitrogen in an organic compound is shown by the following tests:

- (i) **Ignition test** : When heated strongly, smell of burning feathers indicates the presence of nitrogen. However, a negative result is not a proof of the absence of nitrogen.
- (ii) **Soda-lime test** : Liberation of ammonia gas on heating the given organic compound with soda-lime confirms the presence of nitrogen in it.



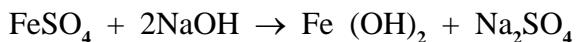
But nitrogenous compounds including nitro and diazo derivatives do not respond to this test, so a negative result is not a proof of the absence of nitrogen.

- (iii) **Lassaigne's test** : This is a confirmatory test for the detection of nitrogen in all cases of nitrogenous compounds. It involves the following steps.
- (a) A freshly cut small piece of sodium metal is melted in a small fusion tube and fused with the organic compound. The red hot tube is broken by immersing in distilled water in a china dish. The contents are boiled in water to extract the fused mass and filtered. This extract is known as *sodium fusion extract*. Nitrogen if present, combines with sodium and carbon of the organic compound to form sodium cyanide.



From $\widetilde{\text{organic compound}}$

- (b) The sodium fusion extract component is boiled with ferrous sulphate solution and cooled.

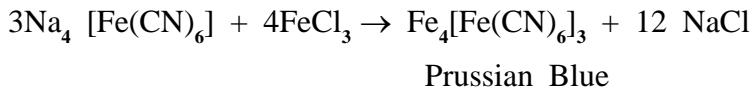


from excess of sodium



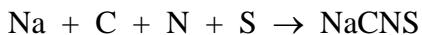
Sodium ferrocyanide.

- (c) To the cooled solution a little ferric chloride solution is added followed by excess of conc. hydrochloric acid.

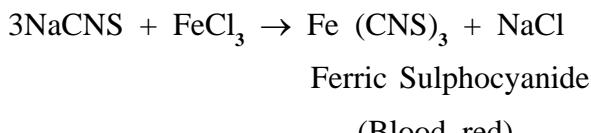


The formation of Prussian blue or green colouration confirms the presence of nitrogen.

In case sulphur is present along with nitrogen in the organic compound, a blood red colouration may appear while performing the test for nitrogen.

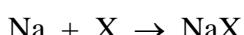


Sodium sulphocyanide.

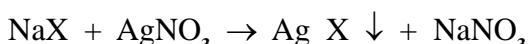


D. Detection of Halogens :

- (i) **Lassaigne's test :** If halogens present in the organic compound, the sodium fusion extract contains sodium halides.

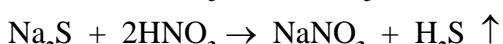
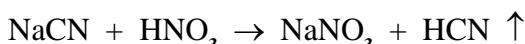
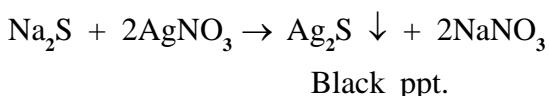
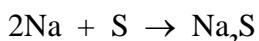
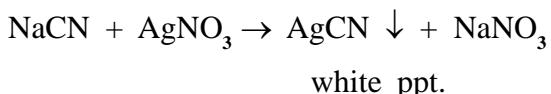


A little amount of sodium extract is acidified with dilute nitric acid and silver nitrate solution is added to it. A precipitate proves the presence of halogen.



White precipitate soluble in dil. NH_4OH indicates chlorine. Yellowish white precipitate insoluble in dil. NH_4OH , but soluble in conc. NH_4OH indicates bromine. Yellow precipitate insoluble even in conc. NH_4OH indicates iodine.

However, when nitrogen or sulphur is also present in the compound. NaCN and/or Na_2S present in the extract interferes in the test of halogens. They can be removed by boiling with strong nitric acid to decompose the cyanide and sulphide. If not removed they will form a white and black precipitate respectively on the addition of silver nitrate.



- (ii) **Beilstein test :** The copper wire flattened at one end is heated in an oxidizing Bunsen flame till it ceases to impart any green colour to the flame. Now a small amount of organic compound is taken on the copper wire and heated in the flame. A green flame, if imparted to the flame, is due to the formation of a volatile copper halide and proves the presence of a halogen. Though sensitive, this test is not always reliable for example, urea imparts green colour though it does not contain halogen.

E. Detection of Sulphur :

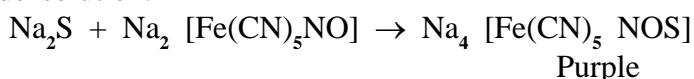
Sulphur may be detected in an organic compound by the following tests :

- (i) **Lassaigne's test :** If sulphur present then the sodium fusion extract contain Na_2S .

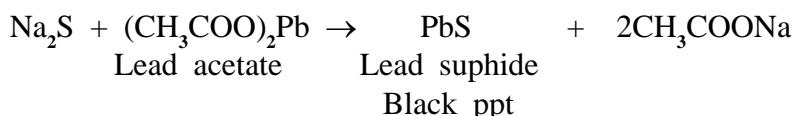


Presence of sodium sulphide in the extract can be confirmed as follows :

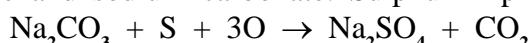
- (a) A purple colour is obtained when a portion of the extract is treated with sodium nitroprusside solution.



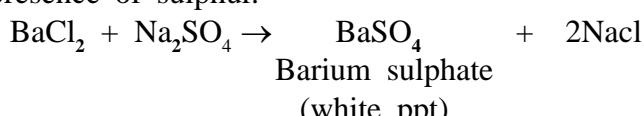
- (b) A black precipitate of lead sulphide is produced when lead acetate solution is added to the sodium fusion extract.



- (ii) **Oxidation test :** The organic compound is fused with a mixture of potassium nitrate and sodium carbonate. Sulphur if present is oxidised to sulphate.

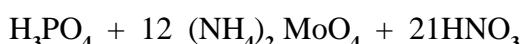


The fused mass is extracted with water, acidified with hydrochloric acid and then barium chloride solution is added to it. A white precipitate of BaSO_4 indicates the presence of sulphur.



F. Detection of Phosphorus :

The compound containing phosphorus when heated with an oxidising agent like hydrogen peroxide, phosphate is formed. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



Ammonium molybdate



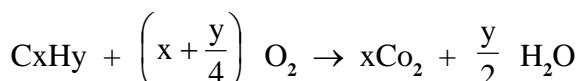
Ammonium phosphomolybdate

16.7 QUANTITATIVE ANALYSIS

After detection of elements, the next step in the molecular diagnosis of an organic compound is its quantitative analysis i.e. finding the percentage composition of the elements by weight which can be done by the following methods.

A. Estimation of Carbon and Hydrogen (Liebig Method) :

- (a) **Principle :** Both carbon and hydrogen are estimated together in one operation. When a known weight of the organic substance is burnt in excess of oxygen, carbon and hydrogen present in it are oxidised to carbon dioxide and water respectively.



The weights of CO_2 and H_2O thus formed are determined and the amounts of carbon and hydrogen in the original substance calculated.

- (b) **Apparatus :** The apparatus for the Liebig method consists of three units as shown in fig. 16.19
- (i) Oxygen supply
 - (ii) Combustion tube
 - (iii) Absorption apparatus.

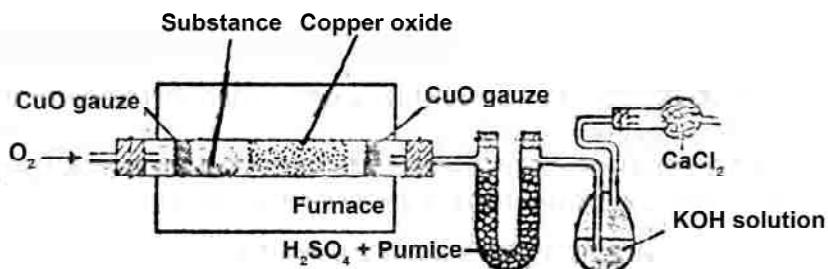


Fig.16.19 Apparatus for the esimation of C and H

The products of combustion containing moisture and carbon dioxide are passed through the absorption apparatus which consists of weighed U-tube packed with anhydrous CaCl_2 or pumice soaked in conc. sulphuric acid to absorb water and another U-tube containing conc. solution of potassium hydroxide to absorb carbon dioxide. These tubes are connected in series. The U-tube and the potash bulb are then detached and the increase in weight of each of them determined.

- (c) **Calculation :** Let the weight of the organic compound = w gm
 Increase in weight of U-tube (H_2O) = x gm
 Increase in weight of potash bulb (CO_2) = y gm

$$\text{Percentage of carbon} = \frac{12y}{44} \times \frac{100}{w}$$

$$\text{Percentage of hydrogen} = \frac{2x}{18} \times \frac{100}{w}$$

Example : 0.2 gm of an organic compound produces 0.5764 gm of CO_2 and 0.1512 gm of water on combustion. Calculate the percentage of carbon and hydrogen in the compound.

Solution : Weight of the organic compound = 0.2 gm

Weight of CO_2 produced = 0.5764 gm

Weight of H_2O produced = 0.1512 gm

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{0.5764}{0.2} \times 100 = 78.5$$

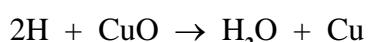
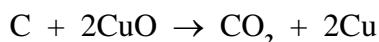
$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{0.1512}{0.2} \times 100 = 8.4$$

B. Estimation of Nitrogen :

The two main method for the estimation of nitrogen in an organic compound are :

(i) Dumas Method :

(a) **Principles :** Duma's method is based on the fact that nitrogenous compounds when heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen.



Traces of oxides of nitrogen formed, if any are reduced to nitrogen by passing the gaseous mixture over a heated copper spiral.



The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig. 16.20)

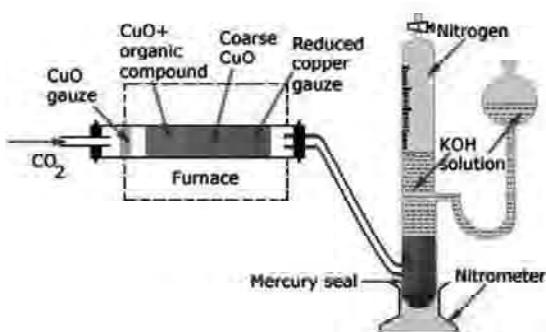


Fig. 16.20 Dumas method for estimation of nitrogen

(b) **Calculation :** Let the weight of the organic compound = W g

Volume of nitrogen collected = V₁ ml

Room temperature = T₁ K

$$V_2 = \text{volume of nitrogen at STP} = \frac{P_1 V_1}{T_1} \times \frac{273}{760}$$

$$\text{by applying the ideal gas equation } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Here P₁ = Atmospheric pressure – aqueous tension = (P–p) mm of Hg.

$$\text{Thus } V_2 = \frac{(P-p)V_1}{T_1} \times \frac{273}{760} = V \text{ ml (say)}$$

How 22,400 ml of N₂ at STP weighs 28 g

$$V \text{ ml of at STP weighs} = \frac{28 \times V}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times W}$$

Example : 0.2 gm of an organic compound yielded 20.7 ml of nitrogen at 15°C and 758 mm of Hg by Duma's method. Calculate the percentage of nitrogen in the compound. (Aqueous tension at 15°C = 12mm)

$$\text{Solution : Volume of N}_2 \text{ at STP} = \frac{(P-p)V_1}{T_1} \times \frac{273}{760}$$

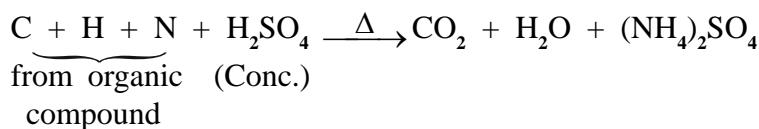
$$= \frac{(758-12) 20.7}{288} \times \frac{273}{760} = 19.2604 \text{ ml}$$

$$\text{Weight of ml of Nitrogen} = \frac{28}{22400} \times 19.2604 \text{ g}$$

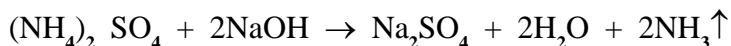
$$\text{Percentage of Nitrogen} = \frac{28 \times 19.2604}{22400} \times \frac{100}{0.2} = 12.04$$

(ii) Kjeldahl's Method :

(a) **Principle :** Kjeldahl's method is based on the fact that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen present in it is quantitatively converted into ammonium sulphate.



The resultant liquid is heated with concentrated alkali and the liberated ammonia gas is passed through a known excess of a standard acid solution. The volume of the unreacted acid is determined by titration with a standard alkali solution. The amount of ammonia and of nitrogen is determined by knowing the amount of acid reacted with ammonia.



(b) **Procedure :** The experiment is carried out in three steps.

- Formation of ammonium sulphate in Kjeldahl's flask (Fig. 16.21)
- Distillation with alkali to get ammonia (Fig. 16.22)
- Titration of excess acid.

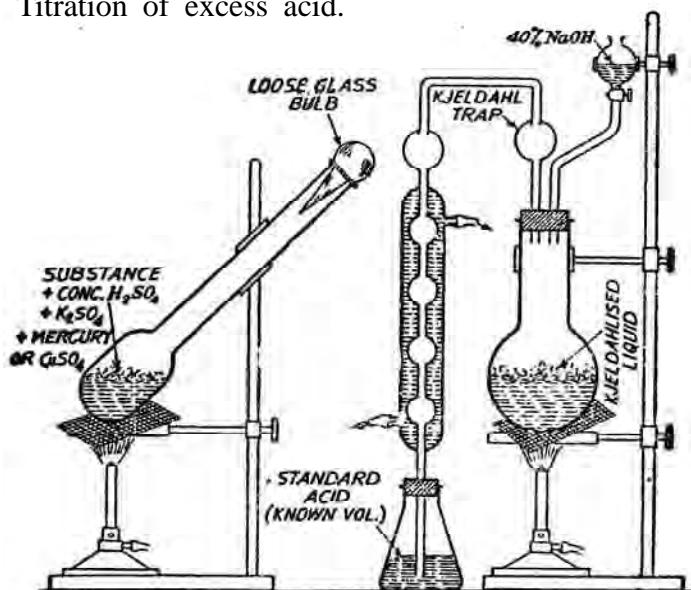


Fig. 16.21 Kjeldahl's flask

Fig. 16.22 Kjeldahl's method
for estimation of nitrogen

(c) **Calculation :**

Let the organic compound = Wg

Volume of H_2SO_4 of molarity M taken = Vml

Volume of NaOH of molarity M used for titration of excess of H_2SO_4 = V_1 ml

$$V_1 \text{ ml of NaOH of molarity M} = \frac{V_1}{2} \text{ ml of } H_2SO_4 \text{ of molarity M}$$

$$\text{Volume of } H_2SO_4 \text{ of molarity M unused} = \left(V - \frac{V_1}{2} \right) \text{ ml}$$

$$\left(V - \frac{V_1}{2} \right) \text{ ml of } H_2SO_4 \text{ of molarity M}$$

$$= 2 \left(V - \frac{V_1}{2} \right) \text{ ml of } NH_3 \text{ solution of molarity M}$$

1000 ml of 1M NH_3 solution contains 17g of NH_3 or 14 g of N.

Hence, $2 \left(V - \frac{V_1}{2} \right)$ ml of NH_3 solution of molarity M contains

$$\frac{14 \times M \times 2 \left(V - \frac{V_1}{2} \right)}{1000} \text{ g of Nitrogen}$$

$$\begin{aligned}\text{Percentage of Nitrogen} &= \frac{14 \times M \times 2 \left(V - \frac{V_1}{2} \right)}{1000} \times \frac{100}{M} \\ &= \frac{1.4 \times M \times 2 \left(V - \frac{V_1}{2} \right)}{M}\end{aligned}$$

- (d) **Limitation :** This method is not applicable to organic compound containing nitro and azo groups and also to pyridine where nitrogen atom is present in the ring.

Problem : 0.4g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 20 ml of 0.1 M H_2SO_4 . Calculate the percentage of nitrogen in the compound.

Solution : Weight of the organic compound = 0.4g

Volume of 0.1 M H_2SO_4 required for neutralisation of ammonia = 20 ml

$20 \text{ ml of } 0.1 \text{ M } \text{H}_2\text{SO}_4 = 2 \times 20 \text{ ml of } 0.1 \text{ M } \text{NH}_3 = 40 \text{ ml of } 0.1 \text{ M } \text{NH}_3$
 $= 4 \text{ ml of } 1 \text{ M } \text{NH}_3$

Now 1000 ml 1M NH_3 = 17g NH_3 = 14g of Nitrogen

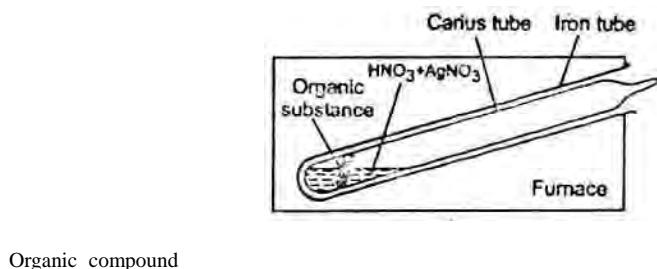
$$4 \text{ ml } 1\text{M } \text{NH}_3 = \frac{14}{1000} \times 4\text{g} = 0.056\text{g of Nitrogen.}$$

$$\text{Percentage of nitrogen} = \frac{0.056}{0.4} \times 100 = 14.0$$

C. Estimation of Halogens by Carius method :

- (a) **Principle :** Carius method for estimation of halogens is dependent on the fact that when a known weight of the organic compound containing halogens is heated in the presence of silver nitrate in a hard glass tube known as Carius tube (Fig. 16.23) in a furnace, silver halide is formed. It is filtered, washed, dried and weighed. From the amount of silver halide produced, the percentage of halogen is calculated.



**Fig. 16.23 Heating the bomb tube in a furnace****(b) Calculation :**

Let the weight of the organic compound = $w\text{g}$

Weight of silver halide formed = $x\text{g}$

Since 1 molecule of $\text{AgX} \equiv 1$ atom of x

(where $X = \text{Cl}, \text{Br}$ or I)

$$\text{Percentage of halogen} = \frac{\text{Atomic weight of } X}{\text{Molecular weight of } \text{AgX}} \times \frac{x}{w} \times 100$$

Problem : 0.1890 g of an organic compound gave 0.2870g of silver chloride in Carius method of estimation of halogen. Find out the percentage of chlorine in the compound.

Solution : Molecular mass of $\text{AgCl} = 108 + 35.5 = 143.5 \text{ g mol}^{-1}$

143.5 g of AgCl contains 35.5 g chlorine.

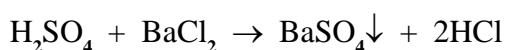
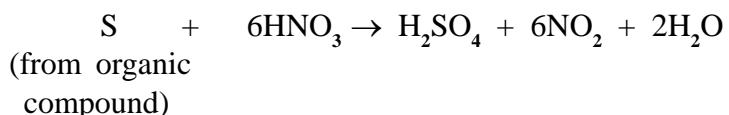
0.2870 g of AgCl contains $\frac{35.5}{143.5} \times 0.2870 \text{ g}$ of chlorine.

Weight of the organic compound = 0.1890 g

$$\therefore \text{Percentage of chlorine} = \frac{35.5 \times 0.2870 \times 100}{143.5 \times 0.1890} = 37.57$$

D. Estimation of Sulphur :

(a) Principle : A known weight of the organic compound is heated with sodium peroxide or fuming nitric acid in the Carius tube at 300°C for six hours. Sulphur present is oxidised to sulphuric acid which is precipitated as barium sulphate by the addition of excess of barium chloride. Barium sulphate so precipitated is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the weight of barium sulphate.



(white ppt.)

- (b) **Calculation :** Let the weight of the organic compound = wg
 Wt. of BaSO_4 formed = xg
 1 mol of BaSO_4 = 233g BaSO_4 = 32 g sulphur

xg BaSO_4 contains $\frac{32 \times x}{233}$ g of sulphur

$$\text{Hence, Percentage of sulphur} = \frac{32 \times x \times 100}{233 \times w}$$

Problem : 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582g of BaSO_4 . Find the percentage of sulphur in the substance.

Solution : Weight of the organic compound = 0.395g

Weight of BaSO_4 formed = 0.582g

233g of BaSO_4 contains 32g of sulphur

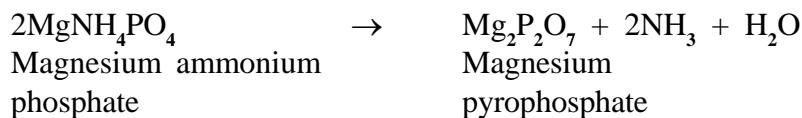
\therefore 0.582g of BaSO_4 contains $\frac{32}{233} \times 0.582$ g of sulphur

Hence, percentage of sulphur in the organic compound

$$= \frac{32}{233} \times 0.582 \times \frac{100}{0.395} = 20.24$$

E. Estimation of Phosphorus :

- (a) **Principle :** A known weight of an organic compound is heated with fuming nitric acid in a Carius tube where upon phosphorus present in the compound is oxidised to phosphoric acid (H_3PO_4). The phosphoric acid is precipitated either as (i) ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ by the addition of ammonia and ammonium molybdate solution or (ii) as magnesium ammonium phosphate by adding magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) which on ignition yeilds magnesium pyrophosphate.



Precipitate of ammonium phosphomolybdate or magnesium pyrophosphate is separated, dried and weighed from which the percentage of phosphorus can be calculated.

- (b) **Calculation :** Let the weight of the organic compound = wg

(i) weight of ammonium phophomolybdate = xg

molecular wt. of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ = 1877 g

Hence, percentage of phosphorus = $\frac{31 \times x \times 100}{1877 \times w}$

(ii) weight of magnesium pyrophosphate = yg

molecular weight of $Mg_2P_2O_7$ = 222

$$\text{Hence, percentage of phosphorous} = \frac{62 \times y \times 100}{222 \times w}$$

Problem : The phosphoric acid formed by heating 0.31g of an organic compound with fuming nitric acid in carius tube was precipitated as $MgNH_4PO_4$ which on ignition left 0.148g of $Mg_2P_2O_7$. find out the percentage of phosphorus in the organic compound.

Solution : wt. of the organic compound = 0.31g

wt. of $Mg_2P_2O_7$ = 0.148g

222g of $Mg_2P_2O_7$ contain 62g of phosphorus.

$$0.148 \text{ g of } Mg_2P_2O_7 \text{ contain phosphorus } \frac{62}{222} \times 0.148 \text{ g}$$

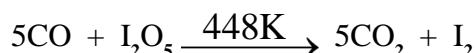
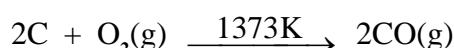
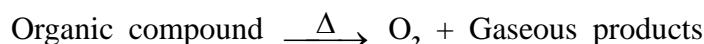
Hence, percentage of phosphorus is the organic compound

$$= \frac{62 \times 0.148 \times 100}{222 \times 0.31} = 13.33$$

F. Estimation of Oxygen :

Though the percentage of oxygen in an organic compound is obtained by subtracting the sum of the percentages of other elements from 100, it can be estimated by a direct method.

- (a) **Principle :** A known weight of the organic compound is pyrolysed in a stream of nitrogen gas. The mixture of gaseous products along with oxygen is passed over red hot coke (1373K) when all the oxygen is converted to carbon monoxide. This when passed through warm (448K) iodine pentoxide (I_2O_5) is oxidised to carbon dioxide producing iodine (Fig. 16.24)



By determining the amount of CO_2 (or I_2) produced, the percentage of oxygen in the original organic compound can be calculated, which can be done by passing the mixture of CO_2 and I_2 over a bed of potassium iodide solution, thus removing iodine. The residual gases containing CO_2 are finally passed through a soda-asbestos U-tube where CO_2 is retained. This U-tube is weighed before and after pyrolysis, the difference of which gives the amount of CO_2 obtained from the given sample of the organic compound (Fig. 16.25)

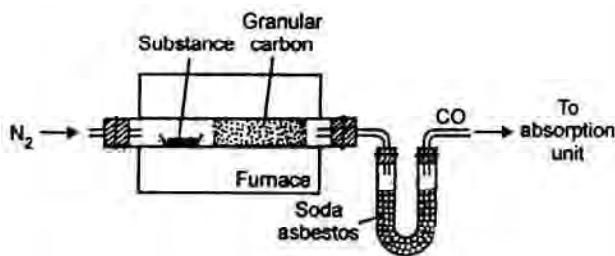


Fig. 16.24 Pyrolysis unit of apparatus for the estimation of oxygen.

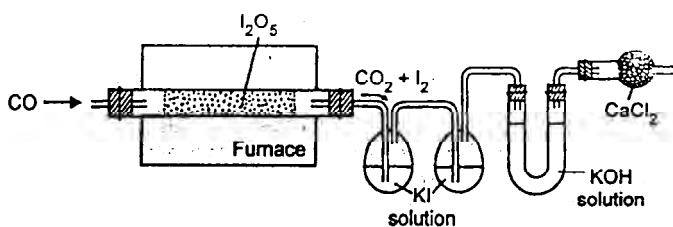


Fig. 16.25 Absorption Unit

- (b) **Calculation :** Let the weight of the organic compound = w g
 The weight of CO_2 produced = x g
 44g of CO_2 contain 32g of oxygen.

$$x\text{g of } \text{CO}_2 \text{ contain oxygen} = \frac{32}{44} \times x \text{ g}$$

$$\text{Hence, percentage of oxygen} = \frac{32}{44} \times x \times \frac{100}{w}$$

G. CHN Analyser :

Recently it has become possible to carry out the estimation of elements like carbon, hydrogen and nitrogen present in an organic compound by using only micro quantities (1–3 mg) of the compound and automatic experimental techniques like CHN Analyser. This instrument displays the results on a screen within a short time.

16.8 CLASSIFICATION OF ORGANIC COMPOUNDS

Classification of organic compounds has been made essentially to systematise and simplify the study of organic compounds. Two main systems of classification are

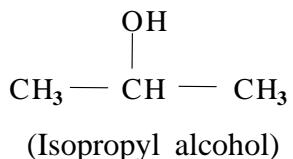
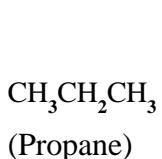
- A. Classification based on carbon skeleton.
- B. Classification based on functional group.

A. Classification based on Carbon skeleton :

Mainly there are two important classes of organic compounds.

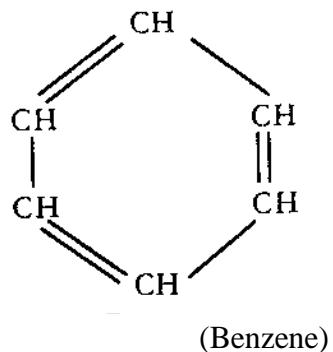
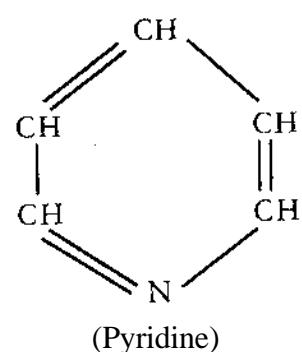
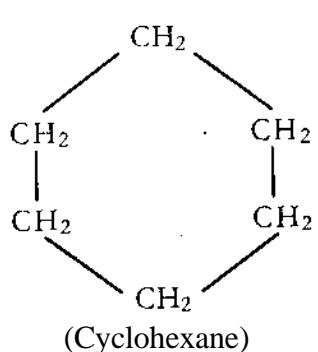
1. Acyclic, open-chain or aliphatic compounds :

Compounds which have an open chain of carbon atoms (branched or straight chained) are called acyclic, open chain or aliphatic compounds. Examples are



2. Cyclic or closed chain compounds :

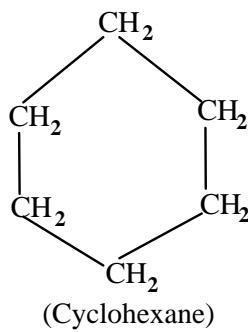
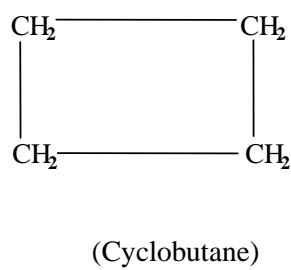
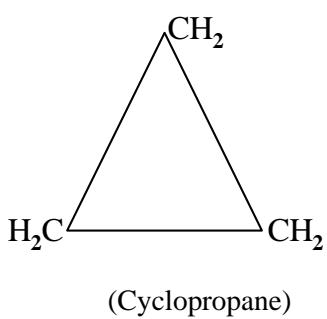
Compounds with a closed chain of atoms (ring structure) are termed as cyclic or closed chain compounds. Examples are cyclohexane, pyridine, benzene etc.



There are two types of cyclic compounds.

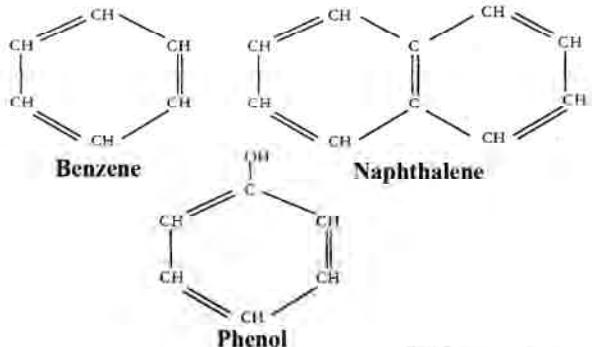
(a) Homocyclic or Carbocyclic compounds : They have one or more rings composed of carbon atoms only. They may be alicyclic or aromatic.

(i) *Alicyclic compounds* : Compounds like cyclopropane, cyclobutane, cyclohexane though cyclic resemble aliphatic compounds. They are called *alicyclic* compounds.



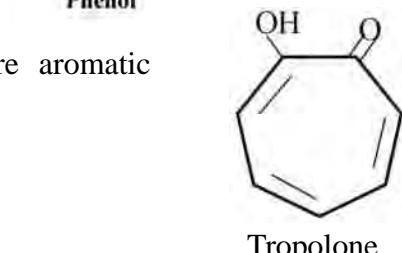
(ii) *Aromatic compounds* : Aromatic compounds can be classified into two categories. These compounds contain one or more benzene rings in their structure. For example,

(a) Benzenoid compounds

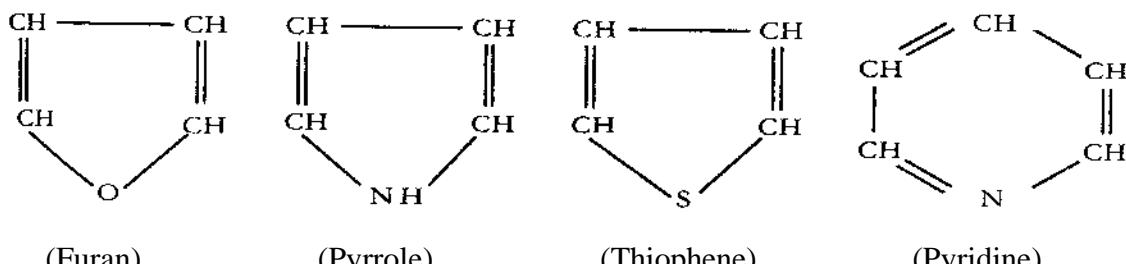


- (b) Non-benzenoid compounds : These are aromatic compounds having no benzene ring.

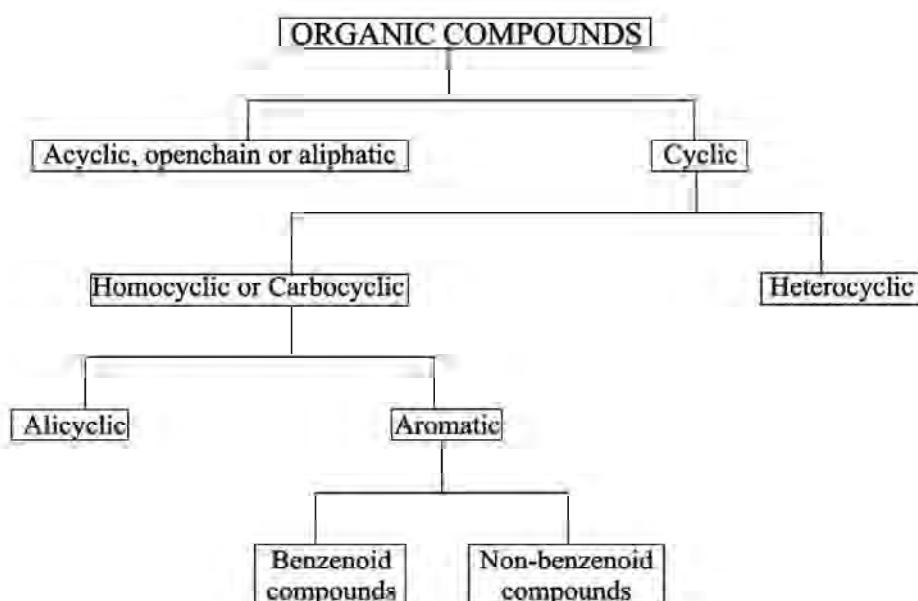
Example- Tropolone



- (b) **Heterocyclic compounds** : Heterocyclic compounds contain one or more atoms or elements other than carbon and hydrogen alongwith carbon atoms in the ring. The atoms of elements other than carbon are termed as hetero atoms which may be N,O,S etc. Example are furan, pyrrole, thiophene, pyridine etc.



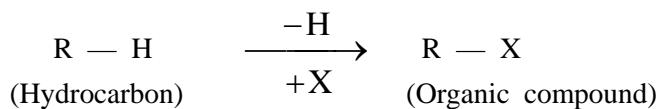
The scheme of classification may be represented as follows :



B. Classification based on Functional Group :

The skeletal classification of organic compounds is very wide and therefore needs further systematisation for study. This is achieved by dividing the above classes of compounds on the basis of functional group or groups present.

Functional group : The simplest compounds are hydrocarbons consisting of carbon and hydrogen only. All other compounds are treated as the derivatives of the hydrocarbons and formed by replacing one or more hydrogen atoms with other atoms or groups.



where R is the hydrocarbon residue and X is a group. Thus, an organic compound can generally be splitted up into two or more groups or radicals. For example, methyl alcohol can be splitted up into methyl (CH_3-) and hydroxyl ($-\text{OH}$) group. A group contains heteroatoms like O,N,S, halogens etc. The groups determine the properties of organic compounds to a great extent. *The reactive groups which determine the chemical characteristics of the organic compounds are termed as functional or characteristic groups.* In fact, all the alcohols are characterised by the presence of the hydroxyl group ($-\text{OH}$) in their molecules. Hence, hydroxyl group ($-\text{OH}$) is functional group. Similarly, all the carboxylic acids are characterised by the presence of the carboxyl group ($-\text{COOH}$) and therefore carboxyl group ($-\text{COOH}$) is a functional group of a class of compounds called carboxylic acids.

In unsaturated compounds, the double bond or triple bond is the reaction site and hence they are considered as functional group(s). Only saturated hydrocarbons do not contain a functional group. The classification of organic compounds on the basis of functional groups present makes the study simple and systematic. Some important functional groups and the class alongwith common examples are listed in Table - 16.1

TABLE - 16.1

Class of compound	Functional group symbol and name	Common examples
1. Alkanes	Nil	Methane(CH_4), Ethane (CH_3CH_3)
2. Alkenes	$\text{C} = \text{C}$ (double bond)	Propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) Ethylene ($\text{CH}_2=\text{CH}_2$) Propylene ($\text{CH}_3-\text{CH}=\text{CH}_2$)
3. Alkynes	$-\text{C} \equiv \text{C}$ – (triple bond)	Acetylene ($\text{CH} \equiv \text{CH}$)
4. Alkyl halides	$-\text{X}$ (F,Cl,Br,I) (halo)	Methyl chloride (CH_3Cl), Ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$), Isopropyl iodide ($\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{I} \end{array}$)
5. Alcohols or Alkanols	$-\text{OH}$ (hydroxy)	Methyl alcohol (CH_3OH) Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$)
6. Ethers	$-\text{O}-\text{R}$ (Alkoxy)	Dimethyl ether ($\text{CH}_3-\text{O}-\text{CH}_3$) Diethyl ether ($\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$)
7. Aldehydes or Alkanals	$-\text{CHO}$ (formyl) or or $-\text{C}^{\text{H}}=\text{O}$ aldehyde)	Formaldehyde ($\text{H}-\text{CHO}$) Acetaldehyde (CH_3-CHO)
8. Ketones or Alkanones	$=\text{CO}$ (carbonyl) or or $>\text{C}=\text{O}$ oxo)	Acetone (CH_3COCH_3)
9. Carboxylic acids or Alkanoic acids	$-\text{COOH}$ or (carboxyl) $-\text{C}^{\text{OH}}=\text{O}$	Formic acid ($\text{H}-\text{COOH}$) Acetic acid (CH_3-COOH)
10. Esters	$-\text{C}^{\text{OR}}=\text{O}$ Ester or alkoxycarbonyl)	Ethyl formate ($\text{H}-\text{COOC}_2\text{H}_5$) Methyl acetate ($\text{CH}_3-\text{COOCH}_3$)
11. Acid chlorides	$-\text{C}^{\text{Cl}}=\text{O}$ (chloroformyl)	Acetyl chloride (CH_3COCl)
12. Acid amides	$-\text{C}^{\text{NH}_2}=\text{O}$ (amide)	Acetamide (CH_3CONH_2)
13. Nitriles	$-\text{C} \equiv \text{N}$ (cyano)	Acetonitrile (CH_3CN)
14. Amines	$-\text{NH}_2$ (amino)	Methylamine (CH_3NH_2)
15. Nitroalkanes	$-\text{NO}_2$ (nitro)	Nitromethane (CH_3-NO_2)
16. Arenes	 (benzene)	Chlorobenzene ($\text{Cl}-\text{C}_6\text{H}_5$) Toluene ($\text{CH}_3-\text{C}_6\text{H}_5$)

HOMOLOGOUS SERIES

A class of compounds containing the same functional group when arranged in the order of increasing molecular mass, each compound differing from the adjacent member by a $-CH_2$ group forms a **homologous series** and the phenomenon is called **homology**. Each member of a homologous series is the homologue of its immediate neighbour.

A homologous series has the following characteristics.

1. All members of a homologous series can be represented by a general formula $R-X$ where R is the hydrocarbon residue and X is the functional group. The homologous series of alcohols can be represented by the general formula $C_nH_{2n+1}OH$ and the formula of various homologues can be obtained by putting 1,2,3....etc. for n.
2. All members of a series can be prepared by the same general method.
3. The physical properties of the members of a series show a regular gradation with increase in molecular mass though the chemical properties of all the members are similar.

A few important homologous series are mentioned in Table 16.2

TABLE – 16.2
Some Important Homologous Series

Name of the series	General Formula	Examples
1. Alkane	C_nH_{2n+2}	$CH_4, C_2H_6, C_3H_8, C_4H_{10}, \dots$
2. Alkene	C_nH_{2n}	$C_2H_4, C_3H_6, C_4H_8, \dots$
3. Alkyne	C_nH_{2n-2}	$C_2H_2, C_3H_4, C_4H_6, \dots$
4. Arene	C_nH_{2n-6}	$C_6H_6, C_7H_8, C_8H_{10}, \dots$
5. Alcohol	$C_nH_{2n+1}OH$	$CH_3OH, C_2H_5OH, C_3H_7OH, \dots$
6. Aldehyde	$C_nH_{2n+1}CHO$	$HCHO, CH_3CHO, C_2H_5CHO, \dots$
7. Ketone	$RCOR'$	$CH_3COCH_3, CH_3CH_2COCH_3, \dots$
8. Carboxylic acid	$C_nH_{2n+1}COOH$	$HCOOH, CH_3COOH, C_2H_5COOH, \dots$
9. Alkyl halide	$C_nH_{2n+1}X$	$CH_3Cl, C_2H_5Cl, C_3H_7Cl, \dots$
10. Amine	$C_nH_{2n+1}NH_2$	$CH_3NH_2, C_2H_5NH_2, C_3H_7NH_2, \dots$
11. Ester	$C_nH_{2n+1}COOR'$	$HCOOCH_3, CH_3COOCH_3, C_2H_5COOCH_3, \dots$
12. Ether	$R - O - R'$	$CH_3-O-CH_3, CH_3OCH_2CH_3, CH_3CH_2OCH_2CH_3, \dots$

16.9 NOMENCLATURE OF ORGANIC COMPOUNDS

Early system of nomenclature of organic compounds was based on the sources from which they were obtained. For example, methyl alcohol was named after its source (Greek word : *methu* means wine and *hule* means wood), since it was obtained by destructive distillation of wood. Thus, the names citric acid (from citrus fruits) formic acid (Latin : *formica* means red ant), uric acid (from urine), acetic acid (Latin : *acetum* means vinegar) etc. have been derived from their sources. These are known as **common or trivial names**.

Due to the unique property of catenation carbon forms a large number of compounds. Problems were raised in naming them by this system. The systematic nomenclature was first developed in an international conference of chemists in 1928 in Geneva. This system was named as Geneva System which was subsequently modified in 1930 in Belgium at the International Union of Chemistry (IUC). The most systematic nomenclature was developed by the International Union of Pure and Applied Chemistry in 1957 referred to as IUPAC system of nomenclature. This system is modified from time to time. The latest rules are mentioned here following "A guide to IUPAC nomenclature of organic compounds" (1994 edition) by R. Panico, W.H. Powell and Jean Claude Richer (Sr.editor), Blackwell Scientific Publications, Oxford. The IUPAC system provides a set of rules for naming the complex organic compounds. Some of the organic compounds have still retained their common names because of familiarity and long usage.

A. GENERAL RULES FOR IUPAC NOMENCLATURE

According to the latest rules, the name of an organic compound is derived from the name of the parent hydrocarbon by using suitable prefixes, infixes and suffixes. The name of the organic compound consists of three parts.

Prefix–Word root – Suffix

Word root is the basic unit of the name. The total number of carbon atoms in the principal chain usually determines the word root. They are fixed as follows :

Word root		Chain length (system)
Meth	–	C ₁ (for one carbon system)
Eth	–	C ₂ (for two carbon system)
Prop	–	C ₃ (for three carbon system)
But	–	C ₄ (for four carbon system)
Pent	–	C ₅ (for five carbon system)
Hex	–	C ₆ (for six carbon system)
Hept	–	C ₇ (for seven carbon system)

Oct	-	C ₈ (for eight carbon system)
Non	-	C ₉ (for nine carbon system)
Dec	-	C ₁₀ (for ten carbon system) and so on

The **suffix** refers to the functional group of a particular class of compound. Suffix may be of two types.

(i) **Primary suffix** : This suggests the nature of linkage between the carbon atom.

Linkage	Suffix
Carbon-Carbon single bond	- - ane
Carbon-Carbon double bond	- - ene
Carbon-Carbon triple bond	- - yne

(ii) **Secondary suffix** : This suggests the characteristic functional groups present in the compound and is added to the name after the primary suffix. Some of the secondary suffixes are :

Functional group	Suffix	Functional group	Suffix
Alcohol (-OH)	-ol	Amide (-CONH ₂)	-amide
Aldehyde (-CHO)	-al	Acyl group (R-CO-)	-oyl
Ketone ($\text{C}=\text{O}$)	-one	Cyanide (-C ≡ N)	-nitrile
Carboxylic acid (-COOH)	-oic acid	Amine (-NH ₂)	-amine
Ester (-COOR)	R.....-oate	Sulphonic acid (-SO ₃ H)	-sulphonic acid
Acid halide (-COX)	-oyl chloride		

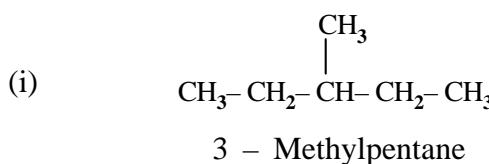
Note : When using secondary suffixes, the carbon of the functional group (if any) is normally included in the principal chain.

Prefixes indicate the substitution of other atom or group in place of hydrogen atom(s) in the main chain of carbon atoms under consideration. They are not regarded as principal functional groups. Commonly used prefixes are :

Substituent	Prefix	Substituent	Prefix
CH_3-	Methyl	$\text{Br}-$	Bromo
CH_3CH_2-	Ethyl	$\text{I}-$	Iodo
$\text{CH}_3\text{CH}_2\text{CH}_2-$	Propyl	$- \text{NO}_2$	Nitro
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	Butyl	$- \text{OR}$	Alkoxy
$\text{F}-$	Fluoro	$-\overset{+}{\text{N}}\equiv \text{N}$	Diazo
$\text{Cl}-$	Chloro	$- \text{N} = \text{O}$	Nitroso

B. COMMON CONVENTIONS IN IUPAC SYSTEM

1. **Position of locants :** A locant is a number (1, 2, 3...) or a letter (*o* –, *m* –, *p* – etc.) used to locate the position of the substituent or a carbon-carbon multiple bond. These locants are placed immediately before the part of the name to which they relate. For example :



(ii) $\text{CH}_3\text{--CH}_2\text{--CH} = \text{CH}_2$ (According to the latest rule, names like
 But-1-ene 1- Butene or Butene - 1 are not correct)

2. **Numerical prefixes** : Numerical prefixes are used to describe a multiplicity of identical features of a structure in nomenclature. Some common numerical prefixes are :

Number	Numerical term	Number	Numerical term
1	mono –	6	hexa –
2	di –	7	hepta –
3.	tri –	8	octa–
4.	tetra –	9	nona –
5.	penta–	10	deca –

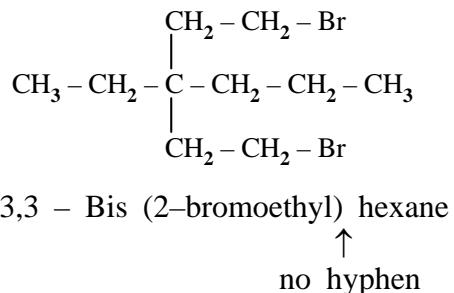
For example : (i) CCl_4
 Tetrachloromethane

(ii) $\begin{array}{c} \text{CH}_2 - \text{OH} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$

Ethane-1,2-diol

In example (i) above, the prefix 'tetra' before chloro indicates the presence of four chlorine atoms in the molecule. Similarly, in the example (ii) above, the prefix 'di' before the suffix 'ol' indicates the presence of two $-OH$ groups in the molecule.

When the substituent itself is substituted (substituted substituent), the multiplicity is indicated by numerical prefixes such as '*bis*' (2), '*tris*' (3), *tetrakis* (4) and so on.

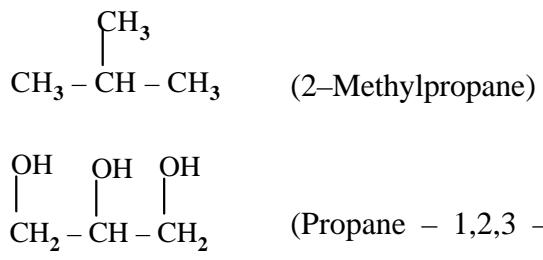


Here, 2 bromoethyl is a substituted substituent because the ethyl group is substituted at the second carbon atom and two such groups are present at position 3. Hence, numerical prefix used is '*bis*' and not '*di*' as in simple substituents.

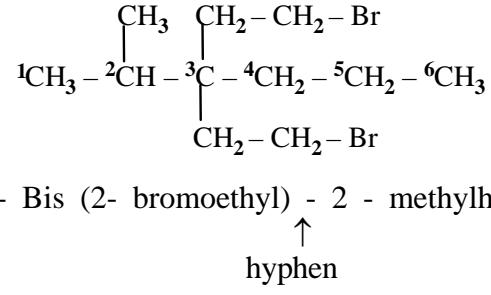
3. Brackets or Parentheses : Brackets or parentheses are used around prefixes defining substituted substituents after the numerical prefix if any.

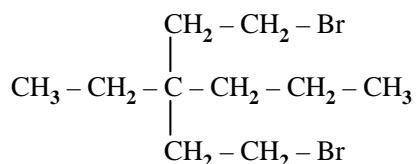
For example : 3,3 – Bis (2–bromoethyl)hexane.

4. Use of hyphen : A hyphen separates a locant from the syllable of the name.



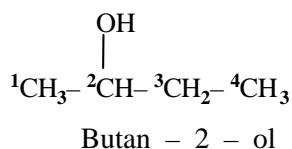
When a substituent is put in the bracket, a hyphen is given after the end of the bracket only if the final bracket is followed by a locant.



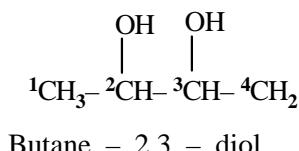


3,3 - Bis (2-bromoethyl) hexane
 ↑
 no hyphen

5. **Omission of 'e'** : The terminal 'e' in the primary suffix is omitted when followed by a second suffix beginning with 'a', 'i', 'o', 'u', or 'y'

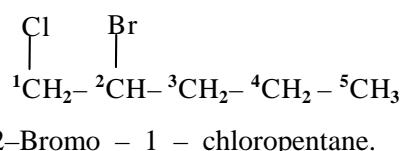


The terminal 'e' of the primary suffix 'ane' is omitted because it is followed by 'o' of the secondary suffix - 'ol'.

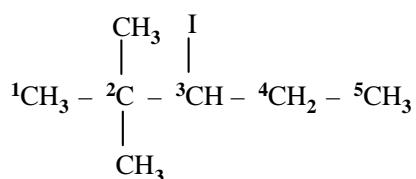


Here, 'e' of the primary suffix 'ane' is not omitted because it is followed by 'd' of secondary suffix 'diol'.

6. **Alphabetical order of the prefixes** : When two or more prefixes are attached to the principal chain, then the prefixes are arranged in the alphabetical order. While arranging prefixes in alphabetical order, di-, tri, tetra - etc (if any) are not considered except for substituted substituents.



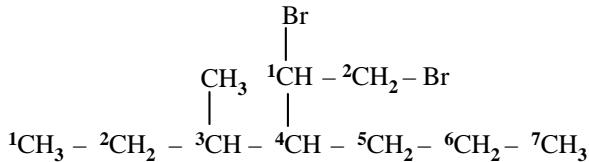
The prefix 'bromo' is placed before 'chloro' because 'b' comes before 'c' in alphabetical order.



3 - Iodo - 2, 2 - dimethylpentane.

Since 'methyl' is a simple substituent, di- is not considered while arranging the prefixes in alphabetical order. 'T' comes before 'm' and therefore 'Iodo' comes first.

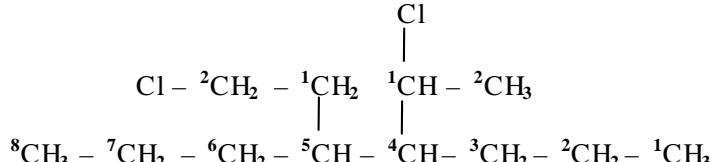
In case of **substituted substituents**, the numerical prefixes 'di', 'tri' etc. are considered while arranging the prefixes. The following example will clarify the rule.



4 – (1,2 – Dibromoethyl) – 3 – methylheptane.

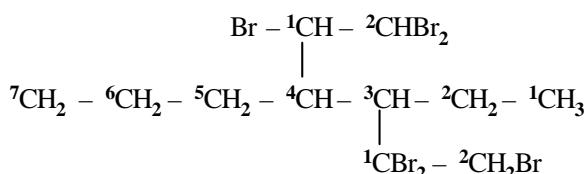
Here, '1,2 – dibromomethyl' is a substituted substituent. Hence, numerical prefix 'di' shall be considered while arranging prefixes. Obviously, 'd' of dibromoethyl comes before 'm' of methyl is alphabetical order and written accordingly.

When two or more prefixes consist of identical words priority for citation is given to that group which contains the lowest locant at the first point of difference. If the locants at the first point are same, the second point of difference is considered and so on and the lowest locant is preferred. This rule can be explained by the following examples :



4 – (1-Chloroethyl) – 5 – (2-chloroethyl)octane

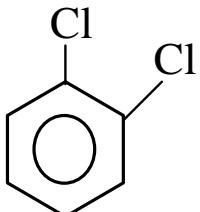
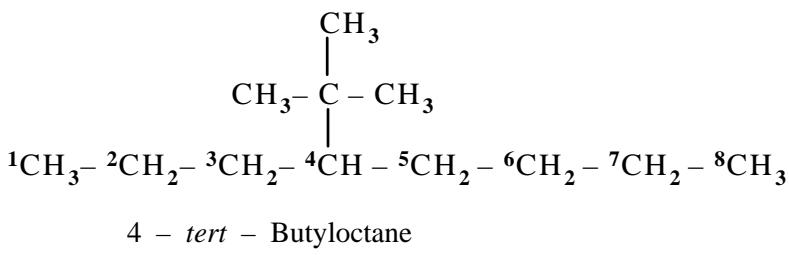
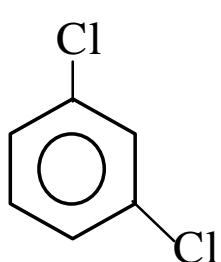
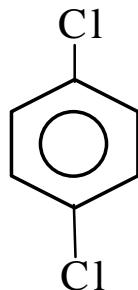
Here, the two prefixes have identical words 'chloroethyl'. Priority for citation is thus given to that group which contains the lowest locant at the first point of difference. Therefore, 1– chloroethyl is written first.



3 – (1,1,2-Tribromoethyl)–4 –(1, 2, 2 –tribromoethyl)heptane

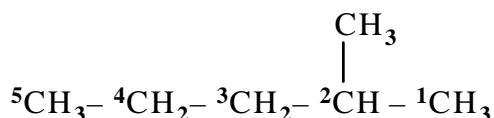
Here, the prefixes have identical words and the locants at the first place in both the prefixes are same. Therefore, the locants at the second place is considered and (1,1,2) set being lower than (1,2,2) set is given priority.

7. The name of an organic compound should start with a capital letter. There are certain exceptions which are given below.

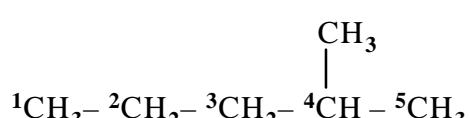
*o* – Dichlorobenzene*m* – Dichlorobenzene*p* – Dichlorobenzene

8. Lowest set of locant rule :

- (a) If there is only one substituent, the carbon atoms of the principal chain is numbered from such an end so as to give the lowest number to the carbon atom carrying the substituent.



2-Methylpentane
(Correct)



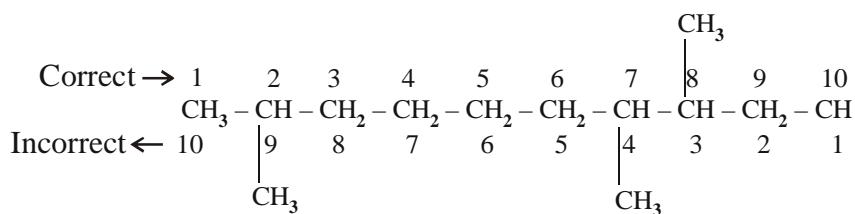
4-Methylpentane
(Incorrect)

In the above example, the correct locant is 2 and not 4, because 2 is lower than 4.

- (b) If two or more number of substituents are present, the carbon atoms of the parent chain is numbered from such an end so as to give the **lowest set of locants** possible.

The lowest set of locants is decided as follows :

- (i) When series of locants containing the same number of terms are compared term by term, then the lowest set is one which contains the lowest number on the occasion of the first difference. (In case the first locant in both the sets is identical, the second set is compared and so on till the lowest locant in a set is obtained and that set shall be the lowest set even though the lowest sum rule applied previously is violated.) The following examples will clarify the situation.



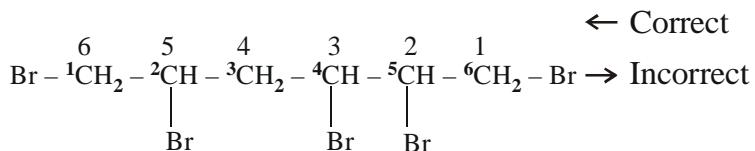
Correct name : 2,7,8 – Trimethyldecane (Sum of locants : $2+7+8 = 17$)

Incorrect name : 3,4,9 – Trimethyldecane (Sum of locants : $3+4+9 = 16$)

Here, the two sets of locants are 2,7,8 and 3,4,9. The first points of difference is the first locant which is 2 in the first set and 3 in the second set. As 2 is the lower locant than 3, the first set of locants i.e. 2,7,8 is the correct set even though the sum of the locants is 17, higher than the second set which is 16 ($3+4+9$). Therefore, the correct name is 2,7,8–Trimethyldecane.

[Note : Commonly used lowest sum rule in the case will lead to incorrect name]

Another example may be taken.



Correct name : 1,2,3,5,6 – Pentabromohexane

(Sum of locants : $1+2+3+5+6 = 17$)

Incorrect name : 1,2,4,5,6 – Pentabromohexane

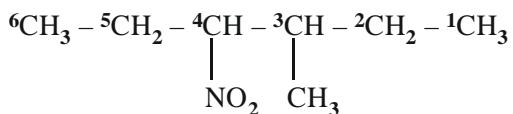
(Sum of locants : $1+2+4+5+6 = 18$)

Here, out of the two sets of locants i.e. 1,2,3,5,6 and 1,2,4,5,6 the first set 1,2,3,5,6 is lower. The first two locants in both the sets are identical and the difference comes in the third locant. 3 being lower than 4 the first set 1,2,3,5,6 is the lowest set. Therefore, the correct name is 1,2,3,5,6 – Pentabromohexane.

[Note : In this case, the lowest set of locant rule and the lowest sum of locant rule give the same set of locants.]

Important : It is important to note that both the lowest set of locant rule and the lowest sum of locant rule lead to the correct name when applied to smaller carbon chain (up to 7 carbon atoms). For the longer carbon chains containing more than 7 carbon atoms. lowest sum of locant rule will lead to incorrect name. Therefore, it is better to use the lowest set of locant rule irrespective of the length of the chain.

9. When two or more different substituents are present to equivalent positions from the two ends of the principal chain (i.e. same set of locants is obtained when numbered from either end), then the numbering is done in such a way that the substituent which comes first in the alphabetical order gets the lower locant.



3–Methyl – 4– nitrohexane.

Both the substituents '*nitro*' and '*methyl*' are present at equivalent positions giving same set of locants (3,4). Since 'm' of '*methyl*' comes before 'n' of '*nitro*', the numbering is done from right end to the left giving the lowest locant to the methyl group.

C. NAMES OF SIMPLER MEMBERS OF ALIPHATIC HOMOLOGOUS SERIES

The names of the aliphatic homologous series and their simpler members are discussed below which will be helpful for naming complex organic compounds.

1. Hydrocarbons

Saturated hydrocarbons are called *paraffins* or *alkanes*. Unsaturated hydrocarbons containing double bond are called *olefins* or *alkenes* and those containing triple bond are called *acetylenes* or *alkynes*. Thus, there are three homologous series in hydrocarbons.

(i) Saturated hydrocarbons or Alkanes or Paraffins

(Suffix – ane)

Alkanes are the parent compounds from which all other compounds are structurally derived. The carbon atoms in the chain are linked by single covalent bonds. Some typical members with their common and IUPAC names are listed below.

TABLE : 16.3 ALKANES

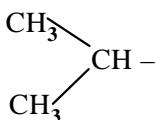
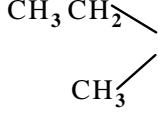
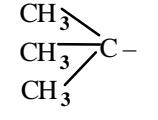
General formula : C_nH_{2n+2} where $n = 1, 2, 3, 4, \dots$ etc.

Formula	Alkane	Common name	IUPAC name
$CH_4(n=1)$	CH_4	Methane	Methane
$C_2H_6(n=2)$	CH_3-CH_3	Ethane	Ethane
$C_3H_8(n=3)$	$CH_3-CH_2-CH_3$	Propane	Propane
$C_4H_{10}(n=4)$	$CH_3-CH_2-CH_2-CH_3$	<i>n</i> -Butane	Butane
$C_4H_{10}(n=4)$	$CH_3-CH(CH_3)-CH_3$	Isobutane	2-Methylpropane
$C_5H_{12} (n=5)$	$CH_3-CH_2-CH_2-CH_2-CH_3$	<i>n</i> -Pentane	Pentane
$C_5H_{12} (n=5)$	$CH_3-CH(CH_3)-CH_2-CH_3$	Isopentane	2-Methylbutane
$C_5H_{12}(n = 5)$	$CH_3-C(CH_3)_3$	Neopentane	2,2-Dimethylpropane

Alkyl groups or radicals :

The monovalent hydrocarbon residue left after removing one hydrogen atom from the alkane is called an **alkyl group** or **radical**, often represented by R^- . The alkyl group is named by removing – **ane** from alkane and adding 'yl'. Thus, CH_3- group is called **methyl** group. CH_3-CH_2- group is called **ethyl** group and so on. The list of a few alkyl groups is given below.

TABLE : 16.4 SOME ALKYL GROUPS OR RADICALS.

Alkyl radical	Structure	Common name	IUPAC name
Methyl (CH_3-)	CH_3-	methyl	methyl
Ethyl (C_2H_5-)	CH_3-CH_2-	ethyl	ethyl
Propyl (C_3H_7-)	$\text{CH}_3\text{CH}_2\text{CH}_2-$	<i>n</i> -propyl	propyl
		Isopropyl	1-methylethyl or Isopropyl
Butyl (C_4H_9-)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	<i>n</i> -butyl	butyl
	Isobutyl		2-methylpropyl or Isobutyl
		<i>sec</i> -Butyl	1-methylpropyl or <i>sec</i> -Butyl
		<i>tert</i> -Butyl	1,1-dimethylethyl or <i>tert</i> -Butyl

(ii) **Olefins or Alkenes (Suffix-ene)****General formula** – C_nH_{2n} where $n = 2, 3, 4$ etc.**Characteristic group** – >C=C<

The IUPAC name of a member is derived from the alkane having the same number of carbon atoms by replacing '*ane*' of alkane by '*ene*'. The first member, obtained by putting $n = 2$, is *ethene* C_2H_4 corresponding to the alkane, ethane. The common name of alkene is **alkylene**. Thus, ethene is named as *ethylene* in common system.

TABLE : 16.5

Alkane	Alkene	Common name	IUPAC name
CH ₄ (Methane)	Does not exist	—	—
C ₂ H ₆ (Ethane)	C ₂ H ₄ (CH ₂ =CH ₂)	Ethylene	Ethene
C ₃ H ₈ (Propane)	C ₃ H ₆ (CH ₃ -CH=CH ₂)	Propylene	Propene
C ₄ H ₁₀ (Butane)	C ₄ H ₈ (CH ₃ -CH ₂ -CH=CH ₂)	α - Butylene	But-1-ene
	C ₄ H ₈ (CH ₃ -CH=CH-CH ₃)	β - Butylene	But-2-ene
	C ₄ H ₈ (CH ₃ - CH ₃ -C = CH ₂)	Iso-butylene	2-Methylprop-1-ene

Alkenyl group :

The monovalent hydrocarbon residue left after removing one hydrogen from the alkene is an alkenyl group. The common names are more prevalent.

TABLE 16.6

Alkenyl group	Formula	Common name	IUPAC name
C ₂ H ₃ -	CH ₂ = CH -	vinyl	Ethenyl
C ₃ H ₅ -	CH ₃ - CH = CH -	propenyl	1-propenyl
	CH ₂ = CH - CH ₂ -	allyl	2-propenyl

In certain cases, one or more multiple bonds are considered to be present in sidechains. For this purpose, the following prefixes are mostly used.



(iii) **Acetylenes or Alkynes (Suffix-yne)**

General formula : C_nH_{2n-2} where n = 2,3,4 etc.

Characteristic group : - C ≡ C -

The IUPAC name of a member is derived from the alkane containing the same number of carbon atoms by replacing the suffix '*ane*' by '*yne*'. The first member is one containing two carbon atoms, C_2H_2 and is commonly known as acetylene.

TABLE : 16.7

Alkane	Alkyne	Common name	IUPAC name
C_2H_6 (Ethane)	$C_2H_2(CH\equiv CH)$	Acetylene	Ethyne
C_3H_8 (Propane)	$C_3H_4(CH_3-C \equiv CH)$	Allylene	Propyne
C_4H_{10} (Butane)	$C_4H_6(CH_3CH_2 - C \equiv CH)$	α – Crotonylene	But-1-yne
	$C_4H_6(CH_3-C \equiv C - CH_3)$	β – Crotonylene	But – 2 – yne

Alkynyl group :

The monovalent hydrocarbon residue left after removing one hydrogen atom from an alkyne is an **alkynyl** group.

TABLE : 16.8

Alkynyl group	Formula	Common name	IUPAC name
C_2H-	$HC \equiv C -$	Acetylide	Ethynyl
C_3H_3-	$HC \equiv C - CH_2 -$	Propargyl	2 – Propynyl
	$CH_3 - C \equiv C ---$		1 – Propynyl

2. Halogen Derivatives of Hydrocarbons

The halogen derivatives of the hydrocarbons are obtained by replacing one or more number of hydrogen atoms by halogen atom or atoms. Thus, a monohalogen compound contains one halogen atom in its molecule. Di –, tri, or polyhalogen compounds contain two, three or more number of halogen atoms in their molecules.

(i) Monohalogen derivatives or Alkyl halides :

Alkyl halides are represented by the general formula $R - X$, where R is an alkyl group and X is a halogen. The common names for these compounds are **alkyl halides** whereas in IUPAC system, they are known as **haloalkanes**.

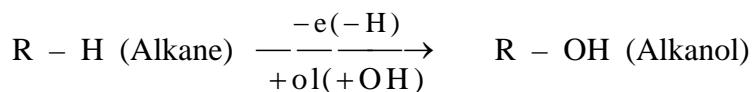
TABLE : 16.9

General formula $C_nH_{2n+1}X$ or $R - X$

Formula	Common name	IUPAC name
$CH_3 - Cl$	Methyl chloride	Chloromethane
$C_2H_5 - Cl$	Ethyl chloride	Chloroethane
$C_3H_7 - Br$	Propyl bromide	Bromopropane
$C_4H_9 - I$	Butyl iodide	Iodobutane

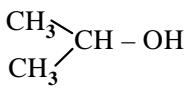
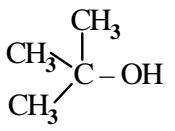
3. Alcohols or Alkanols (Suffix – ol)

Alcohols are the hydroxy derivatives of hydrocarbons. When one hydrogen atom is replaced by a hydroxyl ($-OH$) group, the alcohol formed is called a monohydric alcohol. In trivial system, monohydric alcohols are named as *alkyl alcohols*, whereas in IUPAC system the alcohols are called **alkanols**, obtained by replacing '*e*' of alkane by '*-ol*'.



General formula : $C_nH_{2n+1}OH$ or $R - OH$

TABLE : 16.10

Formula	Common name	IUPAC name
General : $R - OH$	Alkyl alcohol	Alkanol
$CH_3 - OH$	Methyl alcohol	Methanol
$CH_3CH_2 - OH$	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	n – Propyl alcohol	Propan–1–ol
	Isopropyl alcohol	Propan–2–ol
	<i>tert</i> – Butyl alcohol	2-Methylpropan–2–ol

When two hydrogen atoms of a hydrocarbon attached to two different carbon atoms are replaced by two – OH groups, the alcohol formed is called a **dihydric alcohol** or **glycol** or **alkanediol**. Similarly, a compound with three – OH groups attached to three different carbon atoms is called a **trihydric** alcohol or **glycerol** or **alkanetriol**.

4. Ethers or Alkoxyalkanes : (*Prefix - alkoxy*)

When two same or different alkyl groups are linked through oxygen atom, an **ether** results. This is represented by $R - O - R^1$ where R and R^1 may be same or different alkyl groups. In common system, ethers are called **alkyl ethers** (smaller alkyl group goes first) and according to IUPAC system, ethers are treated as **alkoxy** (*alkyl + oxy*) **alkanes** in which one hydrogen atom of the hydrocarbon is replaced by an **alkoxy** group ($RO-$). The parent alkane will be the one containing maximum number of carbon atoms.

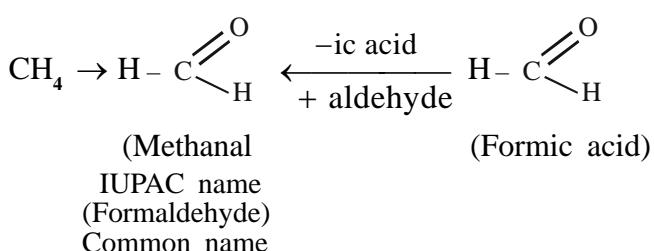
General formula : $C_nH_{2n+2}O$ represented by $R - O - R'$

TABLE : 16.11

Formula	Common name	IUPAC name
General : $R - O - R'$	Dialkyl ether	Alkoxyalkane
$CH_3 - O - CH_3$	Dimethyl ether	Methoxymethane
$CH_3 - O - CH_2CH_3$	Methylethyl ether	Methoxyethane
$CH_3CH_2 - O - CH_2CH_3$	Diethyl ether	Ethoxyethane

5. Aldehydes or Alkanals : (*Suffix* – al)

The functional group of this class of compounds is an **aldehydic** group of **formyl** group, --CHO , structurally represented as $\text{--C}=\overset{\text{O}}{\underset{\text{H}}{\diagdown}}$. Aldehydes have the general formula $\text{R} - \text{CHO}$ where R may be hydrogen or any alkyl group. The common names are derived from the acids they produce on oxidation. But the IUPAC name is obtained by replacing 'e' of the hydrocarbon with 'al'. (The number of carbon atom (s) determines the parent alkane).





Thus, HCHO, structurally represented as $\text{H} - \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{H} \end{array}$ is called *formaldehyde* by common system and **methanal** by IUPAC system of nomenclature.

General formula : $\text{C}_n\text{H}_{2n}\text{O}$

represented by $\text{R} - \text{CHO}$ ($\text{R} = \text{H}$ or alkyl group)

TABLE : 16.12

Formula	Common name	IUPAC name
General : $\text{R} - \text{CHO}$	Aldehyde	Alkanal
$\text{H} - \text{CHO}$	Formaldehyde	Methanal
$\text{CH}_3 - \text{CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{CH}_2 - \text{CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{CH}_2\text{CH}_2 - \text{CHO}$	Butyraldehyde	Butanal

6. Ketones or Alkanones (*Suffix – one*)

This class of compounds contain a bivalent **keto** group or **carbonyl** group ($\text{C}=\text{O}$) and both the valencies are satisfied by two same or different alkyl groups. Ketones are

represented by the general formula $\text{R} - \text{CO} - \text{R}^1$ ($\text{R}-\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{R}^1 \end{array}$). According to the common system, the name ketone is preceded by the alkyl groups arranged in alphabetical order. In IUPAC system, the name of a ketone is obtained by replacing 'e' of the parent hydrocarbon by 'one',

resulting in **alkanone**. Thus, CH_3COCH_3 ($\text{CH}_3 - \begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ | \\ \text{CH}_3 \end{array} - \text{CH}_3$) is named as **dimethyl ketone** or **acetone** in common system and as **propanone** in IUPAC system of nomenclature.

General formula : $C_nH_{2n}O$



represented by $R - C = O - R'$ (R & R' may be same or different)

TABLE : 16.13

Formula	Common name	IUPAC name
General : $R - CO - R'$	Dialkylketone	Alkanone
$CH_3 - CO - CH_3$	Dimethyl ketone or Acetone	Propanone
$CH_3CH_2 - CO - CH_3$	Ethylmethylketone	Butanone
$CH_3CH_2COCH_2CH_3$	Diethylketone	Pentan-3-one

7. Carboxylic Acids (Fatty acids) or Alcanoic acids (*Suffix – oic acid*)



Organic acids are characterised by the presence of **carboxyl** groups ($-C = O - OH$) formed

by CARBOnyl ($>C = O$) and hydroXYL ($-OH$) groups. Compounds containing **carboxyl** group ($-COOH$) are called **carboxylic acids**. The general formula of the carboxylic acid is $R - COOH$ (one hydrogen atom of the hydrogen atom is replaced by $- COOH$), where R may be H or any alkyl group. Compounds containing one, two or three carboxyl groups are called mono, di-or tricarboxylic acids respectively.

The common system of naming the monocarboxylic acids is based on the sources from which they are obtained whereas in IUPAC system, 'e' of the parent hydrocarbon (taking C atom of $-COOH$ group alongwith C atoms of alkyl group) is replaced by '**oic acid**'.

General Formula : $C_nH_{2n+1} COOH$ or $C_nH_{2n}O_2$

represented by : $R - COOH$ (R may be H)

TABLE : 16.14

Formula	Common name	IUPAC name
General : $R - COOH$	Monocarboxylic acid	Alkanoic acid
$H - COOH$	Formic acid	Methanoic acid
$CH_3 - COOH$	Acetic acid	Ethanoic acid
$CH_3CH_2 - COOH$	Propionic acid	Propanoic acid
$CH_3CH_2CH_2 - COOH$	Butyric acid	Butanoic acid
$CH_3CH_2CH_2CH_2 - COOH$	Valeric acid	Pentanoic acid

8. Derivatives of Carboxylic acids :

There are four main derivatives of carboxylic acid.

(i) Acid halides or Acyl halides or Alkanoyl halides

The chloride is most important among all the acid halides. Here, –OH group of –COOH is replaced by chlorine (halogen) to give **acid chloride** or **acylchloride**. The IUPAC names are obtained by substituting 'e' of the corresponding alkane by '*oyl chloride*'. More systematically, '**oic acid**' of corresponding acid is replaced by '**oyl chloride**'.

General formula : R – CO – X

TABLE : 16.15

Formula	Acid	Common name	IUPAC name
General : $\begin{array}{c} \text{O} \\ \parallel \\ \text{R} - \text{C} - \text{X} \end{array}$	Alkanoic acid	Acyl halide	Alkanoyl halide
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{Cl} \end{array}$	Formic acid (Methanoic acid)	Formyl chloride (Methanoyl chloride)	Methanoyl chloride
CH_3COCl	Acetic acid (Ethanoic acid)	Acetyl chloride	Ethanoyl chloride
$\text{CH}_3\text{CH}_2\text{COCl}$	Propionic acid (Propanoic acid)	Propionyl chloride	Propanoyl chloride

(ii) Acid anhydride or Alkanoic anhydride :

Structurally, in these compounds two acyl groups are connected through an oxygen atom. They are considered as acid derivatives formed by elimination of a molecule of water from two carboxyl groups. Hence, they are known as **acid anhydrides** in common system. In IUPAC system their names are obtained by replacing '**acid**' from the name of the alkanoic acid by **anhydride**.

General formula : R – CO – O – CO – R

TABLE : 16.16

Formula	Corresponding		
Formula	Acid	Common name	IUPAC name
R – CO – O – CO – R	Carboxylic acid (Alkanoic acid)	Acid anhydride	Alkanoic anhydride
CH ₃ CO – O – COCH ₃	Acetic acid (Ethanoic acid)	Acetic anhydride	Ethanoic anhydride
C ₂ H ₅ CO – O – COC ₂ H ₅	Propionic acid (Propanoic acid)	Propionic anhydride	Propanoic anhydride

(iii) Esters or alkyl alkanoate :

When the hydrogen atom of the carboxyl group is replaced by an alkyl group, the compound formed is called an **ester**. Esters are represented by the general formula R – COOR¹ (R and R¹ may be same or different) and are named as **alkyl carboxylate** in common system. The IUPAC name for an ester is obtained by replacing 'ic acid' by 'ate' and the name of the alkyl group (R¹) attached to oxygen is prefixed to the word.

General formula : R – COOR¹ (where R may be H or R & R¹ may be same or different alkyl groups.)

TABLE : 16.17

Formula	Corresponding		
Formula	Acid	Common name	IUPAC name
General : R – COOR ¹	Carboxylic acid	Alkyl carboxylate	Alkyl alkanoate
H – COOCH ₃	Formic acid (Methanoic acid)	Methyl formate	Methyl methanoate
CH ₃ – COOCH ₃	Acetic acid (Ethanoic acid)	Methyl acetate	Methyl ethanoate
CH ₃ – COOC ₂ H ₅	Acetic acid (Ethanoic acid)	Ethyl acetate	Ethylethanoate
C ₂ H ₅ – COOCH ₃	Propionic acid (Propanoic acid)	Methyl propionate	Methyl propanoate

(iv) Acid amides or Alkanamides

Acid amides are obtained by replacing $-\text{OH}$ of the carboxyl group by $-\text{NH}_2$ group and can be represented by the general formula $\text{R} - \text{CO} - \text{NH}_2$, where R may be H or any alkyl group. In common system, these are called **acidamides**, whereas in IUPAC system the name of an amide is obtained by replacing 'oic acid' of the corresponding alkanoic acid with 'amide'.

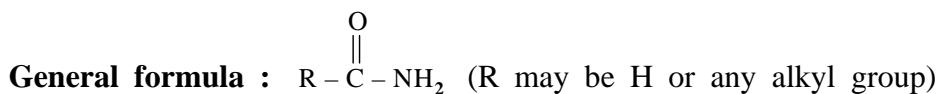
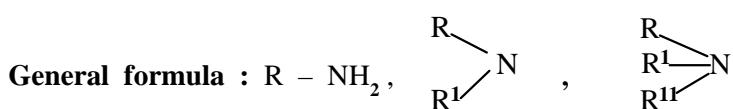


TABLE : 16.18

Formula	Corresponding Acid	Common name	IUPAC name
General : $\text{R} - \text{CO} - \text{NH}_2$	Carboxylic acid (Alkanoic acid)	Acid amide	Alkanamide
$\text{H} - \text{CO} - \text{NH}_2$	Formic acid (Methanoic acid)	Formamide	Methanamide
$\text{CH}_3 - \text{CO} - \text{NH}_2$	Acetic acid (Ethanoic acid)	Acetamide	Ethanamide
$\text{C}_2\text{H}_5 - \text{CO} - \text{NH}_2$	Propionic acid (Propanoic acid)	Propionamide	Propanamide

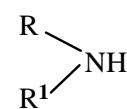
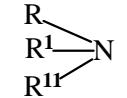
9. Amines :

Amines are alkyl derivatives of ammonia, obtained by replacing hydrogen atom(s) from NH_3 , by the alkyl group(s). According to the common system, monoalkyl derivatives are known as **alkyl amines**, dialkyl derivatives are known as **dialkylamines**, trialkyl derivatives, are known as **trialkylamines**. In IUPAC system, alkylamines are called **alkanamines**, dialkylamines are called **alkylalkanamines** and trialkylamines are called **dialkylalkanamine**. The longer alkyl group present is considered as the parent chain. The remaining alkyl group(s) are named as substituents attached to the nitrogen and a prefix N – is used with the name of the alkyl group.



Where R , R^1 & R^{11} are same or different alkyl groups.

TABLE : 16.19

Formula	Common name	IUPAC name
General :		
$R - NH_2$	Alkylamine	Alkanamine
	Dialkylamine	N -Alkylalkanamine
	Trialkylamine	N -Alkyl- N -alkylalkanamine
$CH_3 - NH_2$	Methylamine	Methanamine
$CH_3 - CH - CH_2CH_2 - NH_2$	Isopentylamine	3-Methyl-1-butanamine
$CH_3 - NH - CH_2 - CH_3$	Ethylmethylamine	N -Methyl ethanamine
$CH_3 - CH_2 - N - CH_3$	Ethyldimethylamine	N,N -Dimethylethanamine
$CH_3CH_2CH_2 - N - CH_3$	Ethyl methylpropylamine	N -Ethyl- N -methylpropanamine
$NH_2 - CH_2 - CH_2 - CH_2 - CH_2 - NH_2$	—	1,4 – Butanediamine

Note : When used as the substituent, the $-NH_2$ group is named as **amino** and is prefixed with a number indicating the carbon atom to which it is attached.

10. Nitroalkanes :

The nitroalkanes are nitro derivatives of the corresponding alkanes and represented

by the general formula, $R - NO_2$ ($R - \overset{+}{N}(\text{O}\Theta)_2$) . Nitro group is always prefixed to the alkane.

The common and IUPAC names are generally same except that in IUPAC system, the position of the nitrogroup is indicated.

General formula : $C_nH_{2n+1}NO_2$ or $R - NO_2$

TABLE : 16.20

Formula	Common name	IUPAC name
General : $R - NO_2$	Nitroalkane	Nitroalkane
$CH_3 - NO_2$	Nitromethane	Nitromethane
$CH_3CH_2CH_2 - NO_2$	Nitropropane	1- Nitropropane
$CH_3 - \begin{matrix} CH - CH_3 \\ \\ NO_2 \end{matrix}$	—	2 - Nitropropane

11. Alkyl cyanides or Alkane nitriles :

The functional group of alkyl cyanides is the $-C \equiv N$ group. The general formula is $R-CN$. These are commonly named either as alkyl cyanides or the nitrile of the acid which is formed on their hydrolysis by changing the suffix *-ic acid* by *-onitrile*. Their IUPAC names, however, follow the parent alkane as illustrated below.

General formula : $C_nH_{2n+1} CN$ or $R - CN$

TABLE : 16.21

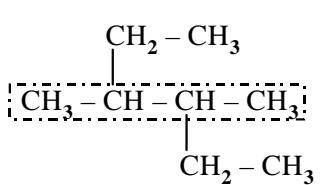
Formula	Common name	IUPAC name
General : $R - CN$	Alkyl cyanide or Acid nitrile	Alkane nitrile
$CH_3 - CN$	Methyl cyanide or Acetonitrile	Ethane nitrile
$CH_3 - CH_2 - CN$	Ethyl cyanide or Propiononitrile	Propane nitrile

D. Nomenclature of branched-chain alkanes and univalent radicals :

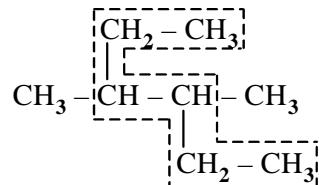
The following rules are adopted while naming the higher branched-chain saturated hydrocarbons or alkanes.

(1) Longest chain rule :

- (a) Select the longest continuous chain of carbon atoms which constitutes the **principal chain** or **parent chain**. Other carbon atoms which are not included in the chain are regarded as substituents and denoted as prefixes. The given alkane is named as a derivative of the alkane representing the parent chain. The longest continuous chain need not be horizontal.



Incorrect chain
(contains only 4 carbon atoms)

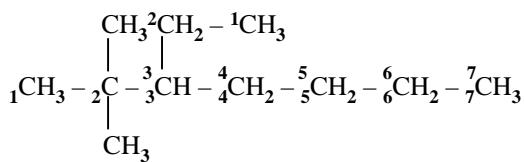


Correct chain
(contains 6 carbon atoms)

In the above example, the longest continuous chain of carbon atoms contains 6 carbon atoms though the chain is not horizontal (straight). So, it is a derivative of the parent hydrocarbon hexane.

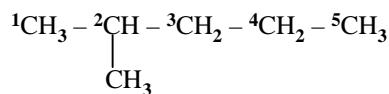
- (b) If the molecule contains two or more chains containing same number of carbon atoms, select the parent chain with greater number of side chains as substituents.

The compound contains two carbon chains containing 7 carbon atoms. The horizontal chain is selected because it contains 3 substituents while the other chain contains only 1 substituent.



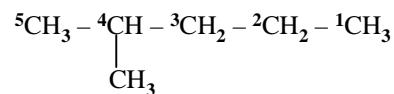
(2) Numbering the principal chain :

- (a) Number the carbon atoms of the parent hydrocarbon by Arabic numerals 1,2,3.....etc. from one end to the other such that the carbon atom carrying the substituent gets the lowest numeral (lowest locant).



Correct numbering

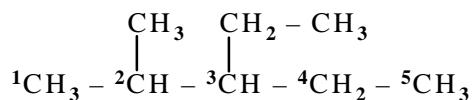
(Substituent has the locant 2)



Incorrect numbering

(Substituent has the locant 4)

- (b) *If more number of substituents are present, number the carbon atoms of the parent chain from such an end so as to give the lowest set of locants possible to the side chains (**Lowest set of locant rule** may be referred to).*

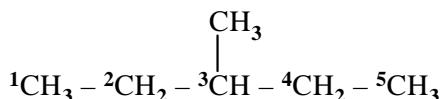


3 – Ethyl – 2 – Methylpentane

Here, numbering from left to right gives the lowest set of locants to the substituent (2,3) and hence, the numbering is done as shown.

- (c) *Prefix the substituent preceded by the locant to the name of parent hydrocarbon. Separate the locant from the name of the substituent by a hyphen.*

The following example will clarify the statement mentioned above.

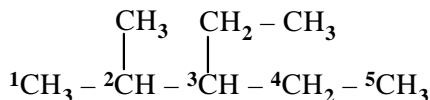


3 – Methylpentane

The parent hydrocarbon contains 5 carbon atoms and a methyl group is attached having the locant 3, Hence, the name of the compound is 3–Methylpentane.

(3) Alphabetical order of substituents :

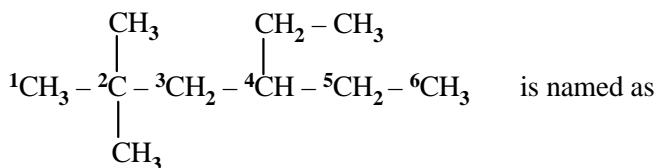
If the number of substituent is more than one, arrange them in alphabetical order prefixed by its positional number.



In this example, 'ethyl' group is alphabetised under 'e' and is written before 'm' of methyl group. Hence, the name of the compound is 3–Ethyl – 2 – methylpentane.

If a particular substituent is present two or three times, attach the prefix di – or tri – respectively to the name of substituent. Write the locants in the increasing order separated by commas amongst themselves and by a hyphen from the name of the substituent. Do not consider di – or tri – while deciding the alphabetical order of the **simple** substituents.

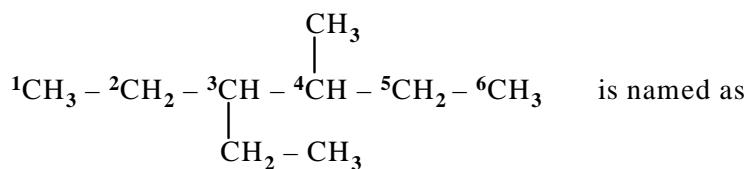
* Thus,



4 – Ethyl – 2, 2 – dimethylhexane and

NOT 2,2 – Dimethyl – 4 – ethylhexane

Note : If two or more different substituents are present at equivalent positions from the two ends of the parent chain, numbering is done from such an end so as to give the lowest locant to the substituent which comes first in the alphabetical order. (Rule – 9 of the common conventions in IUPAC system). Thus,



3 – Ethyl – 4 – methylhexane and

NOT 4-Ethyl – 3– methylhexane (numbering being done from right to left)

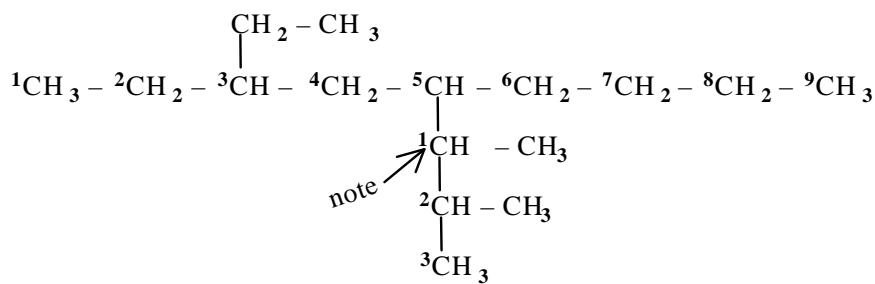
(4) Rule for branched substituents :

If the substituent is itself branched, name it as the substituted alkyl group. Number the carbon chain of the substituent from the carbon atom attached to the parent chain.

The following compound is a derivative of the parent hydrocarbon containing 9 carbon atoms i.e. nonane. Ethyl group is present at position 3 and another complex substituent (substituted alkyl group) is present at position 5. This branched side chain is now numbered in a way so that the carbon atom of the side chain attached to main parent chain gets 1 (longest chain rule is also applicable to such side chains). The compound is named as

* Where names of the complex radicals are composed of identical words, priority is decided by considering the locants in the complex radicals.

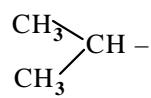
(Rule – 6 of the common convention in IUPAC system)



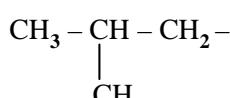
5 – (1,2 Dimethylpropyl) – 3 – ethylnonane.

Important : Complex radicals are alphabetised under the first letter of their complete name i.e. including the numerical affix (if any). Here, 'dimethylpropyl' as a complex single substituent, is alphabetised under 'd' and written before 'e' of ethyl group.

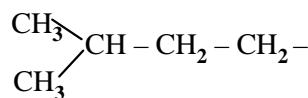
The following trivial, common or semi-systematic names may be used for the unsubstituted radicals.



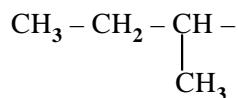
Isopropyl



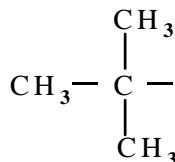
Isobutyl



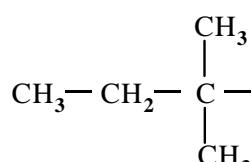
Isopentyl



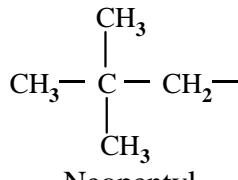
sec – Butyl



tert – Butyl

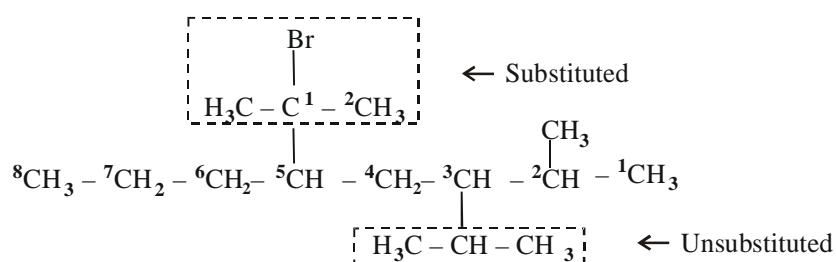


tert – Pentyl



Neopentyl

These trivial or common or semi-systematic prefixes can only be used when they are unsubstituted. This will be clear from the following example.



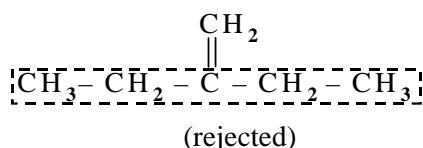
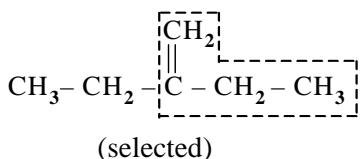
5–(1–Bromo–1–methylene)–3–isopropyl–2–methyloctane.

E. NOMENCLATURE OF UNSATURATED ACYCLIC HYDROCARBONS :

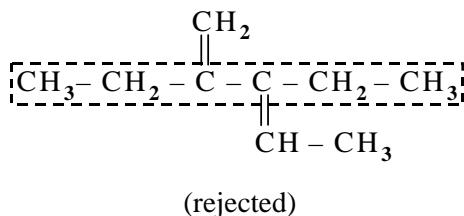
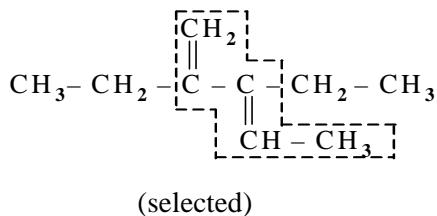
When carbon–carbon multiple bonds are present in an open chain hydrocarbon, the following additional rules are followed while naming these compounds.

(1) Selecting the principal chain :

Select the longest continuous chain of carbon atoms containing maximum number of multiple bonds as the principal chain.



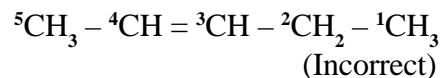
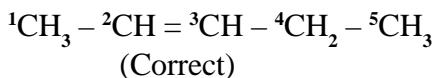
Here, the longest continuous chain containing the double bond has four carbon atoms and is selected though the longest continuous chain without the double bond contains 5 carbon atoms which is rejected.



Though the longest continuous chain of carbon atoms contains 6 carbon atoms, it does not contain double bond whereas two double bonds are present in a chain which contains 5 carbon atoms. Therefore, the chain containing two double bonds is selected.

(2) Numbering the principal chain :

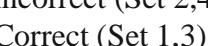
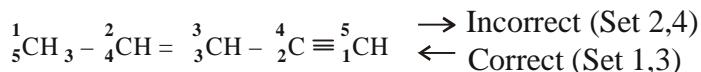
- (i) *If there is one multiple bond, number the principal chain from such an end that the carbon atom containing the multiple bond gets the lowest numeral. For example :*



Numbering from left end gives the lowest numeral to the carbon carrying double bond. Therefore, numbering from left to right will lead to correct nomenclature.

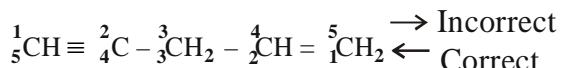
- (ii) *If the principal chain contains two or more multiple bonds, number the principal chain from such an end so that the multiple bonds get the lowest set of locants.*

The following illustration will explain the rule mentioned above.



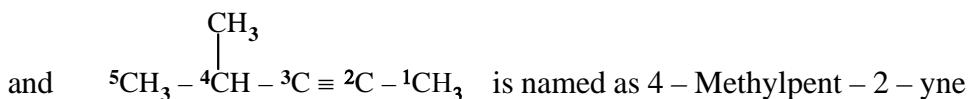
In the above case, numbering from two different ends gives two different sets of locants i.e. 2,4 and 1,3. Out of these two sets of locants set 1, 3 is lower. Hence, numbering is done from right to left.

- (iii) If numbering of the principal chain from both ends give the same set of locants to the multiple bond, then select the set which gives the lower locant to the double bond. This means that if choice exists the double bond gets preference over triple bond in numbering.



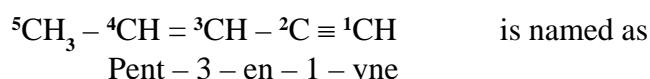
Numbering the carbon atoms of the principal chain from both the ends gives the same set of locants i.e. 1,4. Therefore, the numbering is done from right to left so as to give the lowest numeral to the carbon carrying the double bond (1).

- (3) (i) The primary suffix for double bond is 'ene' and for triple bond, it is 'yne'. For example :

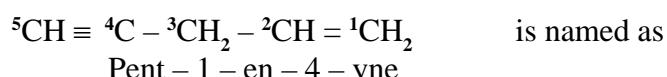


[Note : Old conventional names like 2 – Pentene or Pentene – 2 and 4 – Methyl – 2 – pentyne or 4 – Methylpentyne – 2 are no longer correct]

- (ii) When both double and triple bonds are present in the principal chain, the compound is named as a derivative of **alkyne** i.e. the suffix – 'ene' always comes before –yne. In such cases, 'e' of –ene is deleted if it is followed by suffix starting with 'a', 'i', 'o', 'u' or 'y'. For example :

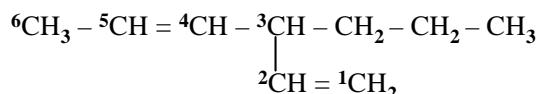


(Numbering as shown above gives the lowest set of locants i.e. 1,3 and 'e' of '-ene' is deleted since it is followed by 'y' of -yne)



(Since numbering from both the ends gives the same set of locants i.e. 1,4, double bond is given preference over the triple bond)

- (iii) If the principal chain contains two double bonds or two triple bonds, then the suffix is *-diene* or *diyne* respectively. In such cases, as per the rule, 'a' is added to the word root. For example –



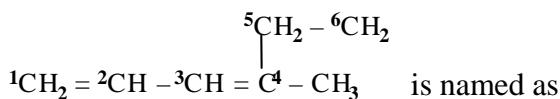
Considering the longest continuous carbon chain containing both the double bonds and lowest set of locants rule, the compound is named as

3 – Propylhexa – 1, 4 – diene

Similarly, $^1\text{CH} \equiv ^2\text{C} - ^3\text{C} \equiv ^4\text{C} - ^5\text{C} \equiv ^6\text{C} - ^7\text{CH}_3$ is named as

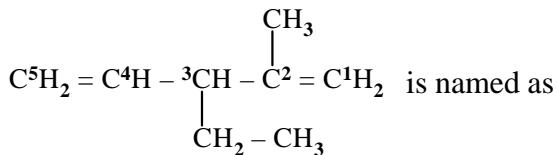
Hepta – 1, 3, 5 – triyne

- (4) *If the unsaturated acyclic hydrocarbon contains side chains alongwith the multiple bonds, number the principal chain in such a way so as to give the lowest set of locants to the multiple bonds. (The side chain may get the higher locant)*



4 – Methylhexa – 1, 3 – diene

But if numbering from both ends gives the same set of locants to the multiple bonds, number the principal chain in a manner so as to give the lowest set of locants to the side chain (s). For example :



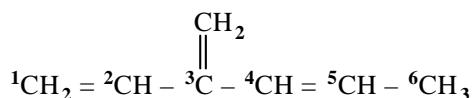
3 – Ethyl – 2 – methylpenta – 1, 4 – diene

Numbering of the parent chain as mentioned above gives the lowest set of locants to the side chains (2&3).

- (5) Sometimes more than two multiple bonds may be present in the unsaturated hydrocarbon and it is not possible to accomodate all the multiple bonds in the principal chain. In such cases, the multiple bonds are considered as side chains. For this purpose, the following prefixes are commonly used.



Such a case is illustrated in the following example.



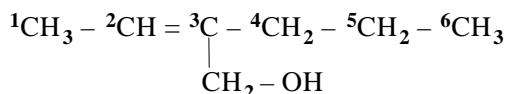
3 – Methylidenehexa – 1, 4 – diene

(Longest continuous chain of carbon atoms with maximum number of double bonds)

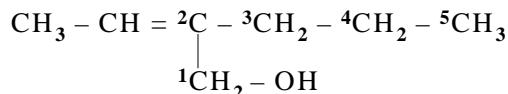
F. NOMENCLATURE OF ORGANIC COMPOUNDS CONTAINING ONE PRINCIPAL FUNCTIONAL GROUP

(1) Selection of principal chain :

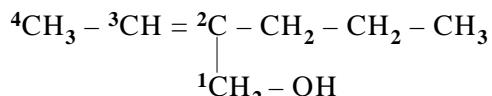
Select the longest continuous chain of carbon atoms which will include the principal functional group and that will constitute the parent chain. If multiple bonds are present, the principal or parent chain should include maximum number of multiple bonds. If there are two or more chains containing equal number of carbon atoms, select the one with maximum number of substituents.



(Incorrect)



(Incorrect)

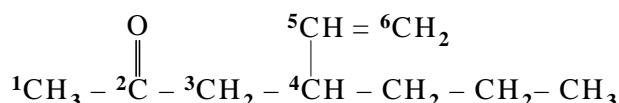


(Correct)

In the above example, the correct principal chain contain the functional group and the double bond and contains only 4 carbon atoms. The other two chains, though contain 6 carbon atoms, do not contain either the functional group or the double bond and hence, they are not selected.

(2) Numbering the principal chain : (Lowest locant to functional group)

Number the principal chain in such a way that the principal functional group gets the lowest locant even if it violates the lowest set of locant rule.



The principal chain, in this case contains six carbon atoms as it must include the double bond. The numbering is done so as to give the lowest numeral to the principal functional group

($\text{C}=\text{O}$) i.e.2.

If characteristic functional group such as – CHO, – COOH, – COOR, – COCl, – C ≡ N etc. is present in the organic compound, then the numbering should be done in such a way that the characteristic functional group gets the lowest locant 1. This locant for the principal functional group is generally omitted if there is no ambiguity.

- (3) Prefix the substituents to the parent hydrocarbon as per IUPAC rules without considering the functional group.
- (4) Add the suffix representing the functional group in place of 'e' of the hydrocarbon.
- (5) Insert the number denoting the position of the functional group before the related suffix and separate on either side by **hyphens**.
- (6) **Halo** and **nitro** groups are always taken as substituents and are prefixed.

A few examples are given below to understand the above rules.

Example - 1 : $\text{CH}_3 - \text{CH}_2 - \overset{2}{\underset{1}{\text{CH}}} - \overset{3}{\text{CH}_2} - \overset{4}{\text{CH}_2} - \overset{5}{\text{CH}_3}$ is named as
 $\text{CH}_2 - \text{OH}$

2 – Ethylpentan – 1 – ol

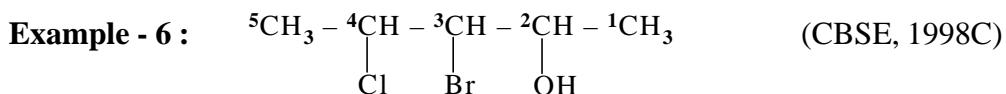
Example - 2 : $\text{CH}_3 - \overset{2}{\underset{1}{\text{C}}} = \overset{3}{\text{CH}_2} - \overset{4}{\underset{5}{\text{CH}}} - \overset{6}{\text{CH}_2} - \text{CH}_2 - \text{CH}_3$
4 – Propylhex – 5 – en – 2 – one

Example - 3 : $\overset{5}{\text{CH}_3} - \overset{4}{\text{C}} \equiv \overset{3}{\text{C}} - \overset{2}{\text{CH}_2} - \overset{1}{\text{CHO}}$
Pent – 3 – yn – 1 – al

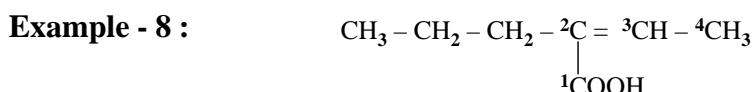
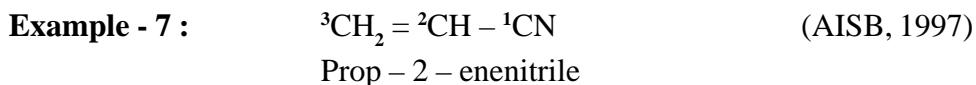
Example - 4 : $\text{CH}_3 - \text{CH}_2 - \overset{2}{\underset{1}{\text{C}}} = \overset{3}{\text{CH}_2} = \overset{4}{\text{O}}$
Methyl – 2 – ethylprop – 2 – enoate

Example - 5 : $\text{CH}_3 - \overset{4}{\underset{\text{OCH}_3}{\text{CH}}} - \overset{3}{\text{C}} = \overset{2}{\underset{\text{CH}_3}{\text{CH}}} - \text{O} - \text{CH}_2 - \text{CH}_3$
2 – Ethoxy – 4 – methoxypentan – 3 – one

(When the position of the principal functional group remains same while numbering from both ends of the parent chain, Ethoxy group gets precedence over Methoxy group)



3 – Bromo – 4 – chloropentan – 2 – ol



2 – Propylbut – 2 – en – 1 – oic acid

G. NOMENCLATURE OF POLYFUNCTIONAL ORGANIC COMPOUNDS

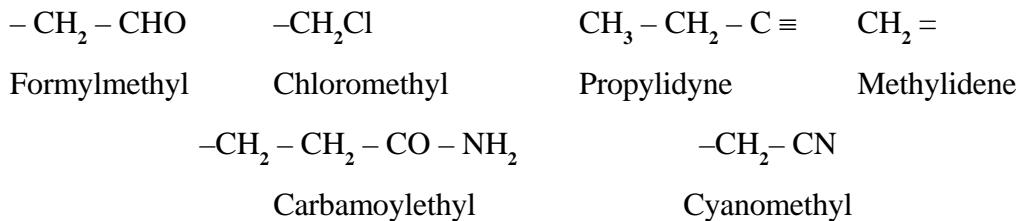
- (1) When a compound has more than one functional group, the group which determines the class of the compound is referred to as the **principal** group and forms the *suffix*. The remaining groups are treated as **substituents**. The order of seniority of some common groups is listed below with prefix and suffix names. The functional group placed higher in the table takes precedence over the others below. The longest continuous chain should contain maximum number of functional groups.

TABLE : 16.22 PRIORITY OF FUNCTIONAL GROUPS

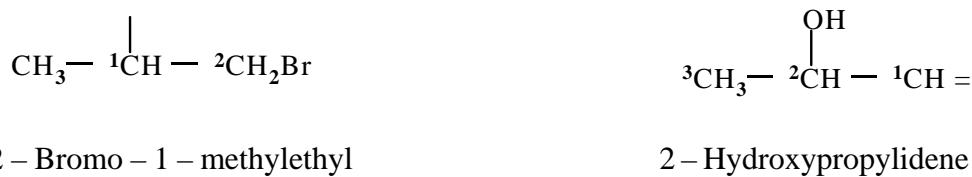
Order of Seniority	Functional Group	Prefix	Suffix
1	– COOH	Carboxy–	–oic acid
2.	– COOR	Alkoxy carbonyl–	Alkyl....oate
3.	– COCl	Chloroformyl–	–oyl chloride
4.	– CONH ₂	Carbamoyl–	–amide
5.	– C ≡ N	Cyano –	– nitrile
6.	– CHO	Formyl –	– al
7.	(C=O)	Oxo	–one
8.	– OH	Hydroxy–	–ol
9.	– NH ₂	Amino–	–amine
10.	C = C	—	–ene
11.	C ≡ C	—	–yne
12.	– NO ₂	Nitro–	—
13.	– X	Halo–	—
(X = F, Cl, Br, I)			

Important : When --CHO , --CN , --COOH , --COCl etc. are used as substituents, their carbon atoms are **not** counted in the principal chain. However, when prefix 'oxo' is used for the keto group, its carbon is counted in the principal chain because of its non-terminal nature. If oxo ($\text{C}=\text{O}$) group occurs at the end of a chain, it is known as an aldehyde group. Therefore, aldehyde group can be represented by two types of prefixes : 'oxo', when carbon of --CHO is counted in the chain and 'formyl', when it is not counted in the chain.

- (2) The principal chain of the polyfunctional compound must be numbered in such a way that the principal functional group gets lowest possible number followed by double bond, triple bond and substituents.
- (3) The substituents must be placed in an alphabetical order before the word root. When two substituents occupy identical positions from either end of the principal chain, then the lowest number must be given to the substituent which comes first in the alphabetical order.
- (4) When the substituent is itself substituted, the nomenclature of the whole substituent follows the rules mentioned earlier. There are a few exceptions.
 - (i) No characteristic group is expressed as suffix. Suffixes such as '*yl*', *ylidene* and *ylydine* are used.

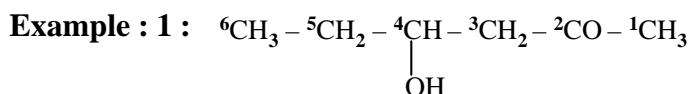


- (ii) The point of attachment of complex substituent has the lowest possible locant. For example,



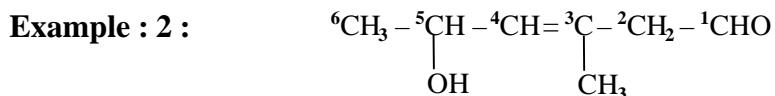
- (iii) Numerical terms used for similar substituted substituent are *bis* (for two), *tris* (for three), *tetrakis* (for four) etc. For simple substituents *di* –, *tri*, *tetra* – etc. are used.

The following examples illustrate the above principle of nomenclature of polyfunctional organic compounds.

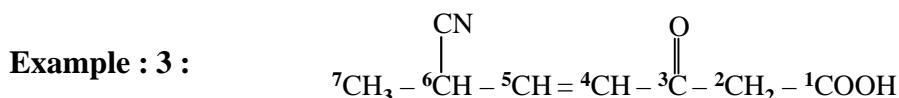


The principal chain contains 6 carbon atoms and the two functional groups $>\text{C}=\text{O}$ and $-\text{OH}$. Keto group being senior takes precedence over $-\text{OH}$ group Therefore $-\text{OH}$ group appears as a substituent. The name of the compound will be

4 – Hydroxyhexan – 2 – one

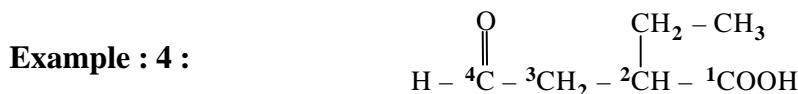


The name of the compound is 5 – Hydroxy – 3 – methylhex – 3 – en – 1 – al.



The principal chain containing maximum number of functional groups contains 7 carbon atoms. $-\text{COOH}$ being the senior most group, the other groups appear as substituents. Further, a double bond is present. Carbon atom of $-\text{COOH}$ group is given the number –1. Thus, the name of the compound is

6 – Cyano – 3 – oxohept – 4 – enoic acid



When $-\text{CHO}$ group is taken in the principal chain, the compound is

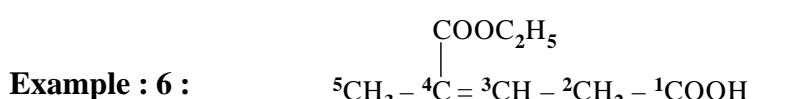
2 – Ethyl – 4 – oxobutanoic acid.

When $-\text{CHO}$ group is taken as a substituent,

2 – Ethyl – 3 – formylpropanoic acid.



2 – Amino – 4 – chloro – 3 – hydroxypentanoic acid



4 – Ethoxycarbonylpent – 3 – enoic acid

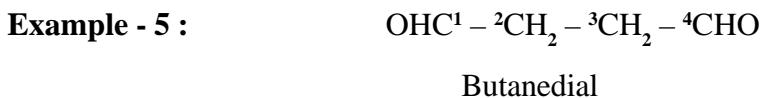
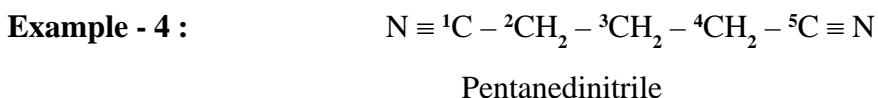
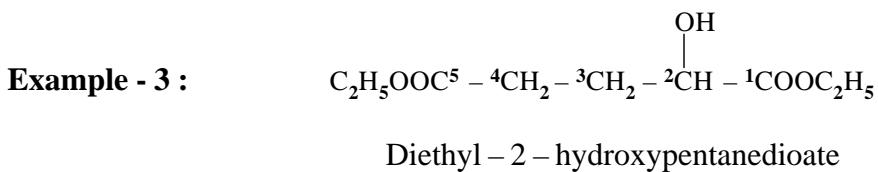
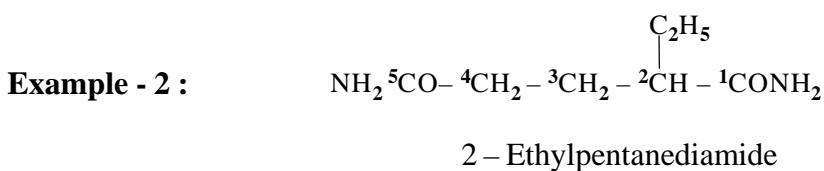
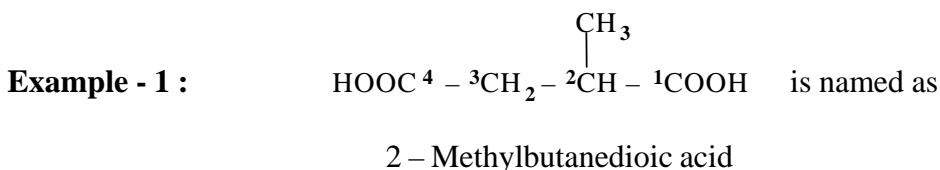
IV (5) Nomenclature of polyfunctional organic compounds containing two or more similar terminal functional groups.

Carbon containing functional groups which occur at the end of a chain are termed as terminal functional groups. They are – COOH, –COOR, –COCl, –CO – O – CO – (anhydride), – CHO and –CN groups. When two or more such groups are present in the organic compound, special rules are followed for their nomenclature.

(i) For organic compounds containing only two similar terminal groups :

In such compounds, the carbon atoms of both the terminal groups are counted in the principal chain and the groups are indicated by a suitable suffix alongwith prefix 'di'.

The following examples will clarify the rule



(ii) For organic compounds containing more than two similar terminal groups :

In such cases, two situations may arise.

- (a) All the similar terminal groups are directly attached to the principal chain

In such cases none of these groups forms a part of the principal chain. Special suffixes are used in these cases and when using special suffixes, the carbon atoms of the terminal groups are **not** counted in the principal chain.

The special suffixes are given below.

Functional group	Suffix
– COOH	–carboxylic acid
– COOR	alkyl.....carboxylate
– COCl	– carbonylhalide
– CONH ₂	–carboxamide
– CN	– carbonitrile
– CHO	– carbaldehyde

This rule is illustrated in the following examples.



Butane – 1, 2, 4 – tricarbaldehyde

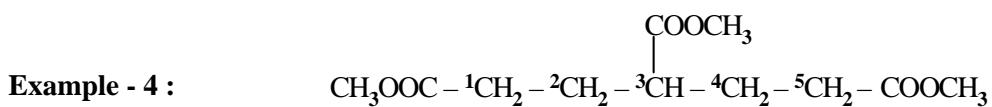


Propane – 1, 2, 3 – tricarbonitrile



Propane – 1, 1, 2, 3 – tetracarboxylic acid

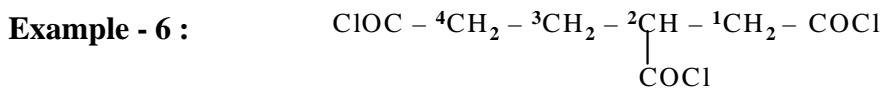
(Numbering from right to left will violate lowest set of locants rule)



Trimethylpentane – 1, 3, 5 – tricarboxylate



Propane – 1, 2, 3 – tricarboxamide.



Butane – 1, 2, 4 – tricarbonylchloride

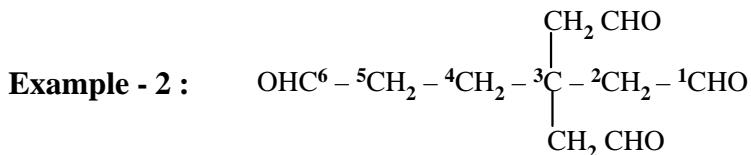
(b) All the similar terminal groups are not directly attached to the principal chain.

In such cases, the longest chain with two such similar terminal groups forms the principal chain and the other similar terminal group is treated as substituent and indicated by suitable prefixes.

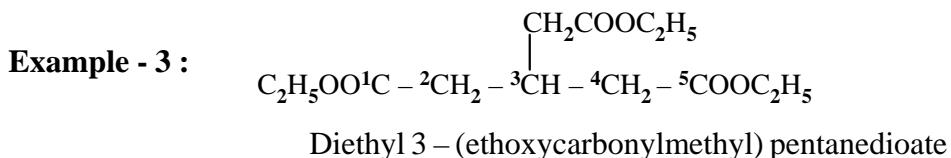


3 – (Carboxymethyl) pentanedioic acid

(Here, note that the carbon atoms of the terminal groups
are counted while numbering the principal chain)



3,3 – Bis (formylmethyl) hexanedral

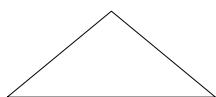


Diethyl 3 – (ethoxycarbonylmethyl) pentanedioate

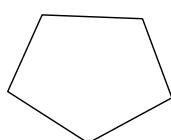
H. NOMENCLATURE OF ALICYCLIC COMPOUNDS

While naming the alicyclic compounds, some additional rules are followed in addition to the rules adopted for acyclic compounds.

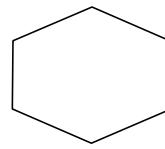
- (1) *The names of the alicyclic compounds are obtained by adding the prefix 'cyclo' to the word root.* For example,



Cyclopropane



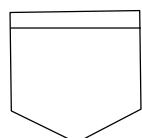
Cyclopentane



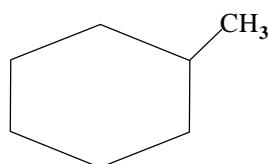
Cyclohexane

- (2) *The substituents present is indicated by Arabic numerals 1,2,3, etc. If only one substituent is present, its position is not mentioned. But if more than one substituent is present, the numbering is done in a manner (i.e. clockwise or anticlockwise) to give the lowest set of locants to the substituents. While writing the substituents, alphabetical order is maintained like the acyclic compounds.*

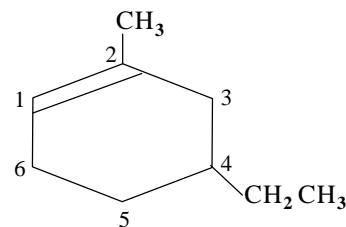
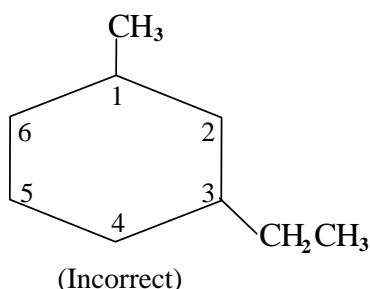
The following examples will illustrate the above rules.



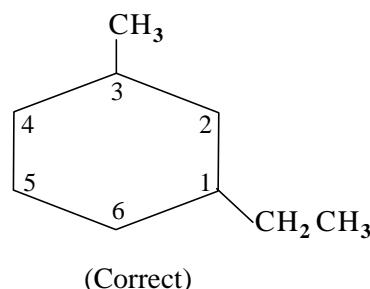
Cyclopentene



Methylcyclohexane

4-Ethyl – 2 – methylcyclohex – 1 – ene
(alphabetical order when writing the name)

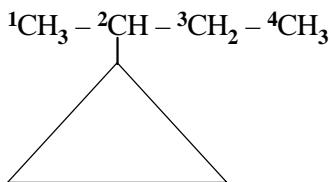
(Incorrect)



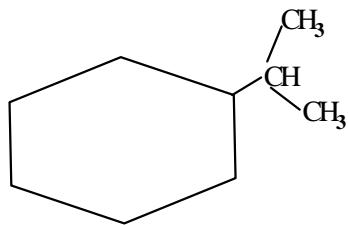
(Correct)

1 – Ethyl – 3 – methylcyclohexane
(alphabetical order when same set of locants are obtained)

- (3) When the number of carbon atoms is more in the side chain alkyl group than the ring, the compound is treated as the cycloalkyl derivative of the alkane. For example,

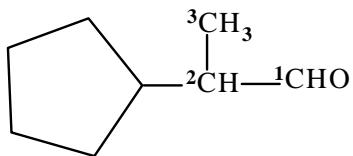


2 – Cyclopropylbutane
(Side chain contains more number of carbon atoms than the ring)

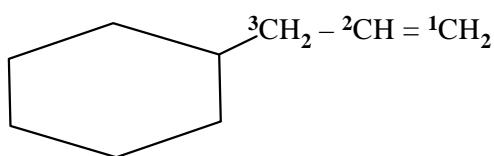


Isopropylcyclohexane
(ring contains more number of carbon atoms than the side chain)

- (4) If the side chain contain multiple bond or functional group, the alicyclic ring is treated as the substituent irrespective of the size of the ring.

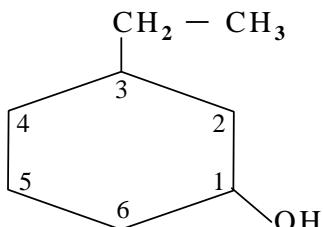


2 – Cyclopentylpropanal

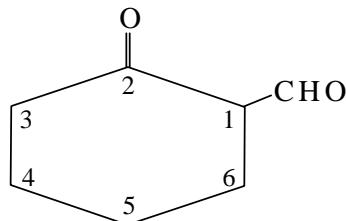


3 – Cyclohexylprop – 1 – ene

- (5) If functional group alongwith other substituent group are present in the ring, it is indicated by suitable prefixes and suffixes as in case of acyclic compounds. If the functional group is directly attached to the ring, its presence is indicated by using suitable suffix, but the carbon atom of such group is not counted in the word root. Suffixes for such groups are as given in III B (ii) (a). For example-

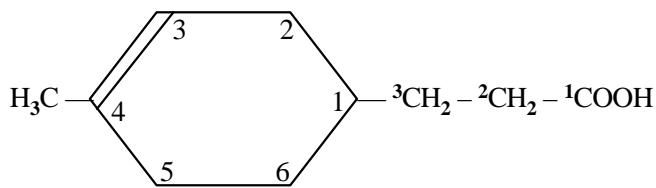


3 – Ethylcyclohexan – 1 – ol



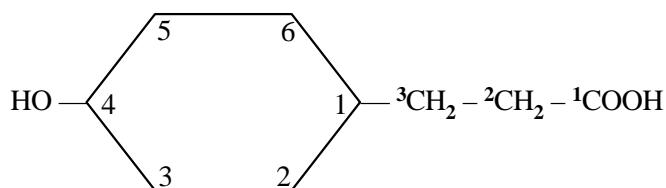
2 – Oxocyclohexane – 1 – carbaldehyde
(-CHO group gets the lowest locant for seniority and suffix 'carbaldehyde' is used instead of 'al' because its carbon is not counted in the ring)

If the ring as well as the side chain contain functional group, then the parent hydrocarbon is decided as in acyclic compounds. For example,



3 – (4–Methylcyclohex – 3 – enyl) propanoic acid

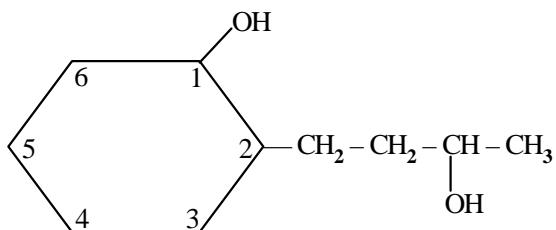
(Side chain contains only functional group)



3 – (4–Hydroxycyclohexyl) propanoic acid

(Both the ring & side chain contain functional groups)

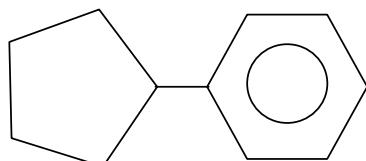
The principal functional group is present in the side chain.



2 – (3–Hydroxybutyl) cyclohexan – 1 – ol.

(Here the ring contains more number of carbon atoms than the side chain)

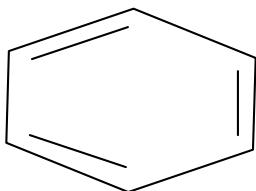
- (6) *If an alicyclic ring is attached to a benzene ring, the compound is named as a derivative of benzene.*



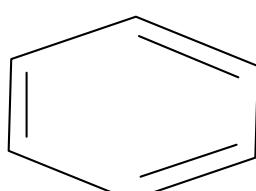
Cyclopentylbenzene

I. NOMENCLATURE OF AROMATIC COMPOUNDS

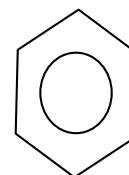
Compounds containing one or more benzene rings are known as aromatic compounds. The parent hydrocarbon in the aromatic series is represented by the molecular formula, C₆H₆. The IUPAC name for the compound is **benzene** and is represented as a regular hexagon with alternate double bonds or a regular hexagon with a circle inside.



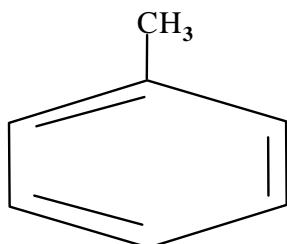
Or



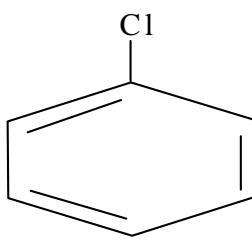
Or



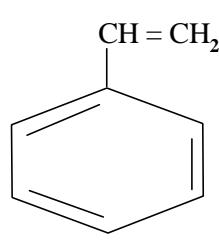
- (1) If only one hydrogen atom of the benzene ring is replaced by another monovalent atom or group of atoms, a monosubstituted derivative results. The substituents present in the ring are prefixed to the word benzene. A monosubstituted derivative can exist in one form only, since all the six hydrogen atoms in benzene are equivalent. For example,



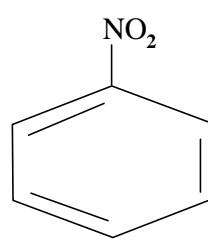
Methylbenzene



Chlorobenzene

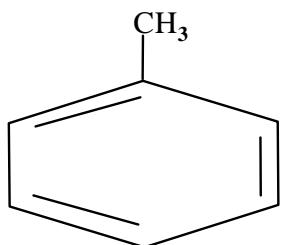


Vinylbenzene

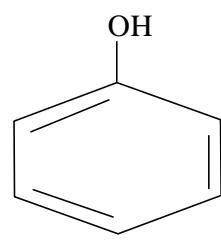


Nitrobenzene

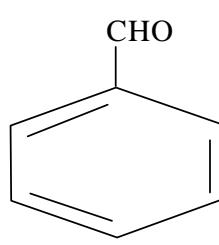
- (2) A number of substituted benzenes have been given special names and have been approved by IUPAC. For example,



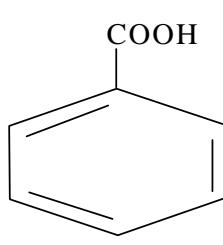
Toluene



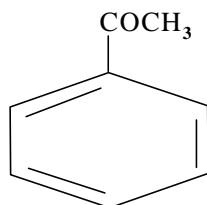
Phenol



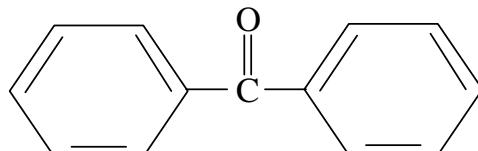
Benzaldehyde



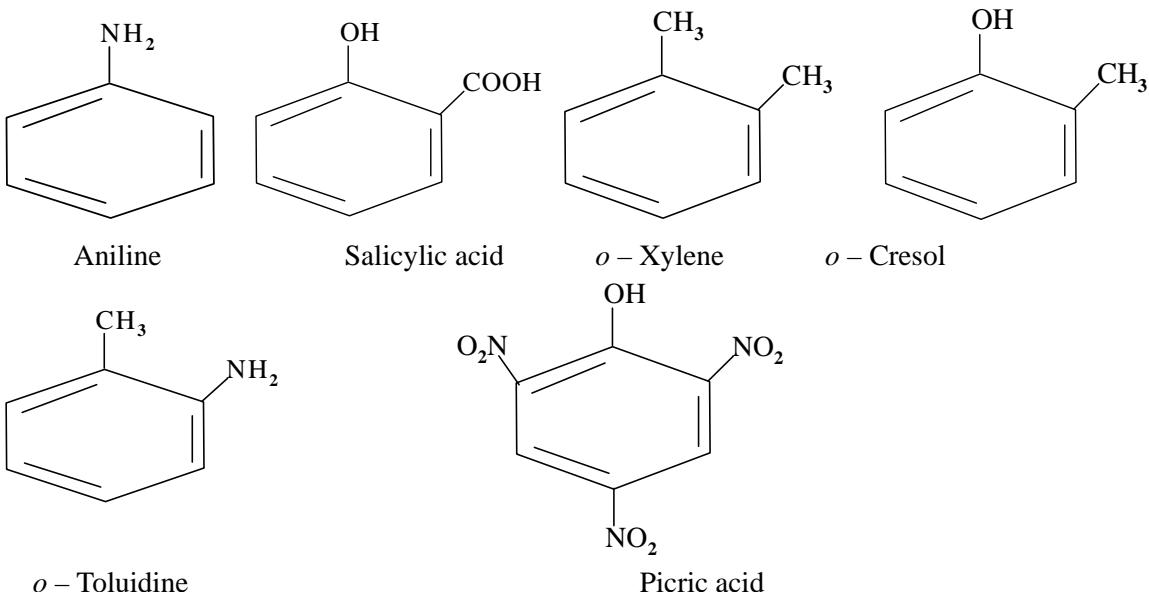
Benzoic acid



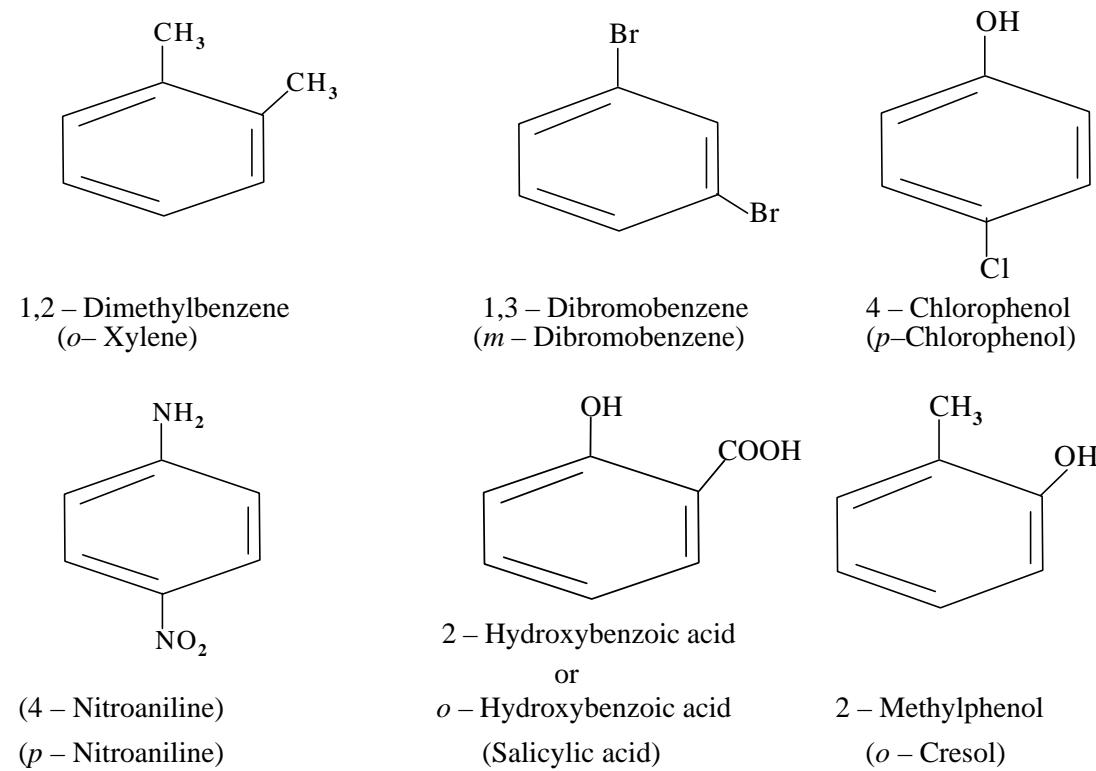
Acetophenone



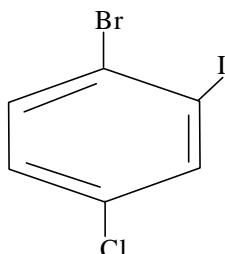
Benzophenone



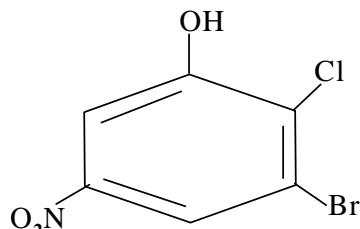
(3) While naming the disubstituted derivatives of benzene, the positions are indicated by numbers. The carbon atom carrying the principal substituent is given the number 1 and the relative position of other substituent is denoted by numbering the carbon atoms of the ring from 2 to 6 either clockwise or anticlockwise so that the lowest number is given to the substituent. Only three disubstituted products are possible – 1,2;1,3 and 1,4. They are referred to as **ortho** (*o*), **meta** (*m*) and **para** (*p*) derivatives respectively. When different substituents are present, they are written in alphabetical order.



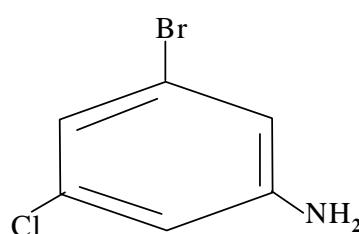
- (4) For polysubstituted benzene derivatives, the positions of the substituents must be numbered in alphabetical order. However, if one of the groups is associated with a special name, the compound is named as a derivative of the monosubstituted compound, numbered from the group designated in the special name.



(1 – Bromo – 4 – chloro – 2 – iodobenzene)
nitrophenol)

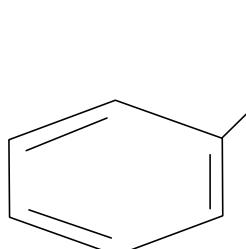


(3 – Bromo – 2 – chloro – 5 –

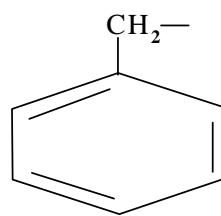


(3 – Bromo – 5 – chloroaniline)

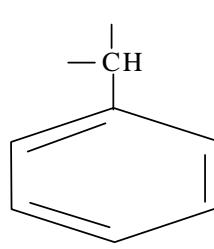
A few aryl groups are mentioned below which will be helpful for nomenclature.



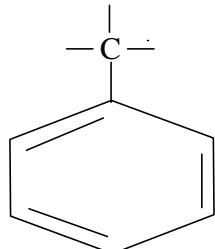
Phenyl



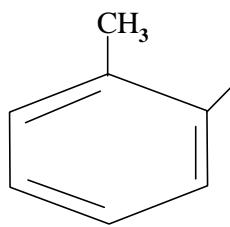
Benzyl



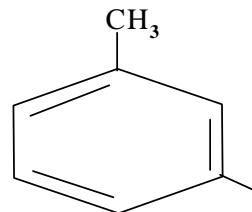
Benzal



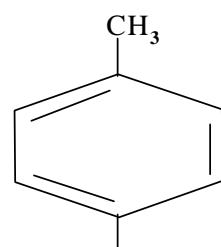
Benzo



o – Tolyl
or
2 – Tolyl



m – Tolyl
or
3 – Tolyl

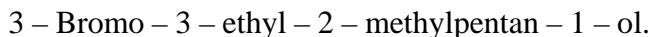


p – Tolyl
or
4 – Tolyl

It may be noted that (a) in case of 'tolyl' groups, no substitution is allowed (b) in case of 'phenyl' group, unlimited substitution is allowed (c) in case of 'benzyl' group, substitution is allowed in the ring.

J. WRITING STRUCTURAL FORMULA FROM IUPAC NAME

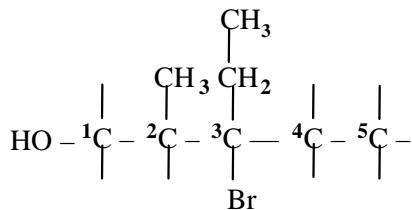
While writing the structural formula from the IUPAC name, the carbon skeleton of the principal chain is first written. The functional group and the substituents are then incorporated in proper positions as described in IUPAC name. Finally, the residual valencies are filled up with hydrogen atoms. The following illustration may be taken. Let us write the structural formula of the organic compound,



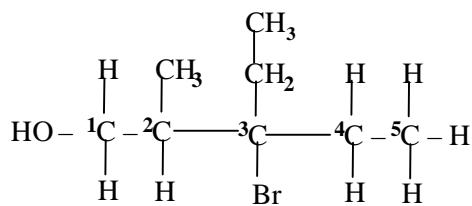
The principal chain consists of 5 carbon atoms and the skeleton is first written and numbered from one end to the other.



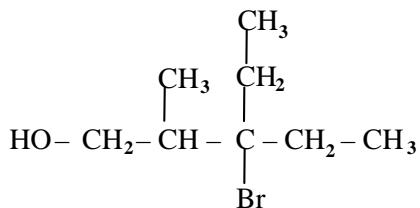
The functional group in the chain, ($-\text{OH}$ group) is placed on C_1 and substituents bromine at C_3 , methyl group at C_2 and ethyl group at C_3 are placed. Now, the skeleton takes the following shape.



Lastly, the remaining valencies of carbon atoms are satisfied by hydrogen atoms.

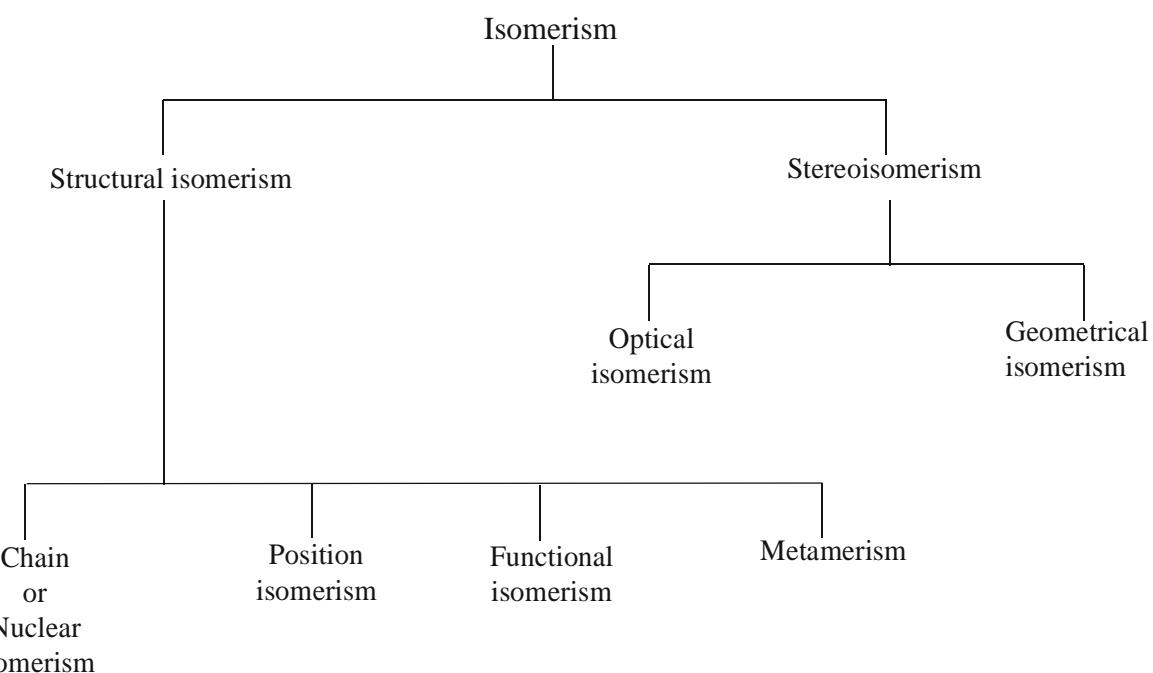


In the condensed form, the compound is written as



16.10 ISOMERISM *

Compounds having the same molecular formula, but differing in physical and chemical properties are called **isomers** or **isomerides** and the phenomenon is known as **isomerism** (Greek : *isos* = equal ; *meros* = part). The difference in properties is due to the difference in the arrangement of atoms within the molecule. Isomerism can be classified as follows :



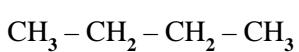
A. STRUCTURAL ISOMERISM

Isomerism due to the arrangement of atoms within the molecule resulting in several structural formulae is termed as **structural isomerism**. Compounds exhibiting such type of isomerism are known as **structural isomers**.

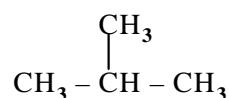
The structural isomerism is of the following types :

- (a) **Chain or Nuclear Isomerism :** This type of isomerism arises due to the difference in the structure of the carbon chain which forms the nucleus of the molecule. Therefore, the isomerism is called **chain or nuclear isomerism**. For example, butane has got the molecular formula C_4H_{10} and two structures can be written, one having a straight chain and another having a branched chain.

* Not in the syllabus



(*n* – butane)

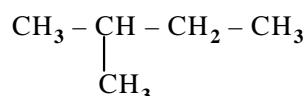
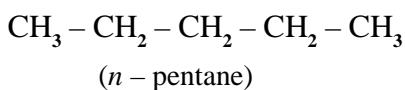


Isobutane

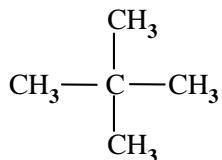
or

2 – Methylpropane

Similarly, three chain isomers are possible for the same molecular formula C₅H₁₂ (pentane)



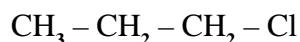
(isopentane or 2 – Methylbutane)



(*neo* – pentane
or
2,2 – Dimethylpropane)

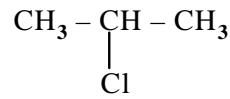
Chain isomerism is also exhibited by alkenes, alkynes, alcohols, ethers, aldehydes, ketones, acids, esters and amines.

(b) **Position Isomerism :** Isomerism arising out of the difference in the position of the same functional group or substituent in the same carbon chain is called position isomerism. For example,



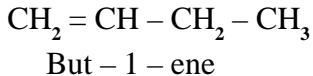
(1 – Chloropropane)

and

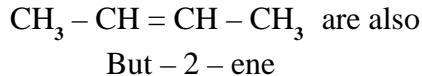


(2 – Chloropropane)

are position isomers. Similarly,

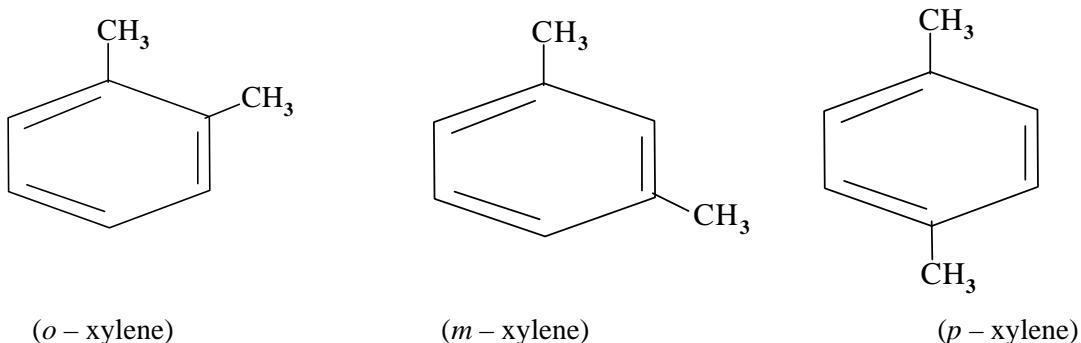


and



position isomers.

Disubstituted aromatic compounds exhibit position isomerism due to the different relative positions occupied by the two substituents on the benzene ring. For example, xylene exhibits the following position isomers.



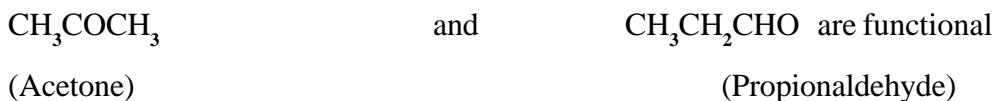
Note : Aldehydes and carboxylic acids do not exhibit position isomerism.

- (c) **Functional Isomerism :** Isomerism arising out of the presence of different functional groups is termed as **functional isomerism**. Alcohols and ethers, aldehydes and ketones, acids and esters, different classes of amines having same molecular formula are functional isomers of each other.

The following examples will justify the above statement. With molecular formula C_2H_6O , two compounds with different functional groups can be written – one is an ether and the other is an alcohol.



thus, functional isomers. Similarly,

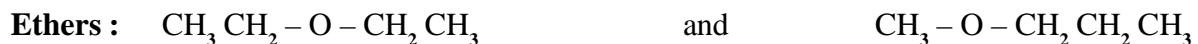


isomers. One is a ketone and the other is an aldehyde.

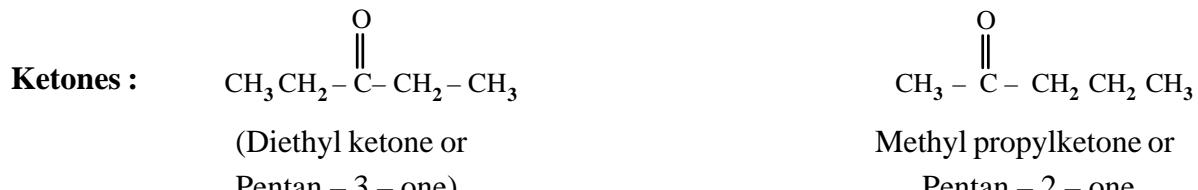
CH_3COOH (acetic acid) and HCOOCH_3 (methyl formate) are functional isomers. One is an acid and the other, an ester.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (*n*-propylamine), $\text{CH}_3 - \text{NH} - \text{CH}_2 - \text{CH}_3$ (ethylmethylamine) and $\text{CH}_3 - \underset{\text{CH}_3}{\text{N}} - \text{CH}_3$ (trimethylamine) are functional isomers.

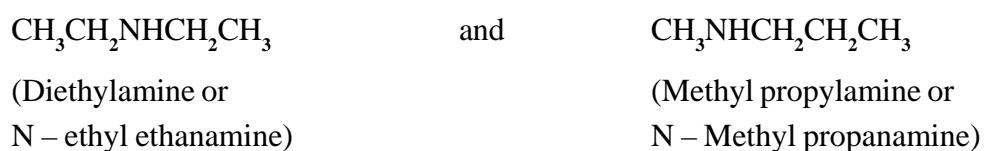
- (d) **Metamerism :** Isomerism arising out of the unequal distribution of carbon atoms on either side of the same functional group in molecules of compounds belonging to the same class is known as **metamerism**. In other words, metamerism occurs due to the difference in the nature of alkyl groups linked to the polyvalent atom of the functional group. For example, **ethers**, **ketones** and **secondary amines** exhibit metamerism.



(Diethyl ether or
Ethoxy ethane) (Methylpropyl ether or
Methoxypropane)

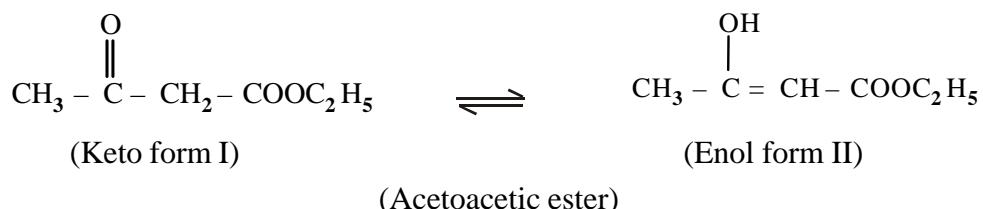


Secondary amines :

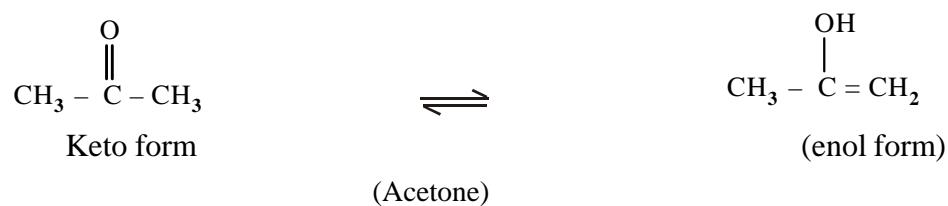


Tautomerism : Two compounds with the same molecular formula, existing in dynamic equilibrium with each other are said to be **tautomers** and the phenomenon is known as **tautomerism**.

When a ketonic substance remains in equilibrium with its enolic form, then it called **keto – enol tautomerism**. Acetoacetic ester exhibits **keto – enol tautomerism**. It gives the reactions of both keto compound and unsaturated hydroxy compound. This can only be explained in terms of the dynamic equilibrium existing between the two isomeric forms.



The keto and enol tautomers of acetone can be represented as :



Tautomerism is considered as a special case of *functional isomerism*.

B. STEREOISOMERISM

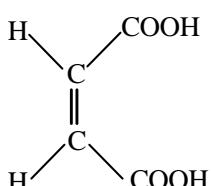
Isomerism exhibited by compounds having the same structural formula, but differing in the relative arrangement of atoms or groups in space within the molecules is termed as **stereoisomerism**. Compounds showing stereoisomerism are called **stereoisomers**.

There are two types of stereoisomerism.

- (a) Geometrical isomerism
- (b) Optical isomerism

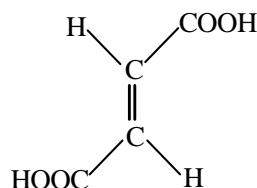
- (a) **Geometrical Isomerism :** When two compounds have the same molecular formula, but different arrangement of atoms or groups in space around the double bond, they are called **geometrical isomers** and the phenomenon is known as **geometrical isomerism**.

Simple examples of this type of isomerism are maleic acid and fumaric acid. Both the acids have the same molecular formula, but the arrangement of atoms and groups in space around C = C is different in both the acid molecules. When two similar atoms or groups lie on the same side, the isomer is a *cis* – isomer and when they lie on the opposite side, the isomer is a *trans* – isomer.



(Maleic acid)

Cis

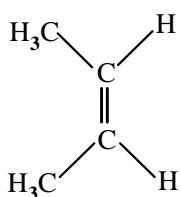


(Fumaric acid)

Trans

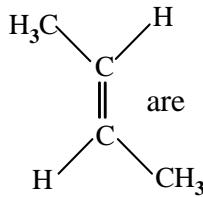
Therefore, geometrical isomerism is also called **cis–trans isomerism**, which arises due to the restricted rotation about a carbon to carbon double bond.

Another example of geometrical isomerism is but – 2 – ene which exists as *cis* but – 2 – ene and *trans* but – 2 – ene.



(*cis* – But – 2 – ene)

and



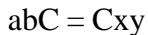
(*trans* – But – 2 – ene)

are geometrical isomers.

E – Z Nomenclature

‘E’ stands for **Entgegen** (German) meaning *opposite* and ‘Z’ stands for **Zusammen** (German) meaning *together*.

Consider the isomers in which all the four atoms attached to C = C bond are different.



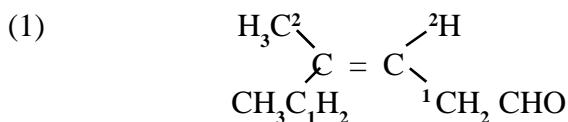
For naming such compounds a system of nomenclature has been introduced. This is called E-Z nomenclature.

Step I - Following the set of sequence rule, priority is given to both the atoms or groups attached to each carbon atom separately. The atom or group of higher priority is numbered 1 and that of lower priority is numbered 2.

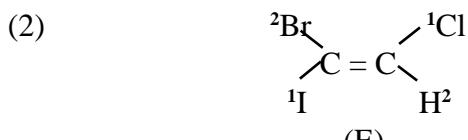
Step II - If the two groups numbered 1 are on same side, the configuration is labelled ‘Z’. If they are on the opposite side the configuration is labelled ‘E’.

Example

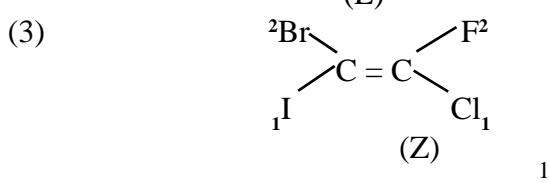
Assign E or Z configuration to the following compounds



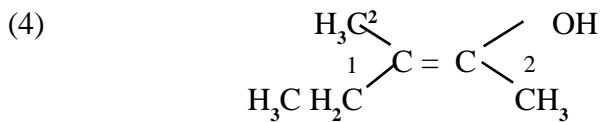
(Z)



(E)



(Z)



(E)

- (b) **Optical Isomerism :** When four different atoms or groups are attached to a carbon atom, two structures can be written for the same compound as in case of lactic acid. This is due to the tetrahedral geometry of the carbon atom. The two structures of lactic acid are represented as follows (Fig. 16.26)

The two structures are related as object and its mirror image and are not superimposable. They represent two different compounds. When plane polarised light is passed through these compounds separately, one rotates the plane of polarised light towards left and the other rotates

towards right. But the magnitude of rotation is same. However, these two compounds have similar chemical and almost similar physical properties due to identical structures except that they rotate the plane of polarised light in different directions due to the arrangement of atoms or groups in space around the central carbon atoms to which they are attached.

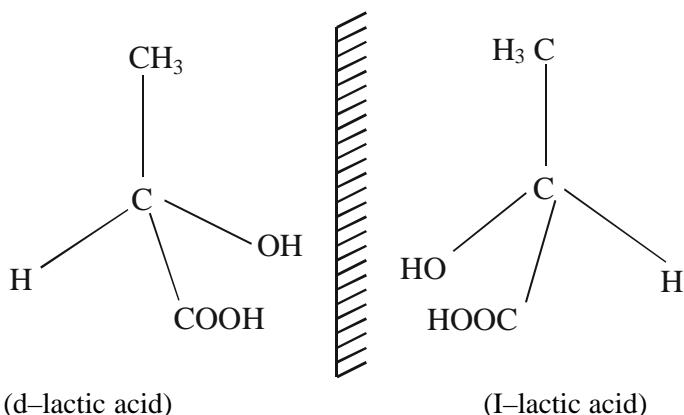


Fig.16.26 Optical isomers of lactic acid

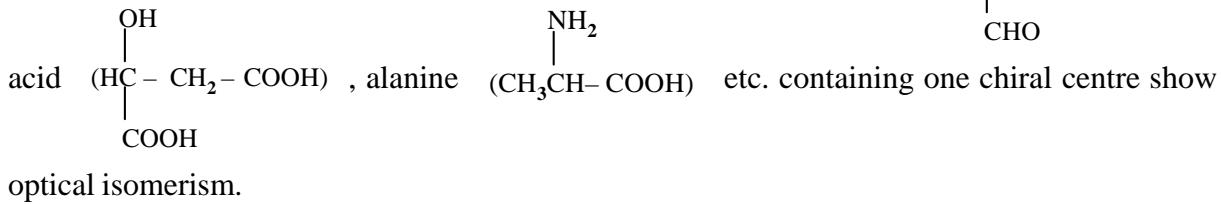
Compounds having the same molecular formula, but different spatial arrangement of atoms or groups within the molecule and possessing the property of rotating the plane of polarised light are known as **optical isomers** or **enantiomers** or **enantiomorphs** or **antipodes** and the phenomenon is called **optical isomerism or enantiomerism**. The enantiomers have similar chemical and almost similar physical properties except that they behave differently towards the plane polarised light.

The enantiomer rotating the plane of polarised light towards right is called **dextrorotatory** and is represented by the letter *d* – or a (+) sign. Its mirror image enantiomer which rotates the plane of polarised light towards left is called **laevo-rotatory** and is represented by the letter *l* – or a (–) sign. The *d* – and *l* – forms of lactic acid are shown in Fig. 15.7. Since the *d* – and *l* – isomers rotate the plane of polarised light to the same extent either to right or to left, a mixture containing equal amount of *d* – and *l* – isomers of an optically active compound will not rotate the plane of polarised light at all and such a mixture is called a **racemic mixture** or **racemic modification** represented by *dl* – or (±) sign. A racemic mixutre is optically inactive due to **external compensation** and can be resolved (separated) into its optically active antipodes.

CONDITIONS FOR OPTICAL ACTIVITY

A compound to show optical activity should possess in its molecule atleast one **asymmetric** carbon atom or **chiral** carbon i.e. a carbon atom to which four different atoms or groups are attached. Secondly, the molecule should not have a **plane of symmetry**, so that the molecule and its image are non-superimposable (**dissymmetric** nature of the molecule). These are the two condition for a compound to show optical isomerism.

Compounds like 2 – chlorobutane, butan – 2 – ol, glyceraldehyde ($\text{H}_2\text{C} = \text{CH}(\text{OH})\text{CH}_2\text{CH}_3$), malic



Specification of Configuration about a Chiral atom

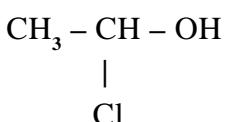
R,S Nomenclature : To assign a particular configuration to an optically active compound in terms of prefixes R and S, the following procedure is to be followed, ‘R’ stands for **rectus** (latin) meaning right. ‘S’ stands for **sinister** (latin) meaning left. The following steps are involved.

Step - I (Fixing of Priorities)- A set of rules known as **sequence rules** are to be obeyed while, assigning the order of priority to the four groups attached to chiral or asymmetric carbon atom.

Rule - 1

The atom with highest atomic number gets the highest priority and the atom with lowest atomic number gets the least priority. Atom or group with highest priority as given number 1 and that with least priority is given number 4.

e.g. 1 - chloroethanal

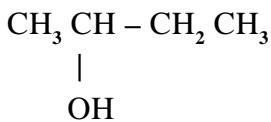


Order of priority is Cl (1), OH(2), CH₃ (3), H (4)

Rule - 2

If the first atom of two or more groups is the same, then priority is decided taking the second or even the third atom of the group as the case may be.

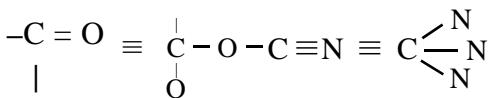
e.g. Between CH₃- and CH₃ – CH₂ – group CH₃ – CH₂ – group is given priority since in CH₃- the second atom is Hydrogen whereas in CH₃ – CH₂ the second atom is Carbon having higher atomic number. In secondary butyl alcohol



Order of priority is OH(1), CH₃- CH₂- (2), CH₃- (3), H (4)

Rule - 3

If the group or atom linked to chiral carbon contains = bond or ≡ bond, then that becomes equivalent to two and three single bonds respectively.



e.g. in case of glyceraldehyde



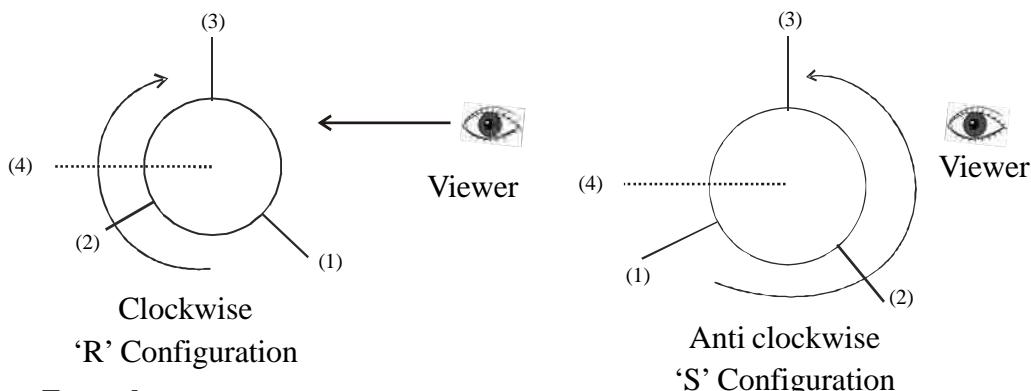
*CHOH , order of priority –OH, –CHO, CH₂ OH, H



Step II (Assigning Configuration)

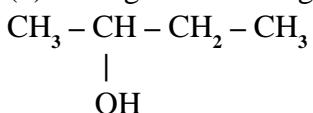
The molecule is to be viewed in such a way that the atom or group of the lowest priority is directed away from the eye.

If the atoms or groups attached to chiral carbon be 1, 2, 3, 4 and order of priority is also 1, 2, 3, 4, then orientation of the molecule is made in such a way that atom of lowest priority (4) is pointed to the back. If the eye traces a sequence 1 → 2 → 3 in a clockwise direction, the configuration is 'R'. If it traces the sequence 1 → 2 → 3 in an anticlockwise direction, the configuration is 'S'



Examples

(1) Configurations assigned to two enantiomers of secondary butyl alcohol



Sequence, $-\text{OH}$ (1), $-\text{CH}_2 - \text{CH}_3$ (2), $-\text{CH}_3$ (3), $-\text{H}$ (4)

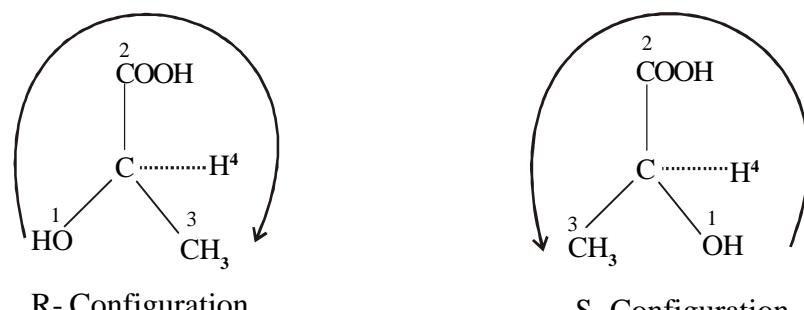


R- Configuration (clockwise)

S- Configuration (anticlockwise)

(2) Configuration assigned to two *i* somers of lactic acid [$\text{CH}_3 - \text{CH}(\text{OH}) - \text{COOH}$]

Priority, $\overset{(1)}{\text{OH}}$, $\overset{(2)}{\text{COOH}}$, $\overset{(3)}{\text{CH}_3}$, $\overset{(4)}{\text{H}}$

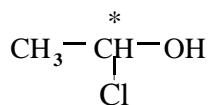


R- Configuration

S- Configuration

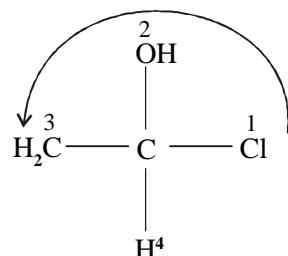
Configuration of the molecule drawn on the plane of the paper by Fischer Projection.

Consider the configuration of 1-chloroethanol



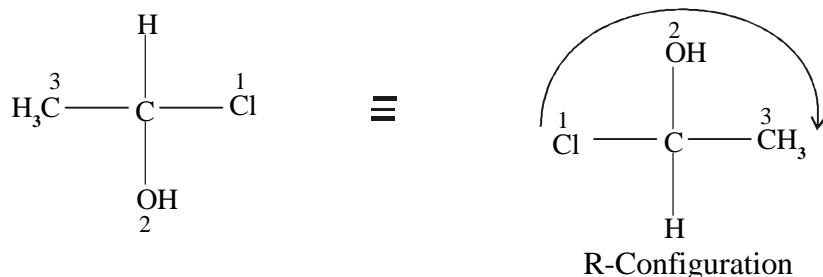
Priority is – Cl (1), – OH (2), – CH₃ (3), – H (4)

Case - 1 Bring the atom of lowest priority to the bottom. Rotate the eye in order of decreasing priority. If it is clockwise → ‘R’ configuration. If, anticlockwise → ‘S’ configuration.



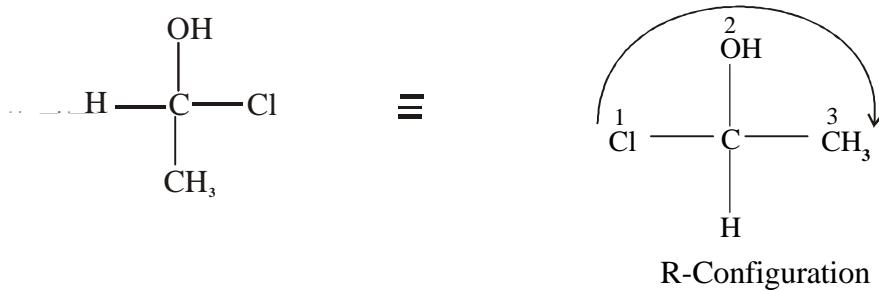
S- Configuration

Case - 2 If the atom of lowest priority is at the top, rotate the molecule by 180° so as to bring it to the bottom. Rotate the eye in order of decreasing priority and assign the configuration.



R-Configuration

Case - 3 If the atom of lowest priority is at the left side of horizontal line, keep the top position fixed and change the position of remaining atoms in the clockwise direction so as to bring the atom of lowest priority to the bottom. Rotate the eye in order of decreasing priority and assign configuration.

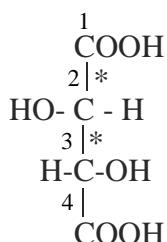


R-Configuration

Case - 4 If the atom of lowest priority is at the right side of the horizontal line, keep the top position fixed and change the position of other atoms or groups in the clockwise direction so as to bring the atom of lowest priority to the bottom. Rotate the eye in the order of decreasing priority and assign configuration.

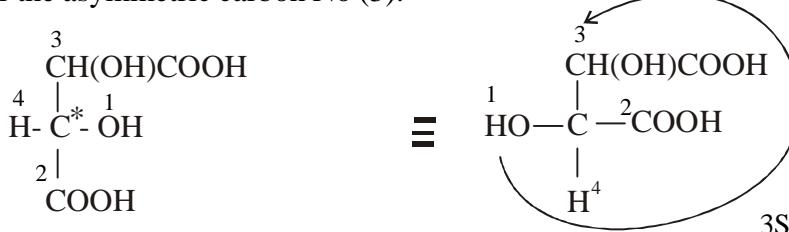
Assignment of configuration to the molecule containing more than one chiral carbon.

Example - (1) Consider tartaric acid HOOC – CH (OH) CH (OH) (COOH)



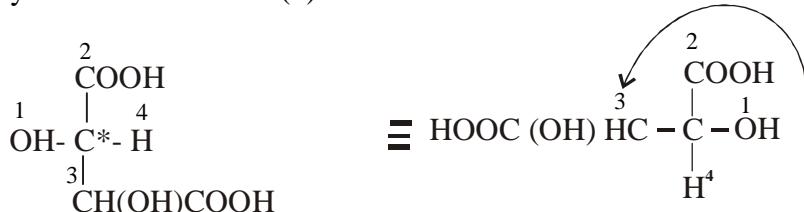
The sequence of priority is –OH (1), –COOH (2), CH (OH) COOH (3), H (4)

Consider the asymmetric carbon No (3).



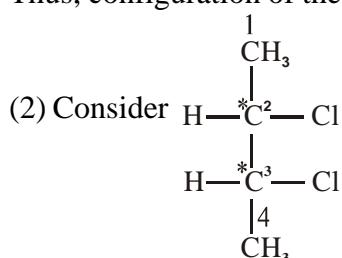
Here atom of lowest priority is at the left so keep the top group fixed and change the position of other atom in the clockwise direction so as to bring the atom of lowest priority to the bottom. Rotate the eye in order of decreasing priority and assign configuration.

Consider the asymmetric carbon No (2).



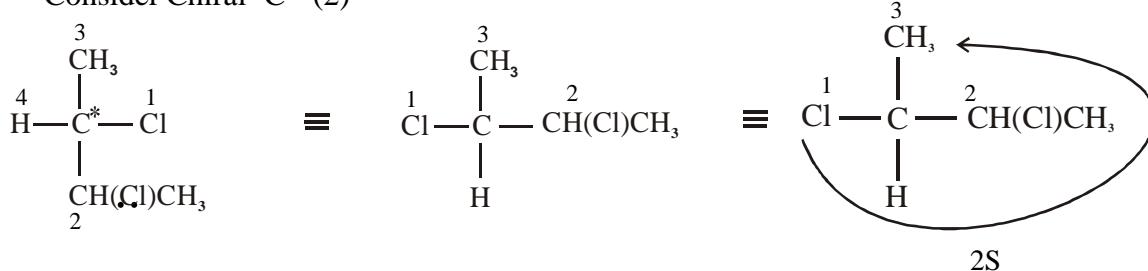
Here the atom of lowest priority is at the right side of horizontal line. Keeping the top position fixed the change of position of other groups is made in the clockwise direction so as to bring the atom of lowest priority to the bottom. Rotate the eye in the order of decreasing priority.

Thus, configuration of the compound is (2S, 3S)

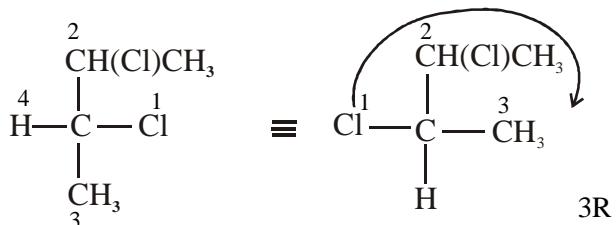


Sequence is – Cl (1), – CH (Cl) CH₃ (2), – CH₃ (3), – H(4)

Consider Chiral ‘C’* (2)



Consider chiral 'C*' (3)



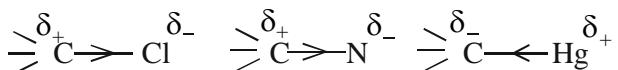
The configuration is (2S, 3R).

16.11 ELECTRONIC DISPLACEMENTS IN A COVALENT BOND

The covalent bond which is formed by the mutual sharing of two electrons between the participating atoms may not be an ideal one, because an attacking agent always bears either a positive or a negative charge and for a reaction to occur on the covalent bond, it must possess oppositely charged centres. In other words, the substrate molecule although as a whole electrically neutral, must develop polarity on some of its carbon atoms and substituents linked together which is made possible by the partial or complete displacement of the bonding electrons. These displacements may be permanent (e.g. inductive, resonance and hyperconjugative effects) otherwise called as polarisation effects or temporary (e.g. electromeric and inductomeric effect) known as polarisability effects.

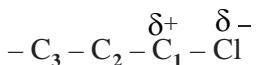
A. INDUCTIVE EFFECT

When two electrically dissimilar (having different electronegativities) atoms are connected by a single bond, the more electronegative atom will attract the shared electron pair of the bond towards it than the other atom. As a result, a fractional negative charge is developed (δ^-) on the more electronegative atom and a fractional positive charge (δ^+) is developed on the less electronegative atom. The extent of fractional charge created on atom depends on the electronegativity difference between the atoms.



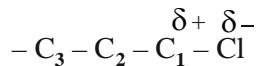
The polarisation of electrons (or electron density) towards more electronegative atom is a permanent effect and therefore, called **permanent polarisation** effect or **inductive effect**. Electron repelling groups (alkyl groups, metal atoms) have +I effect whereas electron withdrawing groups (NO_2 , F, Cl, Br, I, OCH_3 , OH, CN, COOH etc.) have -I effect.

Consider a chain of carbon atoms with a chlorine atom joined to the end carbon atom.



As stated earlier, chlorine being more electronegative than carbon acquires a small negative charge and C_1 acquires a small positive charge. As C_1 is positively charged, it attracts the electron pair shared between C_1 and C_2 towards itself. This causes C_2 to acquire a small positive charge, but this charge is smaller than the charge on C_1 , which is now almost neutralised. Similarly, C_3 acquires a positive charge which is less than that on C_2 . This effect is the inductive effect and

decreases rapidly as the distance from Cl increases. Practically, the inductive effect is ignored after the second carbon atom.

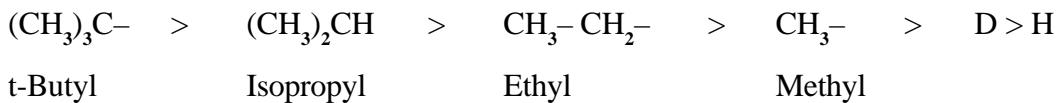


Inductive effects are of two types. These are :

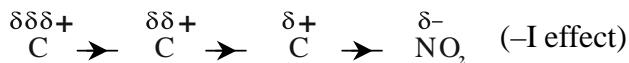
(i) +I effect : If the substituent attached to the end of the carbon chain is electron donating, the effect is called +I effect. For example,



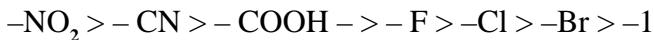
The +I effect of some of the atoms or groups in the decreasing order is :



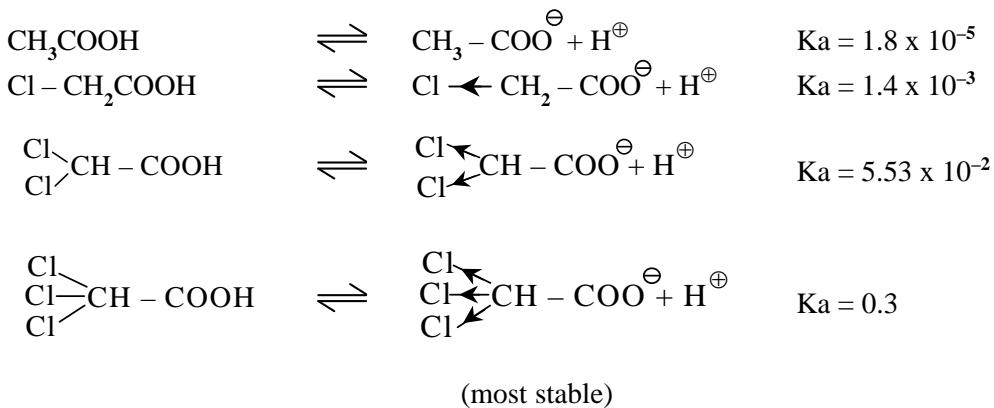
(ii) -I effect : If the substituent attached to the end of the carbon chain is electron withdrawing, the effect is called -I effect. For example,



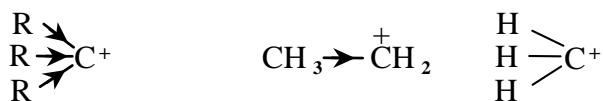
The -I effect of some of the atoms and groups in the decreasing order is :



Inductive effect is reflected in the acidity of the various chloroacetic acids. If we consider monochloroacetic acid ($\text{Cl} - \text{CH}_2 - \text{COOH}$) and trichloroacetic acid ($\text{Cl}_3\text{C} - \text{COOH}$), we find that the trichloroacetic acid is the strongest of all these three substituted acids. That is because the negative charge of the carboxylate ion is attracted by the chlorine atoms, thus stabilizing the anion very strongly. As the number of chlorine atom increases, the anion gets more and more stabilized.



Inductive effect can also be used to explain the stability of carbocations. Carbocations are planar and positively charged.



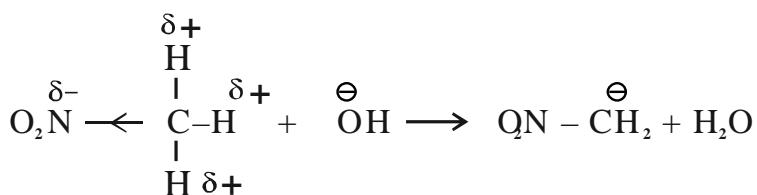
Alkyl groups release electrons and disperse the positive charge by inductive effect. Electrons in a C – C bond are more polarisable than those in a C – H bond. Hence, replacing hydrogen by alkyl group reduces the net charge on positively charged carbon. Thus, the stability of carbocations follows the order,



B. INDUCTOMERIC EFFECT

The temporary effect which increases the permanent inductive effect present in a molecule due to the approach of a charged ion (attacking reagent) is termed as **inductomeric** or **inductometric effect**.

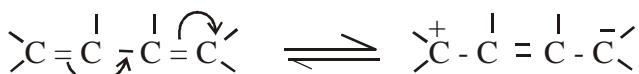
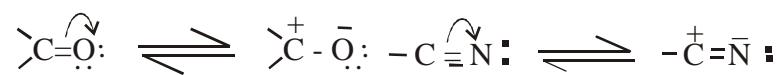
For example, in nitromethane, the $-I$ effect of $-\text{NO}_2$ group is further increased temporarily by the approach of hydroxyl ion to the hydrogen atom which is ultimately removed as water.



Since inductomeric effect is time dependent, it always favours the reaction and never inhibits it.

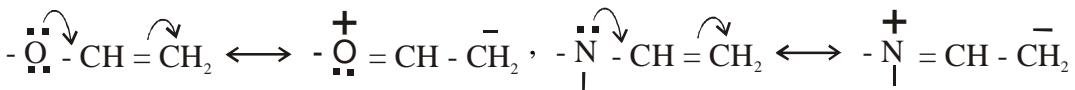
C. ELECTROMERIC EFFECT

When multiple bonds such as, >C=O: , >C=O , $-\text{C}\equiv\text{N}$, $-\text{C}\equiv\text{C}-$ are present in an organic molecule, the shared pair of electrons of the π -bond may be completely displaced towards one of the bonded atoms depending upon its electronegativity when a charged reagent is brought near the molecule. This effect is **temporary**, because the polarisation of the molecule to positive or negative poles and the displaced electron pair reverts back to its original position when the charge is removed from the vicinity of the molecule. This effect is known as "**Electromeric effect**" and is represented by E. This effect is more prominent in conjugated systems. When two atoms with different electronegativities are involved in displacement process, the displacement occurs towards the more electronegative atom. Electromeric effect may be represented as given below.

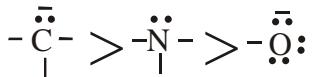


(curved arrow indicates the electron displacement with direction)

When a multiple bond is conjugated to an atom with non-bonded pair of electrons, then that non-bonded pair can also participate to enhance the electromeric effect, Thus,



The ease of electron release will depend upon the ease of polarisation of the non-bonded electron pair. Thus, one of the sequence is



D. RESONANCE :

Occasionally no reasonable single electronic structure can be written for a molecule which can satisfactorily explain all its observed properties. For example, carbon dioxide can be represented by atleast three possible structures.



The calculated heat of formation of carbon dioxide for one formula is 350kcals/mol. and the O – O distance should be 2.40A⁰. However, the observed heat of formation is 380kcals/mol. and O – O distance is 2.30A⁰ indicating that none of these three structures satisfactorily accounts for its observed properties. Thus the actual structure is one which can not be represented on the paper and all these structures make some contribution to the actual structure of carbondioxide molecule. The actual molecule is a **hybrid** of all these individual structures, which differ in the location of electrons around the constituent atoms. They are called the **contributing** structures or **canonical** structures or **resonating** structures which are purely hypothetical and individually do not represent any real molecule. This phenomenon is called **resonance**, a term coined by **Heisenberg. Ingold** had called this phenomenon **mesomerism**.

The true structure of the molecule is called **resonance hybrid**.

Benzene can be represented by the following structures :

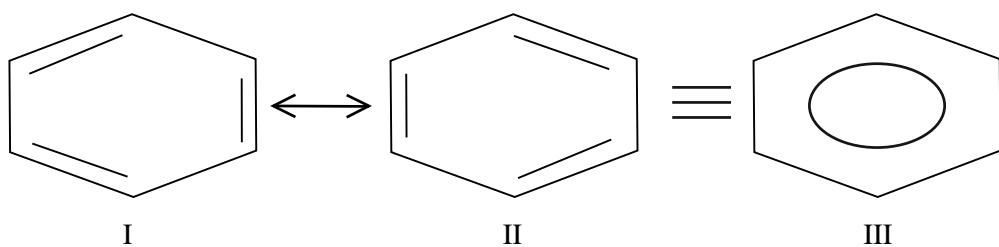


Fig 16.27 I & II are the resonating Structures of Benzene whereas III is the resonance hybrid

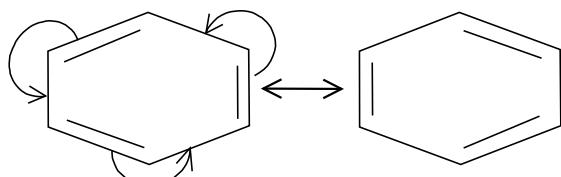
None of these structures truly represents the actual structure of benzene. Both the structures contribute significantly (nearly 93%) to the actual structure of benzene. Hence, benzene is said to be a resonance hybrid of these contributing structures.

*When several structures may be assumed to contribute to the actual structure of a molecule, but no one of them can be said to represent it uniquely, then the true structure of the molecule is referred to as a **resonance hybrid** and the phenomenon is termed as **resonance**.*

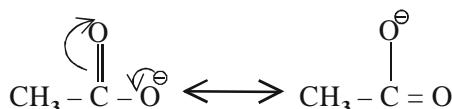
The situation of resonance is represented by a double headed arrow (\leftrightarrow) connecting the resonating structures. A resonance hybrid exhibits unusual stability. The difference between the energy of the hybrid and the energy of the most stable resonating structure is called the **resonance energy**. The resonance energy for carbon dioxide is 30 kcals/mol. whereas for benzene, it is 36 kcals/mol.

Chief Conditions of Resonance :

- (i) The various resonating structures should have the same positions of nuclei differing only in the position of electrons.
- (ii) The energy content of all the canonical structures must nearly be same.
- (iii) Each canonical form must have the same number of unpaired electrons (including zero).
- (iv) Resonance occurs in a molecule only when all the atoms lie in the same plane.
- (v) All resonating structures do not contribute to the same extent to the hybrid. Stable structures having less energy contribute most and the hybrid behaves more like that form. Among the resonating structures, the one which has (a) more number of covalent bonds, (b) all the atoms with octet of electrons excepting hydrogen which has a duplet, (c) less separation of opposite charges and (d) more dispersal of charge, is more stable than others.
- (vi) Resonating structures are interconvertible by one or a series of short electron shifts.
For instance -



(Benzene)



(Acetate ion)

Characteristics of Rosonance hybrid :

- (i) **Stability :** The resonance hybrid is always more stable than any of the contributing structures.
- (ii) **Resonance energy :** Resonance energy is the measure of the stability of the resonance hybrid. Higher its value, greater is its stability.

- (iii) **Unusual bond lengths :** In a resonance hybrid, the bond lengths are totally different from those of any of the contributing structures. For example, all the (C – C) bond lengths are equal in benzene having value 1.39A° , which is in between the bond length of 1.54A° for C–C single bond and 1.34A° for C = C double bond.

Resonance effect or Mesomeric effect :

The flow of π electrons from one part of conjugated system to the other creating centres of low and high electron density due to the phenomenon of resonance is termed as **resonance effect** (R effect) or **mesomeric effect** (M effect) which is of two types :

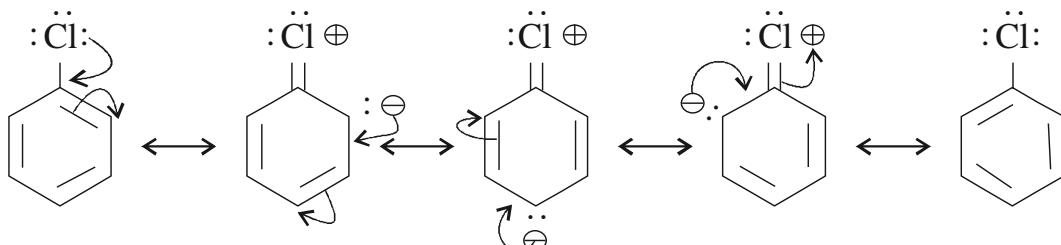
- (i) **Positive resonance (+R) or positive mesomeric (+M) effect:**

Groups which donate electrons to a conjugated system are said to have +R or +M effect.

– OH, – OR, – NH₂, – NHR, – NR₂, – Cl, – Br, – I etc.



Vinyl chloride

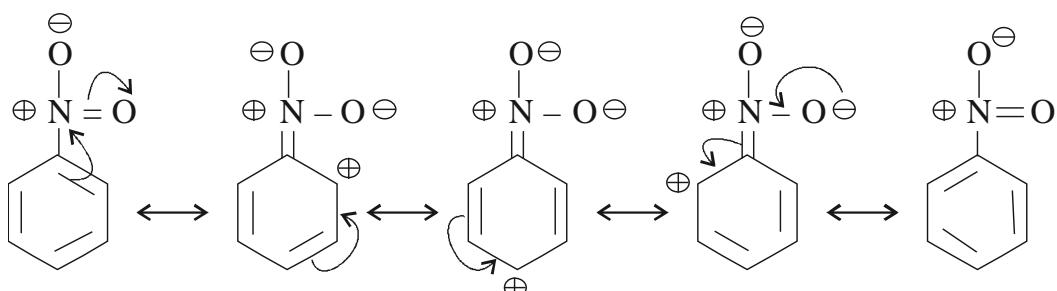
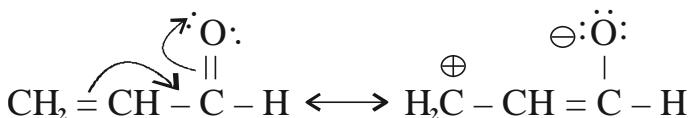


Chlorobenzene

- (ii) **Negative resonance (–R) or negative mesomeric (–M) effect :**

Groups which withdraw electrons from the conjugated system towards themselves are said to exhibit – R or – M effect.

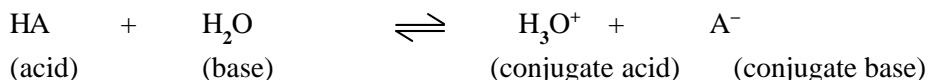
Examples are – NO₂, – CN, – COOH – CHO, – COR etc.



Effects of resonance :

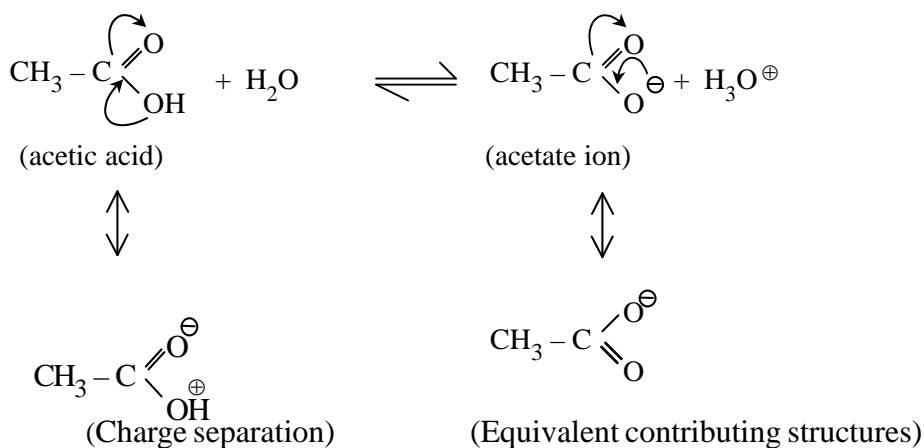
Resonance helps to explain the acidity and basicity of organic compounds. A few common examples are given below.

- (a) **Acidity of organic acids :** The acidity of an acid depends upon its ability to donate proton. The equilibrium can be written as



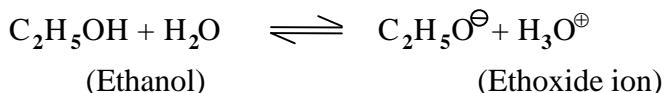
HA is an acid and it donates a proton to H_2O (base) and forms a conjugate base (A^-). If the conjugate base is more stable than the acid, then the equilibrium shifts towards the right and HA behaves as an acid.

Acetic acid is an acid and ethanol is not an acid.



The conjugate base (acetate ion) is more stable than the acid because of the equivalence of the contributing structures. Though resonance occurs in the acid, it does not contribute to its stability due to charge separation which acts as a restoring force. Hence, the equilibrium shifts towards right and acetic acid is an acid

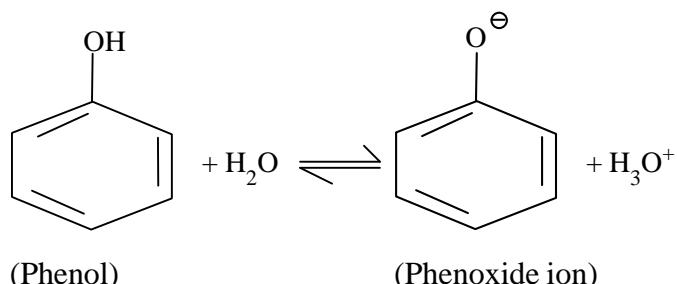
Consider the case of ethanol $\text{C}_2\text{H}_5\text{OH}$. The equilibrium can be represented as



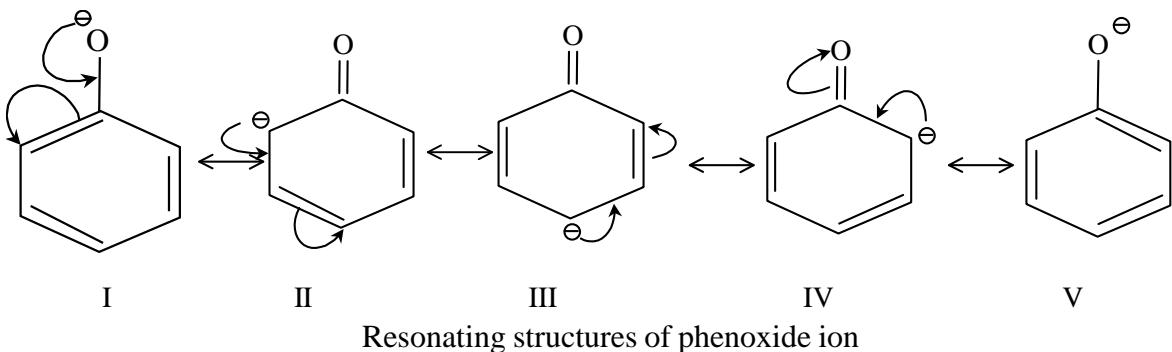
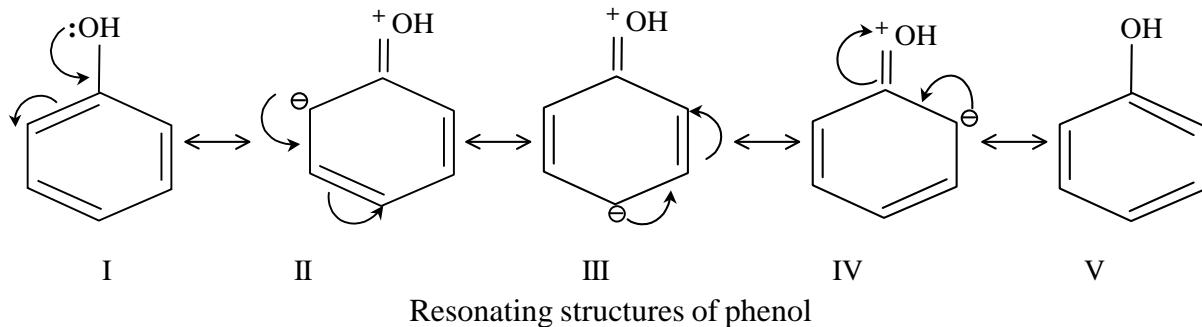
Resonance does not occur in ethoxide ion. Ethyl group being electron repelling does not accommodate the negative charge. Hence the equilibrium does not shift to the right since the ethoxide ion is not stabilised by resonance.

Phenol is acidic

Consider the following equilibrium for phenol.

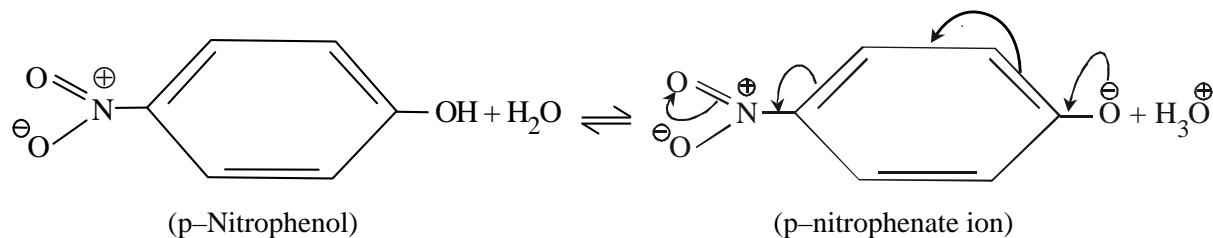
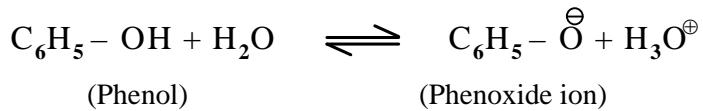


Phenol will be acidic only if the phenoxide ion will be more stable than phenol, so that the equilibrium will shift towards right hand side. Let us write the resonating structures for both the phenol and phenoxide ion.



For both phenol and phenoxide ion five resonating structures can be written. In case of phenol, besides the two Kekulé structures (I & V), other structures contribute negligibly towards the stability because of charge separation. On the other hand, in case of phenoxide ion, the other structures (II, III & IV) do not involve charge separation, but instead delocalise the charge leading to greater stability of the ion. Hence, phenoxide ion is more stable than phenol due to resonance and phenol is acidic.

p- Nitrophenol is more acidic than phenol



p- Nitrophenate is more stable than phenoxide because of resonance. More number of resonating can be written for p- nitrophenate leading to greater stability. Therefore, p- nitrophenol is more acidic ($pK_a = 7.16$) than phenol ($pK_a = 10$).

(b) Basicity of organic bases :

All organic compounds containing unshared pair of electrons or acquiring unshared pair of electrons through electron shifts can be considered as bases. The unshared pair of electrons accepts a proton, thus behaving as a base. The equilibrium for basicity is expressed as

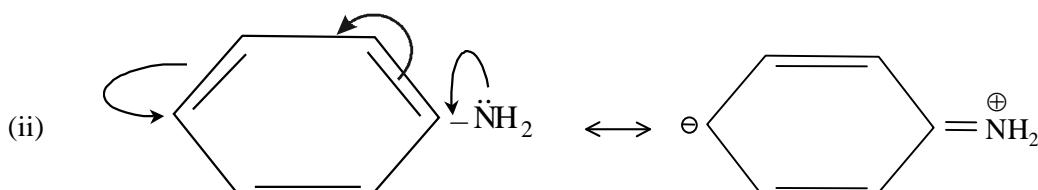


The conjugate acid is weak for a strong base and strong for weak base.

Basicity of methylamine and aniline



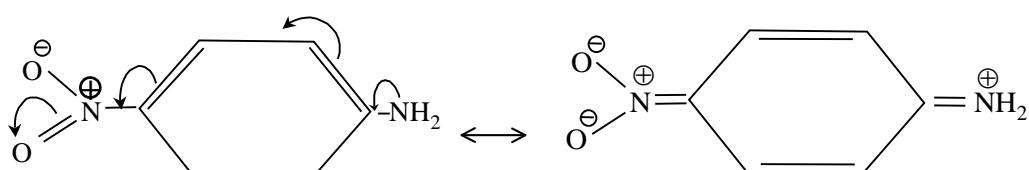
- (i) In case of methylamine, methyl group is electron repelling (+ I effect) whereas phenyl group is electron withdrawing (- I effect) in aniline.



The conjugative effect of phenyl group withdraws electron density from nitrogen. This is a consequence of resonance. As a result the basicity of aniline decreases. No such effect is observed in methylamine and hence methylamine is quite basic in nature.

Basicity of aniline and p- nitroaniline

When nitro group is present at para position, there is greater resonance interaction of the lone pair of electron of nitrogen with p- nitrophenyl system than with phenyl group, thus decreasing its basicity.

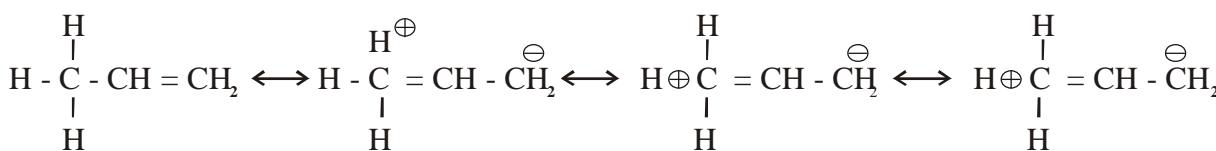


E. HYPERCONJUGATION (NO BOND RESONANCE)

A special type of resonance involving σ - electrons and π - electrons is called **hyperconjugation**. When alkyl groups like $\text{H}_3\text{C}-$, C_2H_5- are directly attached to multiple bonds like $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, the electron repelling property of the former groups are considerably enhanced. The +I effect of the alkyl groups can not explain this phenomenon properly.

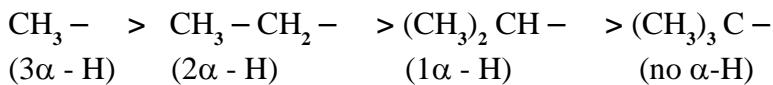
To account for this, **Baker** and **Nathan** suggested that when $\text{C}-\text{H}$ bond is attached to an unsaturated carbon atom, the σ - electrons of $\text{H}-\text{C}$ bond become delocalised by entering into partial conjugation with the adjacent π -electrons of unsaturated system, which means $\sigma-\pi$ conjugation occurs.

This type of conjugation between the electrons of single bond and those of multiple bond is termed **hyperconjugation** (Mulliken, 1941). Hyperconjugation causes a permanent polarity in the molecule and that polar effect is called *hyperconjugative effect*, Hyperconjugation is represented as follows:

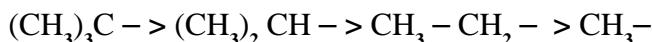


In the above resonating structures, one of the $\text{H}-\text{C}$ bond is considered to be cleaved. From this point of view, hyperconjugation is often called “**no bond resonance**”. Though $\text{H}-\text{C}$ bond is shown to be broken, H^{\oplus} is never free from the system or changes its position in the molecule. This effect is also called **Baker-Nathan effect** or **Anchimeric assistance**. (Please note that the above resonating structures have been written taking one $\text{H}-\text{C}$ bond only. Other two $\text{H}-\text{C}$ bonds can also result in different resonating or hyperconjugative structures)

Thus it is evident that hydrogen atoms attached to the carbon atom (α -carbon atom) next to the multiple bond (called the α - hydrogen atoms) are responsible for this hyperconjugation. Therefore, with the increased number of α -hydrogen atoms, more number of hyperconjugative structures can be written leading to greater inductive effect. Thus, the order of hyperconjugative effect is



This order is the reverse of inductive effect i.e.



Effect of Hyperconjugation

Hyperconjugation effect is certainly weaker than resonance effect. Due to this effect, the electron density of the unsaturated part of the molecule increases and therefore, the multiple bonds in these systems are found to be more reactive than what is expected from +I effect only.

Various physical and chemical properties have been explained through hyperconjugation.

Physical : Bond length – In ethane (CH_3-CH_3), $\text{C}-\text{C}$ bond length is 1.54\AA^0 .

But in $\text{CH}_3-\text{C}\equiv\text{CH}$,

CH_3-C single bond distance is found to be 1.46\AA^0 . This is due to hyperconjugation and the

CH_3-C bond develops a partial double bond character resulting in the shortening of bond distance.

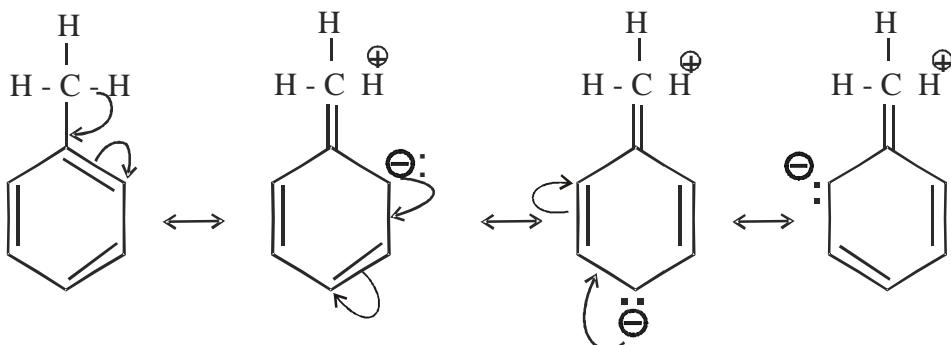
Chemical

(i) Stability of alkenes : The stabilities of alkenes can be known from their heat of hydrogenation values. Lower the heat of hydrogenation, greater will be the stability. Greater the number of alkyl groups attached to C = C, greater is the stability. This is evident from the following table.

Compound	No. of α -H	Heat of hydrogenation in kcals mol ⁻¹
I. $\text{CH}_2 = \text{CH}_2$ (Ethene)	nil	32.8
II. $\text{CH}_3 - \text{CH} = \text{CH}_2$ (Propene)	3	30.1
III. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ But - 2 - ene	6	cis 28.6 trans 27.6
IV. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{C} = \text{CH} - \text{CH}_3 \end{array}$ 2-methylbut -2-ene	9	26.9
V. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{C} = \text{C} \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array} \end{array}$ 2,3-Dimethylbut-2-ene	12	26.6

On the basis of heat of hydrogenation, the stability of alkenes follow the order, V > IV > III > II > I. This is in perfect agreement with the number of α -hydrogen atoms of alkyl groups attached to carbon-carbon double bond

(ii) Directive Influence of Alkyl groups



(For other two α -dydrogens, similar structures can be written)

CH_3- and other alkyl groups have o- and p-directive influence in electrophilic substitution reaction. In case of toluene, the electron density at o- and p-positions with respect to methyl group increases due to hyperconjugation (3- α hydrogens). Hence, electrophilic substitution will preferably be at o- and p- positions in case of toluene and other alkyl benzenes.

(iii) Stability of carbocations and free radicals.

The order of relative stability of the carbocations and free radicals is tertiary > secondary > primary.

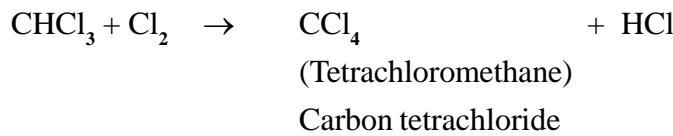
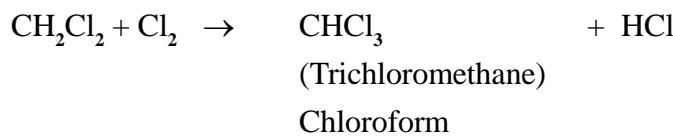
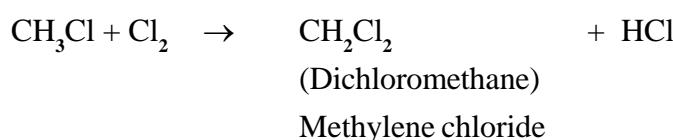
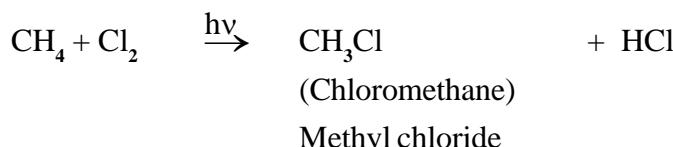
This can be explained on the basis of hyperconjugation. Greater the number of alkyl groups attached to carbocation, greater is the hyperconjugative interaction leading to the stability of the carbocation. Similar explanation can hold good for free radicals also.

16.12 TYPES OF ORGANIC REACTION

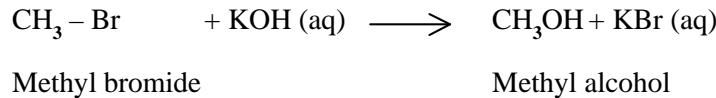
Organic reactions may be classified into four fundamental types basing on the nature of the products formed. These are :

- (i) Substitution reaction
- (ii) Addition reaction
- (iii) Elimination reaction
- (iv) Rearrangement reaction

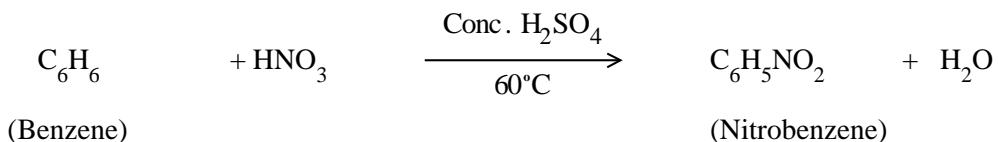
(i) **Substitution reaction :** When one or more atoms or groups of an organic compound are replaced by an equivalent number of atoms or groups, without any change in the remaining part of the molecule the reaction is termed as a **substitution reaction**. In substitution reaction, one or more covalent bonds are broken and formed at the same carbon atom of the reactant. The new atom or group which enters the molecule is called the *substituent* and the product is called a *substitution product*. Substitution reactions are characteristic reactions of saturated compounds. For example, when methane reacts with chlorine in the presence of diffused sunlight, all the four hydrogen atoms are substituted by chlorine atoms, subsequently forming a mixture of chloromethanes.



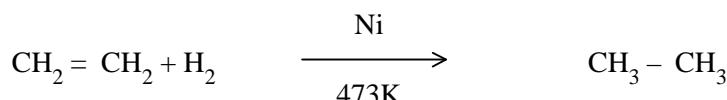
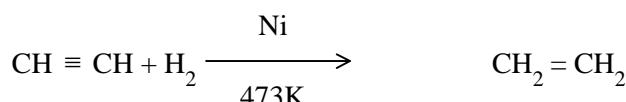
When methyl bromide is treated with aqueous KOH solution, the bromine atom is substituted by the hydroxy group and methyl alcohol is formed.



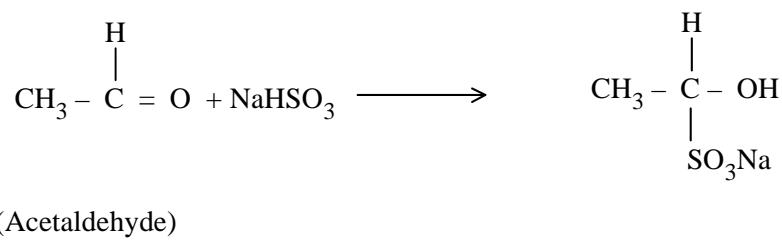
When benzene is treated with a mixture of conc. HNO_3 and conc. H_2SO_4 at 60°C , the hydrogen atom of the benzene ring is substituted by a nitro group, forming nitrobenzene.



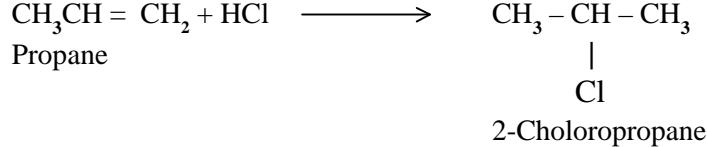
- (ii) **Addition reaction :** A reaction in which two reacting molecules combine to give a single molecule as the product is called **addition reaction**. Addition reactions are characteristic reaction of unsaturated compounds. For example : acetylene adds on hydrogen in two steps forming ethylene and ethane respectively.



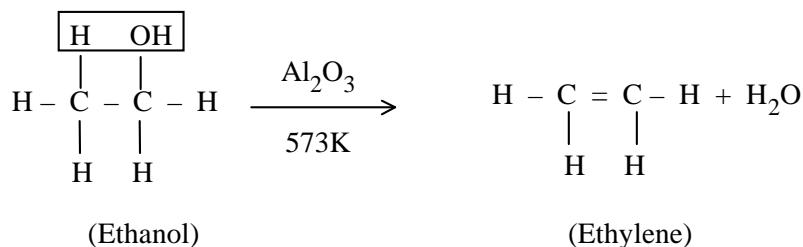
Similarly, NaHSO_3 adds to $>\text{C}=\text{O}$ group of acetaldehyde forming a bisulphite compound.



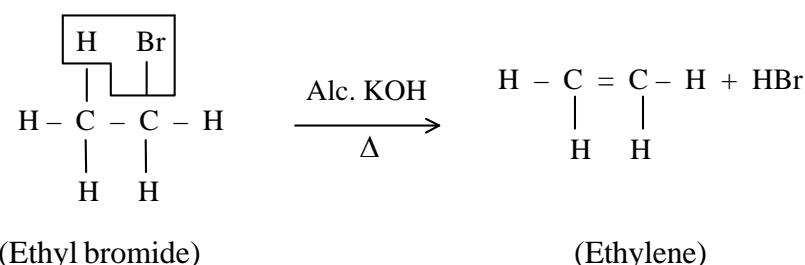
Addition of HCl to propene results in 2-chloropropane as the addition product.



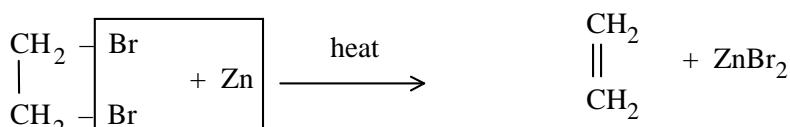
- (iii) **Elimination reaction :** Reaction in which two or more atoms or groups attached to the adjacent carbon atoms of the reactant molecule are eliminated in form of simple molecules like H_2O , H_2 , NH_3 , HCl etc. leading to the formation of a multiple bond are called **elimination reactions**. Due to such elimination, a multiple bond (double or triple) is formed. For example, when vapour of ethanol is passed over heated Al_2O_3 , ethylene is formed. A molecule of water is eliminated.



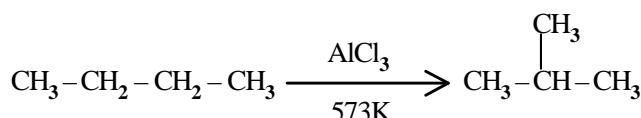
Similarly, when ethyl bromide is treated with alcoholic KOH, ethylene is formed.



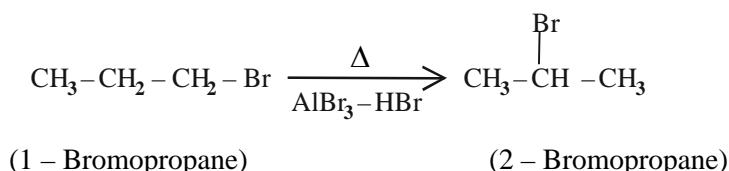
When ethylene dibromide is heated with Zn, ethylene is formed.



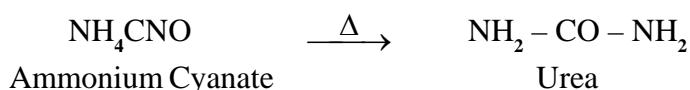
- (iv) **Rearrangement reaction :** These types of reactions involve migration of an atom or group from one site to another within the same molecule. The product is always a structural isomer of the original compound. For example, when n-butane is heated with AlCl_3 at 573K, 2 – methylpropane is formed.



Similarly, 1 – bromopropane rearranges to form 2 – bromopropane when heated with AlBr_3 and HBr.



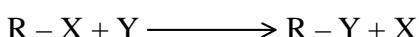
Ammonium cyanate on heating forms urea involving a rearrangement reaction.



16.13 FISSION OF A COVALENT BOND :

Irrespective of the organic reaction each reaction involves the breaking of a covalent bond in the substrate in the presence of a reagent and formation of a new covalent bond resulting with the product.

For example, the substrate R – X reacts with an attacking agent Y to give product R – Y.



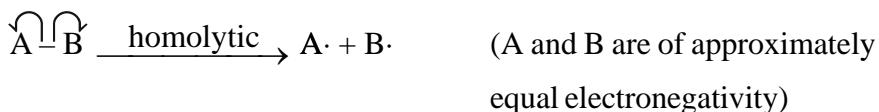
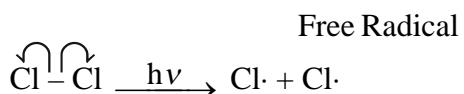
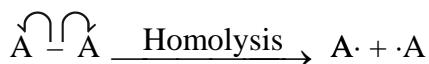
In this reaction the covalent bond R – X is broken and a new covalent bond R – Y is formed. Depending on the nature of R, the attacking agent Y, the leaving group X and experimental condition, bond cleavage or bond fission can take place in two ways.

(i) Homolysis or homolytic cleavage :

Homolysis of covalent bond may be defined as that type of cleavage where the shared pair of electrons is distributed equally between two bonded atoms resulting in two free radicals.

Homolytic fission usually occurs in non-polar bonds on heating at high temperature or in the presence of ultraviolet radiation or in the presence of peroxide compounds.

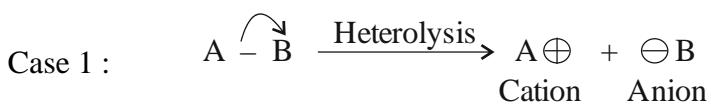
Homolysis can be represented by a fish arrow which shows one-electron displacement.



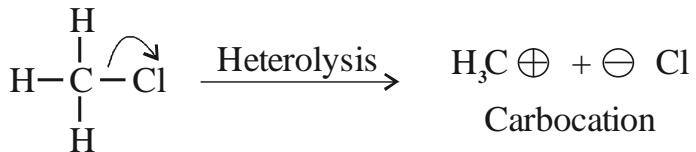
(ii) Heterolysis or heterolytic cleavage :

The type of cleavage of a covalent bond where the shared pair of electrons is donated to one of the bonded atoms resulting with an ion pair is termed as heterolysis or heterolytic cleavage.

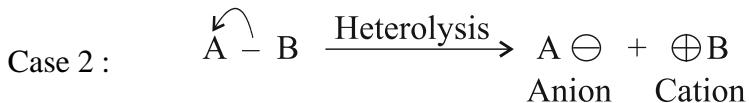
Heterolytic fission which occurs in a polar bond is represented by curved arrow which shows a two electron displacement towards more electronegative atom.



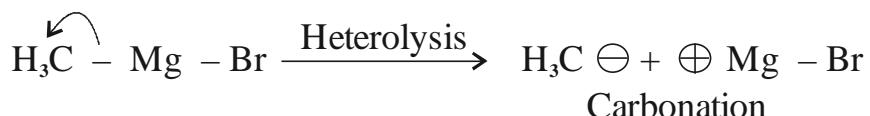
where B is more electronegative than A.



where chlorine is more electronegative than carbon.



where A is more electronegative than B

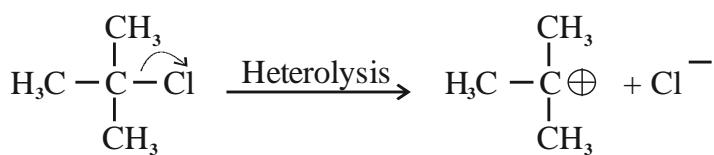


REACTIVE INTERMEDIATES:

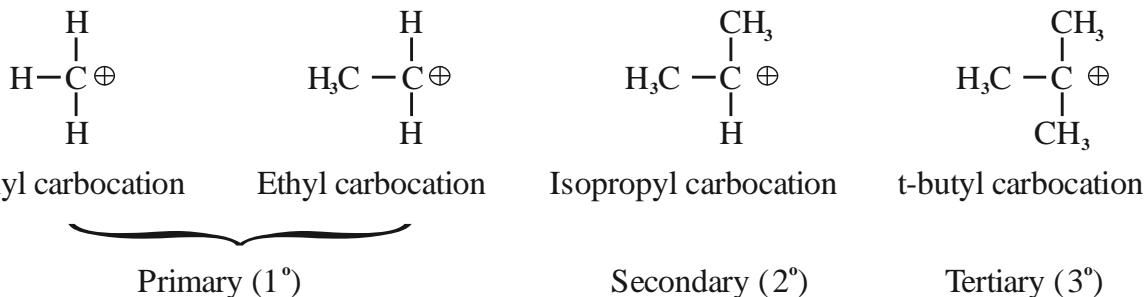
Homolytic and heterolytic cleavage of a covalent bond of the substrate result in short lived and highly reactive fragments called reactive intermediates which may be ionic or neutral.

(a) Carbocations :

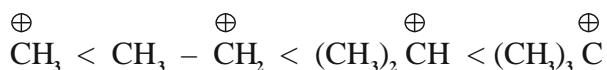
A carbocation is a positively charged species where the positive charge resides on a carbon atom with six electrons or three pairs of electron in its valence shell being formed by the heterolysis of a covalent bond.



- (i) Carbocations are classified as primary (1°), secondary (2°) and tertiary (3°) depending on the nature of the carbon atom bearing positive charge.

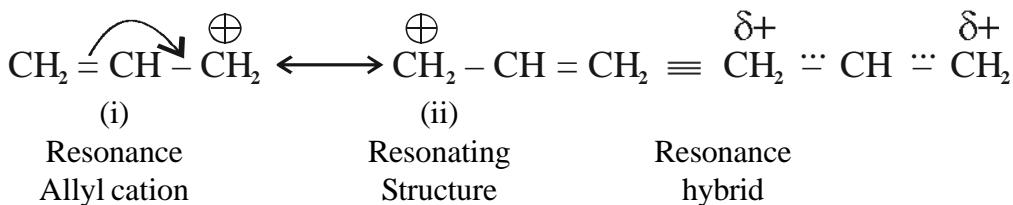


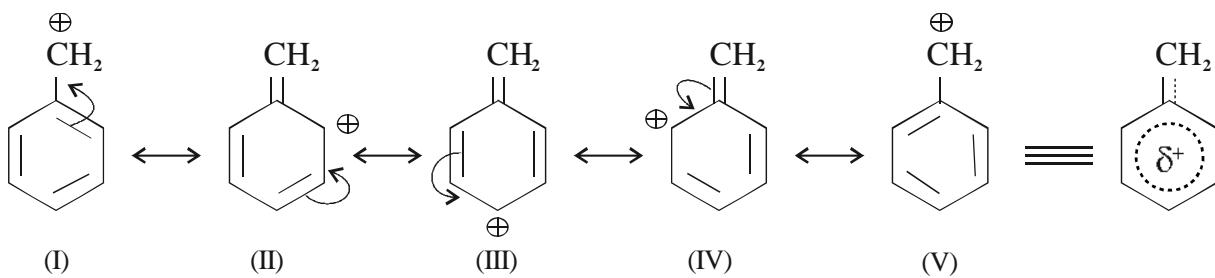
- (ii) The observed order stability of the carbocations is :



because alkyl group attached directly to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.

The high stability of allyl and benzyl cations can be explained by resonance. Benzyl cation because of having higher number of resonating structures is more stable than allyl cation.



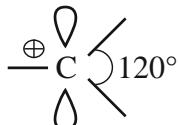


Resonating structures

Resonance hybrid

Resonance in Benzyl cation

- (iii) The carbocations have trigonal planar structure with bond angle 120° , the carbon atom carrying positive charge being Sp^2 hybridized. The unhybridized 2p orbital is empty lying perpendicular to the molecular axis.

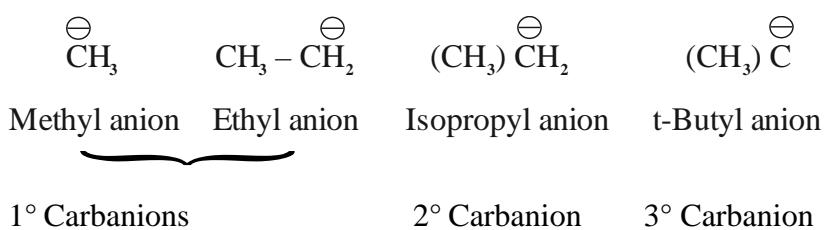


Structure of carbocation

(b) Carbanions :

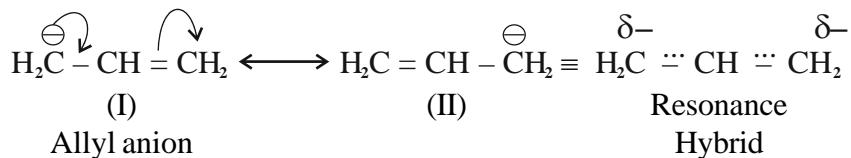
Carbanions may be defined as the negatively charged species with negative charge on the carbon atom possessing eight electrons or four pairs of electrons in its valence shell being formed by the heterolytic fission of a covalent bond.

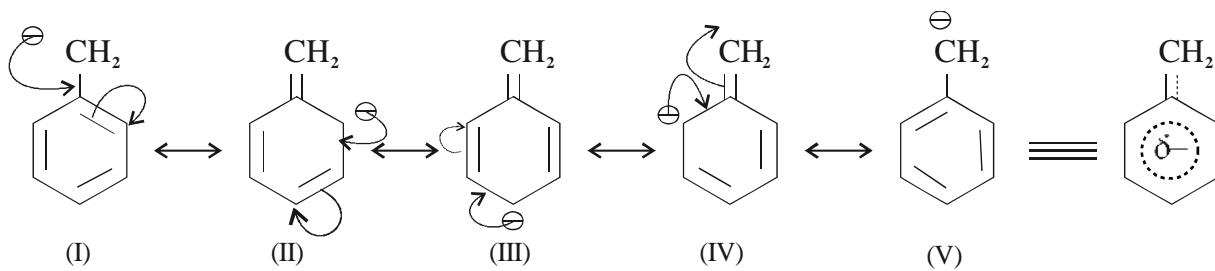
- (i) Carbanions can be categorised into three types : primary (1°), secondary (2°) and tertiary (3°) depending on the nature of the carbon atom bearing the negative charge.



- (ii) The order of stability of carbanions is $1^\circ > 2^\circ > 3^\circ$ which can be explained by inductive effect. The presence of alkyl group with + I effect intensifies the negative charge on carbon making it unstable.

But the stability of allyl and benzyl anions can be explained by the phenomenon of resonance.

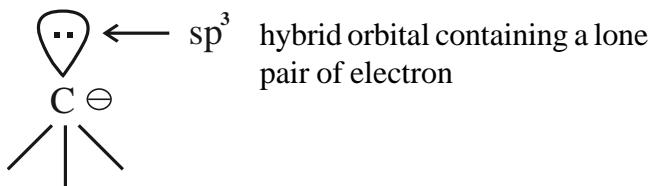




Benzyl anion

Resonance hybrid

- (iii) The carbanion is having a pyramidal i.e. a distorted tetrahedral structure like ammonia where the negatively charged carbon atom is sp^3 hybridized with bond angle 107° . The fourth sp^3 hybrid orbital contain a lone pair of electrons.

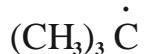
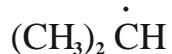
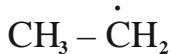


Structure of carbanion

(c) Free Radicals :

Free radicals may be defined as the odd electron neutral species which are formed by homolytic fission of a covalent bond.

- (i) Free radicals are of three types, such as primary (1°), secondary (2°) and tertiary (3°) depending on the nature of carbon atom carrying the unpaired electron.



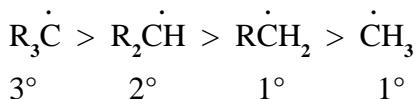
Methyl free radical
Primary (1°)

Ethyl free radical
Primary (1°)

Isopropyl free radical
Secondary (2°)

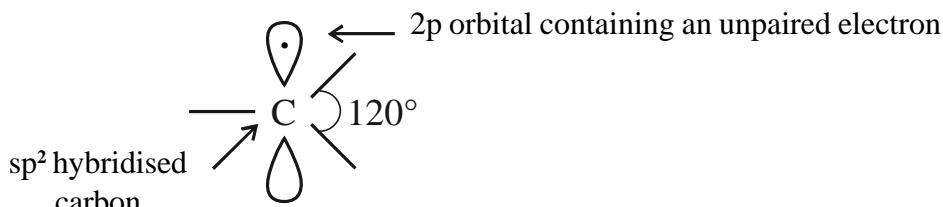
t-Butyl free radical
Tertiary (3°)

- (ii) The relative stability of simple alkyl free radicals has the order

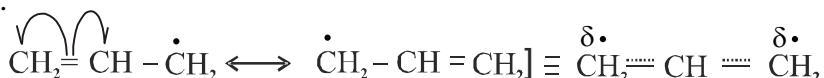


which can only be explained on the basis of hyperconjugation. Higher the number of α -H atoms, greater will be the delocalization of the odd electron and hence more stable will the alkyl free radical.

- (iii) Alkyl free radical is having trigonal planar structure with the central carbon atom being Sp^2 hybridized like carbocation. But in case of free radical the unhybridized 2p orbital contains a single electron.

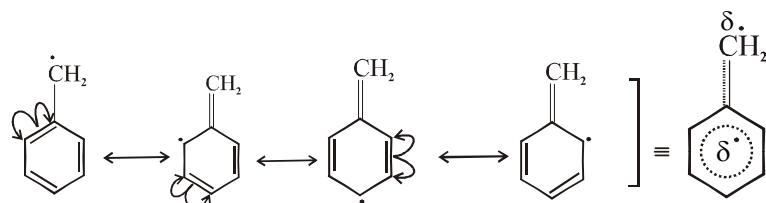


- (iv) The stability of allyl and benzyl radicals can be explained through resonance. Though these are 1° free radicals, they are more stable than 1° alkyl radicals. The stability is attributed to the resonance effect. In both allyl and benzyl radicals the p-orbital on carbon carrying a single electron is in conjugation with π bond and thus delocalisation occurs through p- π overlap.



(Resonance stabilisation of allyl radical)

The benzyl radical is more stable compared to allyl radical because in benzylic radical, the number of contributing structure is more.



(Resonance stabilisation of benzyl radical)

Due to resonance effect, the allyl and benzyl radicals are more stable than 1° , 2° , or 3° alkyl free radicals. Thus we can summarise the stability order of free radicals as Benzyllic > Allylic > 3° > 2° > 1° > CH_3 .

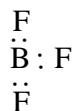
16.14 ELECTROPHILES AND NUCLEOPHILES

Ionic or polar reagents are classified into two subdivisions as

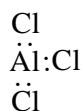
- (a) Electrophiles or Electrophilic reagents
- (b) Nucleophiles or Nucleophilic reagents

- (a) **Electrophiles or Electrophilic Reagents :** The reagents which are positively charged and electron deficient having a tendency to form a bond by accepting an electron pair from another species are called **electrophiles** (*electron loving*). An electrophile is thus electron deficient and attacks regions of high electron density (negative centres) in the substrate molecule.

Electrophilic reagents may be divided into two types : Positive electrophiles and neutral electrophiles. The positive electrophiles refer to those which carry a positive charge and include proton, cations and carbocations. Examples are H^+ , Cl^+ , Br^+ , I^+ , NO_2^+ , NO^+ , R_3C^+ , RN_2^+ , H_3O^+ etc. The neutral electrophiles though deficient in electrons do not carry positive charge. Examples are AlCl_3 , ZnCl_2 , BF_3 , SO_3 , carbenes. All these reagents have six electrons in their outermost orbit and are thus short of a pair of electrons for acquiring stable configuration and therefore behave as electron seeking reagent.



(Boron trifluoride)



(Aluminium chloride)

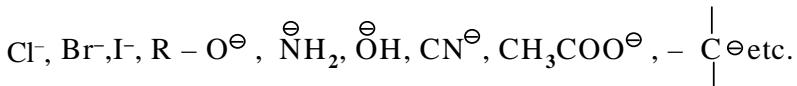


(Dichlorocarbene)

It should be noted that an electrophile need not be a positively charged ion, but it must possess an atom or centre which is electron deficient.

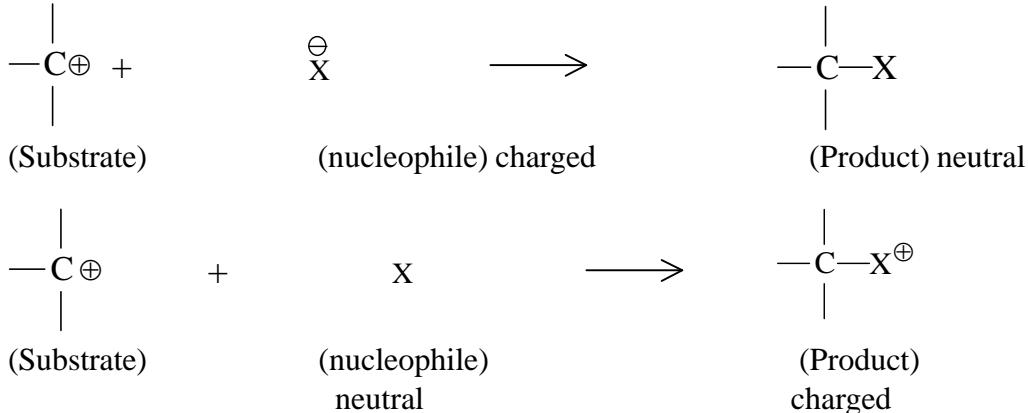
- (b) **Nucleophiles or Nucleophilic Reagents :** Anions and molecules with unshared pair of electrons having a tendency to donate a pair of electron to another species, capable of accepting it are **nucleophiles** (*nucleus loving*). Nucleophiles are electron rich centres and enter into reactions with electron acceptors. Nucleophiles may be negative nucleophiles or neutral nucleophiles.

Negative nucleophiles are those which carry negative charge. Examples are



The neutral nucleophiles are rich in electrons due to the presence of unshared electron pair. For example – $\text{H}_2\ddot{\text{O}}$, $\dot{\text{N}}\text{H}_3$, $\text{R}_3\dot{\text{N}}$, $\text{R}_2\dot{\text{S}}$, $\text{R} - \ddot{\text{O}}\text{H}$, $\text{R}\dot{\text{S}}\text{H}$ etc.

The addition of a negatively charged nucleophile to positively charged substance gives rise to a neutral product while the addition of a neutral nucleophile will give rise to a positively charged product.



CHAPTER (16) AT A GLANCE

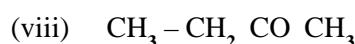
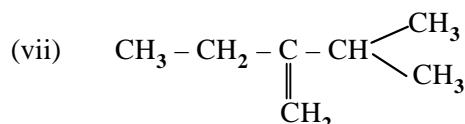
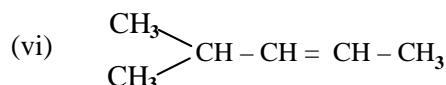
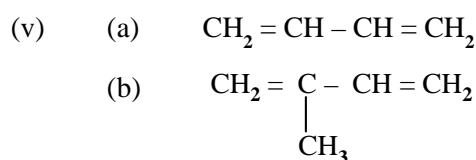
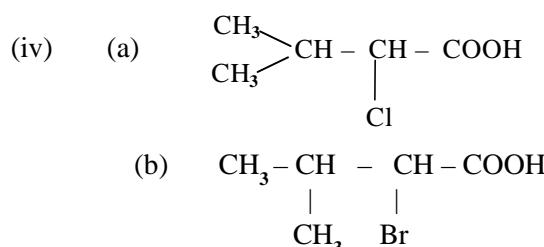
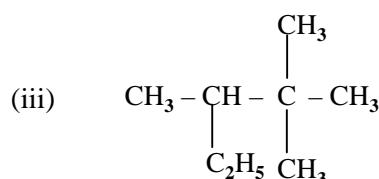
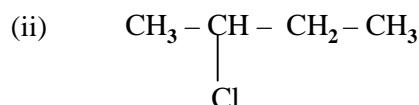
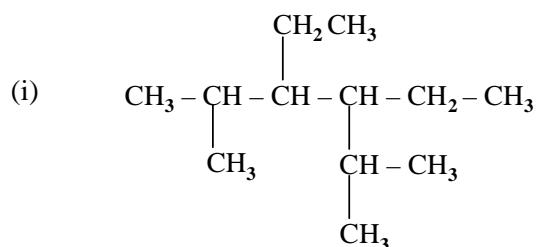
1. Organic compounds are defined as the compounds of carbon containing hydrogen and one or more additional elements like oxygen, nitrogen, sulphur, phosphorus, halogen etc.
2. Organic compounds are studied separately due to their characteristic features like vast number, complex nature, homology, isomerism, non-ionic and reversible nature of reaction and vast application in our life.
3. Carbon is tetravalent and all the four valencies are equivalent. It possesses the unique property of catenation.
4. Carbon utilises sp^3 hybrid orbitals for bond formation in saturated compounds, sp^2 hybrid orbitals in unsaturated compounds containing $C = C$ and sp hybrid orbitals in unsaturated compounds containing $C \equiv C$.
5. To elucidate the structure of the organic compounds the following steps are to be followed.
 - (i) Purification of the organic compounds involving crystallization, sublimation, distillation and differential extraction basing on the difference of one or more physical properties. Chromatography is the modern technology now mostly used for the separation, identification and purification of organic compounds basing on mainly principles of adsorption and partition, thus leading to different types of chromatography like adsorption chromatography (column chromatography and thin layer chromatography) and partition chromatography (paper chromatography).
 - (ii) Qualitative analysis of the organic compounds to detect the elements present like nitrogen, sulphur, halogens and phosphorus by Lassaigne's test in addition to carbon and hydrogen by estimating the amount of CO_2 and H_2O formed on oxidation.
 - (iii) Quantitative analysis of nitrogen is carried out either by Duma's method by Kjeldahl's method. Halogens can be estimated by Carius method, whereas phosphorus and sulphur can be oxidized to form phosphoric acid and sulphuric acid from which the amount present can be calculated. Liebig method is helpful in estimating carbon and hydrogen and percentage of oxygen is usually calculated by taking difference between 100% and the sum of percentages of all other elements present in the organic compound under observation.
6. Organic compounds are classified basing on carbon skeleton and functional groups.
7. Compounds containing the same functional group show homology. In a homologous series, two consecutive members differ by a $-CH_2-$ group.
8. Organic compounds are conveniently named according to the IUPAC system which is modified from time to time. According to the recent rule, the prefixes and suffixes are preceded by the locants. A compound may have several names, but a single name should not represent more than one structure.

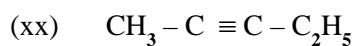
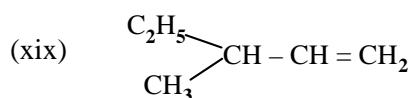
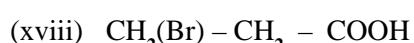
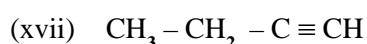
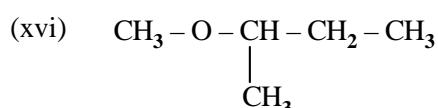
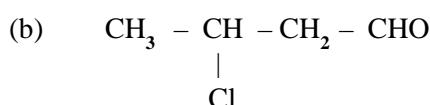
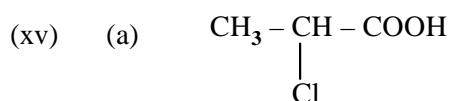
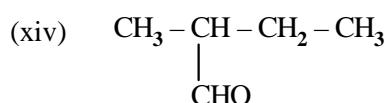
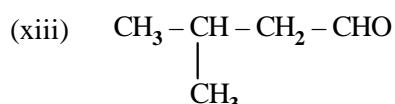
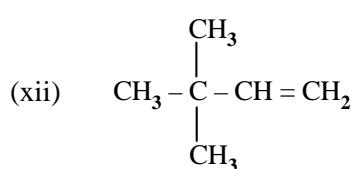
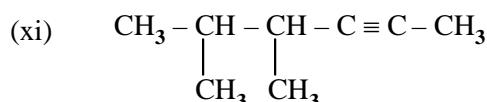
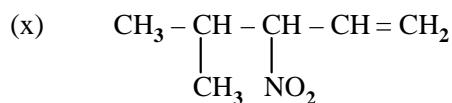
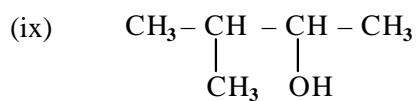
9. Organic compounds show **structural** and **stereoisomerism**. **Structural isomerism** arises due to the arrangement of atoms within the molecule resulting in several structural formulae whereas **stereoisomerism** arises due to the relative arrangement of atoms or groups in space within the molecule.
10. For a compound to show **optical isomerism**, the four atoms or groups attached to the carbon atom must be different. **Geometrical isomerism** arises due to the restricted rotation about a carbon to carbon double bond.
11. **Inductive effect** arises due to the electronegativity difference between atoms in a bond. There are +I substituents repelling electrons (alkyl groups, COO^- etc.) and -I substituents attracting electrons (-F, -Cl, -OH, NO_2 etc.) Inductive effect operates through a short distance (i.e. up to about 3\AA). The acidity of substituted acids, stability of carbocations etc. can be explained through inductive effect.
12. **Electromeric effect** - It is a temporary effect. On the approach of a charged reagent, the π -electron of the multiple bond present in an organic molecule has a tendency to get polarised in the direction of more electronegative atom. The effect is known as electromeric effect.
13. When several structures can be written for a particular compound by simply redistribution of electron density, no one of these structures satisfactorily account for all the observed properties. The actual structure is represented by a hybrid of all these structures. The molecule is referred to as a **resonance hybrid**.
14. Resonance confers stability to the molecule.
15. Resonance helps to explain certain observed phenomena like acidity and basicity of organic compounds.
16. **Hyperconjugation**- The electron releasing tendency of alkyl group gets enhanced if it is linked to a multiple bond present in an organic molecule. The effect is known as hyperconjugation or no bond resonance which causes permanent polarity in the molecule.
17. Organic reactions may be classified into four fundamental types basing on the nature of products. They are **substitution**, **addition**, **elimination** and **rearrangement** reactions.
18. **Homolytic cleavage** of a covalent bond results in the formation of **free radicals** whereas **heterolytic cleavage** results in the formation of **ions**. Carbon carrying negative charge is called a **carbanion** and carbon carrying positive charge is called a **carbocation**.
19. Reagents having negative charge (CH_3^- , $\text{C}_2\text{H}_5\text{O}^-$, COO^- etc.) or a lone pair of electrons in a complete shell ($\dot{\text{N}}\text{H}_3$, $\text{H}_2\ddot{\text{O}}$, $\text{H}_2\ddot{\text{S}}$ etc) are called **nucleophiles**.
20. Reagents having a positive charge (Br^+ , NO_2^+ , I^+ etc.) or electron deficiency are called **electrophiles**.
21. Reactions taking place with nucleophilic reagents are called **nucleophilic reactions** and the reactions taking place with electrophilic reagents are called **electrophilic reactions**.

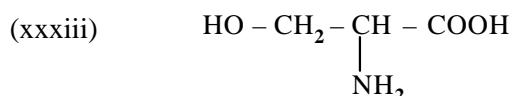
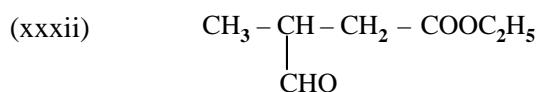
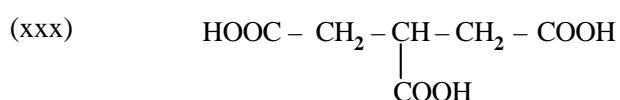
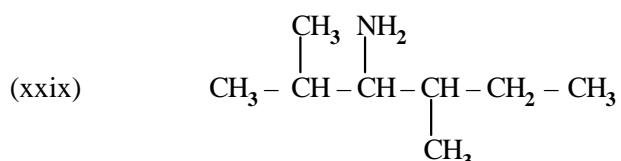
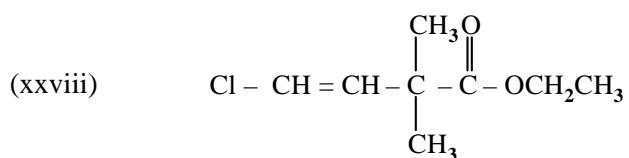
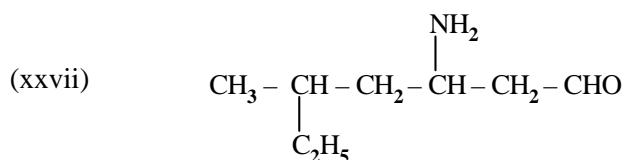
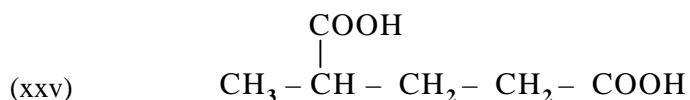
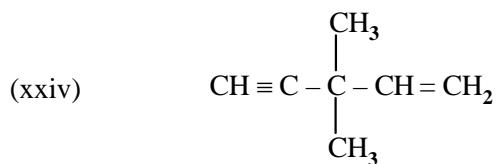
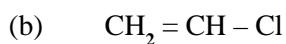
QUESTIONS

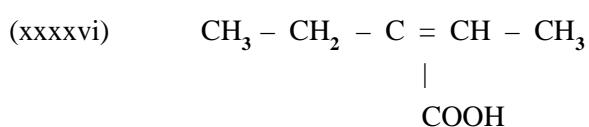
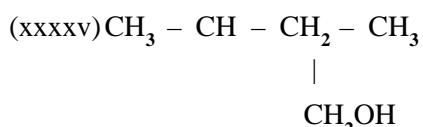
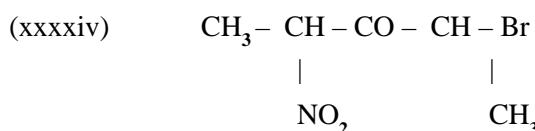
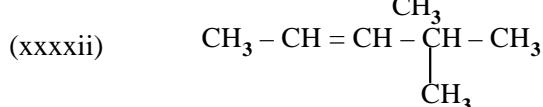
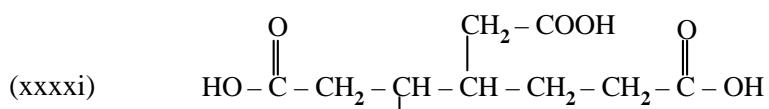
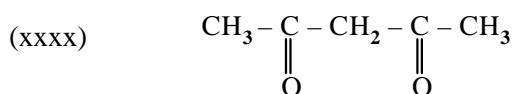
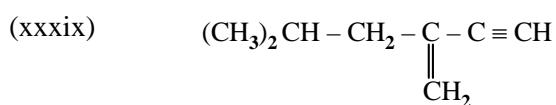
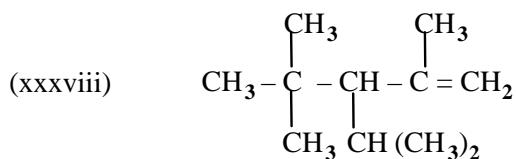
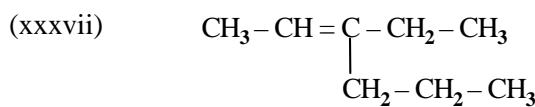
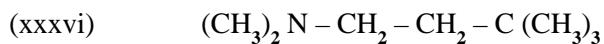
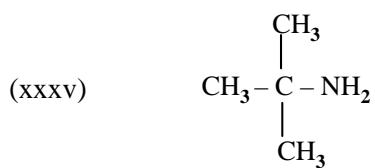
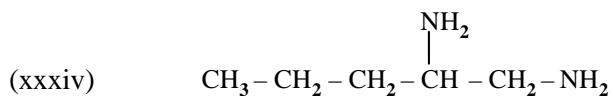
A. SHORT QUESTIONS : (one mark each)

1. Give the IUPAC names of the following compounds :







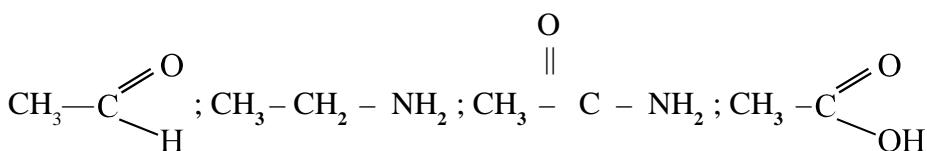


2. Write down the structural formulae of the following compounds :

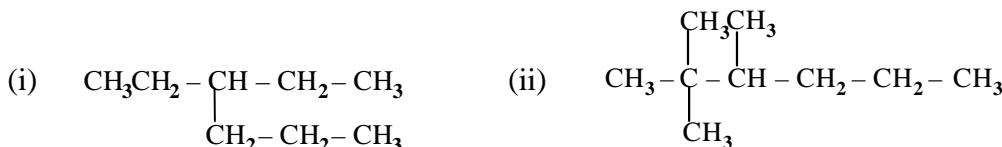
- (i) 1-Bromo – 3 – pentanone
 - (ii) 2 – Pentanone
 - (iii) 2 – Methyl – 1 – pentene
 - (iv) 3,3 – Dimethyl – 1 – butene
 - (v) 3 – Methyl – 3 – pentanol
 - (vi) 1 – Bromo – 2 methylbutane
 - (vii) 4,5 – Dimethyl – 2 – hexyne
 - (viii) 4 – Methyl – 2 – pentene
 - (ix) Ethyl formate
 - (x) 3 – Hydroxybutanoic acid
 - (xi) 2 – Butanol
 - (xii) 1,3 – Butadiene
 - (xiii) 3 – Pentanol
 - (xiv) 2,2 – Dimethyl – 1 – propanal
 - (xv) 3 – Methylpent – 4 – en – 2 – one.
 - (xvi) 2 – Bromo – 4 – chloropentanal
 - (xvii) Pentane – 2,4 – dione
 - (xviii) 2 – Methyl propane
 - (xix) Ethyl-4 amino-3-chlorobut-2-enoate
 - (xx) Benzoic acid
 - (xxi) 2-Methyl buta-1, 3-diene
 - (xxii) Propadiene
3. Which of the following is basic ?
- (i) $\text{CH}_3\text{CH}_2\text{OH}$ (ii) CH_3COCH_3 (iii) $\text{CH}_3\text{CH}_2\text{NH}_2$ (iv) $\text{CH}_3 - \text{O} - \text{CH}_3$
4. Name the compound which is isomeric with diethyl ether.
5. Give the IUPAC name of a compound which is isomeric with acetone
6. (a) How many sigma and pi-bonds are present in methyl cyanide ?
 (b) How many sigma and pi-bonds are present in vinyl cyanide ?
7. Name the functional isomer of propanone.
8. Indicate the hybridised state of carbon atoms in acetylene.
9. How many isomers are possible for C_5H_{12} .
10. Write formula of one alkynyl group.
11. How many sigma and pi-bonds are present in acetylene molecule ?

B. Short Questions : (two marks each)

1. Write the structure of the following compounds :
 - (a) 2 – Methylpentene (b) 2 – butanol
2. Circle the functional groups in the following :
 - (a) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$; $\text{CH}_3 - \text{COOH}$; $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$; CH_3CONH_2
 - (b) Name the functional groups :



3. What do you understand by functional group in organic compounds ?
4. Write a short note on – "Isomerism in organic compounds".
5. Name the functional groups in the following compounds.
 CH_3CHO ; $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CONH_2
6. The following names are incorrect. Give correct names.



(3 – Propylpentane) (4,5,5 – trimethylhexane)

7. What is homologous series ? Give an example of it.
8. What is resonance ? Give one example.
9. Explain with one example the term electrophile.
10. What is a nucleophile ? Give an example of nucleophilic substitution reaction.

C. Short questions : (Three marks each)

1. What is Rf value ? How can it be used for identification of organic compounds in a mixture ?
2. What is the principle behind the soda lime test for nitrogen? Why is this test not dependable ?
3. Is Beilstein's test a satisfactory test for the detection of halogens ?
4. Why is H_2SO_4 added after addition of ferrous sulphate in Lassaigne's test for nitrogen ? Give reasons.
5. Why is dry copper oxide used in the detection of hydrogen ?
6. What is the principle behind Duma's method for the estimation of nitrogen?
7. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?
8. Why is it necessary to used acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test ?

D. Multiple Choice Questions

1. The concept of vital force theory was given by

(a) Lavoisier	(b) Wohler
(c) Berzelius	(d) Berthelot
2. Carbon forms a large number of compounds because of

(a) catenation	(b) high electron affinity
(c) high ionisation energy	(d) variable valency.
3. A compound with molecular formula C_2H_2 must contain

(a) all sigma bonds	(b) all pi-bonds
(c) three sigma and two pi-bonds	(d) two sigma and three pi-bonds.
4. Alicyclic compound is

(a) an aromatic compound	(b) a carbocyclic compound
(c) an acyclic compound	(d) a heterocyclic compound.
5. The compound $R - CO - NH_2$ is an example of

(a) an amide	(b) an amine
(c) a ketone	(d) a cyanide.
6. The hybridisation of carbons C_1 and C_3 in the compound is

$$^1CH_3 - ^2CH = ^3CH - ^4CH_3$$

(a) sp^2, sp^3	(b) sp^3, sp^2
(c) sp, sp^3	(d) sp^2, sp^2
7. The IUPAC name of $OHC - CH = CH - \overset{CH_2}{\underset{CH_2 - CH_2 - CH_2 - CH_3}{|}} CH - CH = CH_2$ is

(a) 4 – Butyl – 2, 5 – hexadien – 1 – al. (b) 5 – Vinyloct – 3 – en – 1 – al
(c) 5 – Vinyloct – 5 – en – 8 – al (d) 3 – Butyl – 1,4 – hexadien – 8 – al
8. Which of the following IUPAC names is correct ?

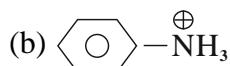
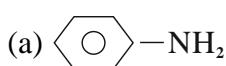
(a) 2 – Methyl – 3 – ethylpentane	(b) 2 – Ethyl – 3 – methylpentane
(c) 3 – Ethyl – 2 – methylpentane	(d) 3 – Methyl – 2 – ethylpentane
9. The IUPAC name of $CH_2 = CH - CH(CH_3)_2$ is

(a) 1,1 – Dimethyl – 2 – propene	(b) 3 – Methyl – 1 – butene
(c) 2 – Vinylpropane	(d) 1 – Isopropylethylene
10. The IUPAC name of $CH \equiv C - CH = CH_2$ is

(a) 3 – Buten – 1 – yne	(b) 1 – Buten – 3 – yne
(c) But – 1 – yn – 3 – ene	(d) 1 – Butyn – 3 – ene

11. IUPAC name of the compound $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ is :
- (a) Buten – 1, 4 – dioic acid
 - (b) 3 – carboxypropanoic acid
 - (c) Succinic acid
 - (d) 1,2 – Dicarboxyethane
12. Which of the following compounds has isopropyl group ?
- (a) 2,2,3,3 – Tetramethylpentane
 - (b) 2,2 – Dimethylpentane
 - (c) 2,2,3 – Trimethylpentane
 - (d) 2 – Methylpentane
13. Isomerism exhibited by acetic acid and methyl formate is
- (a) functional
 - (b) geometrical
 - (c) chain
 - (d) position.
14. Electrophiles are
- (a) electron loving species
 - (b) electron hating species
 - (c) nucleus loving reagents
 - (d) nucleus hating reagents.
15. Nucleophiles are
- (a) electron loving species
 - (b) electron hating species
 - (c) nucleus loving species
 - (d) nucleus hating species.
16. Heterolytic cleavage of a carbon – carbon covalent bond gives
- (a) carbanion
 - (b) carbocation
 - (c) free radical
 - (d) both carbanion and carbocation
17. A π – bond is formed by the overlapping of
- (a) hybridised orbitals
 - (b) π – orbitals only
 - (c) any two p-orbitals
 - (d) orbitals oriented perpendicular to the molecular axis.
18. Chemically similar compounds differing by $-\text{CH}_2$ group are
- (a) isomers
 - (b) allotropes
 - (c) homologues
 - (d) tautomers.
19. Which of the following is the most stable ion ?
- (a) $\text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{C}}\text{H} - \text{CH}_3$
 - (b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\oplus}{\text{C}}\text{H}_2$
 - (c) $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\oplus}{\text{C}}} - \text{CH}_3$
 - (d) $\overset{\oplus}{\text{C}}\text{H}_3$
20. Which of the following would be optically active ?
- (a) tert. butanol
 - (b) sec. butanol
 - (c) n – butanol
 - (d) 1 – chloro – 4 – hydroxybutane

31. In which of the following molecules, the resonance effect is not present ?



32. An electrophilic reagent must have

(a) a vacant orbital

(b) an orbital containing one electron

(c) an orbital containing two electrons

(d) all completely filled orbitals

33. Methanol and acetone can be separated by

(a) fractional distillation

(b) distillation

(c) steam distillation

(d) vacuum distillation

34. Which of the following mixture would steam distillation be the most appropriate method of separation

(a) Diethyl ether and water

(b) Ethyl alcohol and water

(c) Aniline and sodium chloride

(d) none of these

35. In quantitative estimation of hydrogen 0.1g of an organic compound yielded 0.09g of water. The percentage of hydrogen in the compound is

(a) 8

(b) 10

(c) 12

(d) 15

36. In Duma's method for the estimation of nitrogen the sample is heated with copper oxide and the gas evolved is passed over

(a) Nickel

(b) Copper oxide

(c) Copper gauze

(d) None of these.

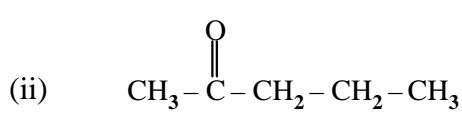
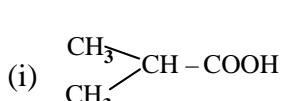
37. In the Carius method for the estimation of halogens, the sample is heated with

(a) Conc. HNO_3 (b) Conc. H_2SO_4 and Ag(c) Conc. HNO_3 and AgNO_3

(d) None of these

E. SHORT QUESTIONS

1. Write the IUPAC names of the following compounds



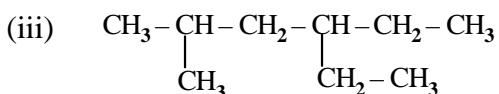
2. Write the structural formulae of the following :

(i) 2,2,3 – Trimethylbutane

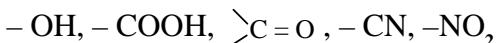
(ii) 1 – Chloropropan – 2 – one

(iii) Benzoyl chloride

3. Name each of following compounds on the basis of IUPAC system.



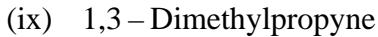
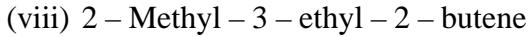
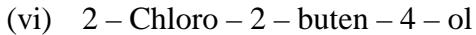
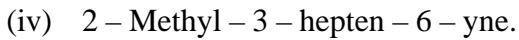
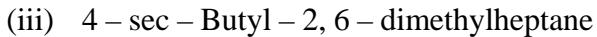
4. Arrange the following functional groups in the increasing order of priority.



5. Write down all the possible structural isomers of



6. Correct the following IUPAC names of the compounds :



F. ESSAY TYPE QUESTIONS

- What are different types of organic reactions ? Name them with one suitable example in each case.
- What are optical isomers ? Mention two conditions for optical activity.
- Explain the terms –
 - Homolytic and heterolytic cleavage
 - Nucleophile and electrophile
- What is a homologous series ? What are its characteristics ?
- Write down the structure of isomeric pentyl radicals. Name them by IUPAC system.
- Name the type of isomers the following pair represents (with justification)
 - $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3

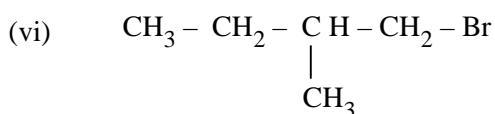
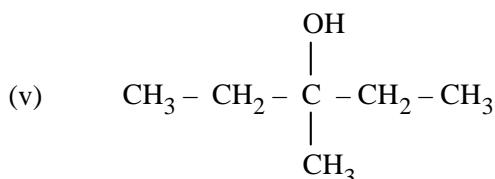
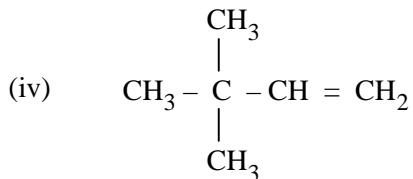
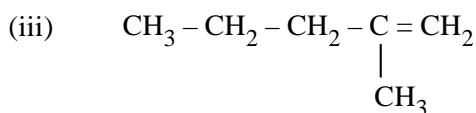
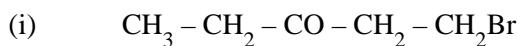
- (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ and $\text{CH}_3 - \begin{array}{c} \text{CH} - \text{CH}_3 \\ | \\ \text{CHO} \end{array}$
- (iii) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ and $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$
 (iv) $\text{CH}_3 - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{CH}_3$ and $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{CH}_3$,
 (v) $\text{CH}_3 - \text{CHO}$ and $\text{CH}_2 = \text{CHOH}$
7. What is the cause of geometrical isomerism ? Write the structures of the two geometrical isomers of 2 – butene. Name them. Why don't you expect geometrical isomers in case of 2 – butyne ?
8. Give reasons–
- Trichloroacetic acid is more acidic than acetic acid
 - phenol is acidic, but alcohol is neutral
 - Aniline is less basic than methylamine.
 - Acetic acid is acidic.
 - Acid amides are less basic than amines.
9. Discuss the chemistry for the detection of nitrogen in an organic compound. How is this test modified when both nitrogen and sulphur present in the organic compound are to be detected simultaneously ?
10. (a) How are carbon and hydrogen estimated in an organic compound ?
 (b) 0.6g of an organic compound gave an combustion 0.09g of H_2O and 0.55g of CO_2 . Calculate the percentage composition of the compound if it contains only C, H and oxygen. (Answer C = 25%, H = 1.66%, O = 73.34%)
11. Write a note on chromatography.
12. Describe Carius method for the estimation of
- Phosphorus
 - Halogens
 - Sulphur
13. (a) How is nitrogen estimated in an organic compound by Kjeldahl's method ?
 (b) If NH_3 obtained from 0.2g of an organic compound by Kjeldahl's method neutralises 25 ml of 0.1 N H_2SO_4 , what is the percentage of nitrogen in the compound ? (Answer: 17.50)
14. (a) How are halogens estimated in organic compound ?
 (b) 0.147g of an organic compound containing chlorine was heated with nitric acid and silver nitrate and gave 0.287g of silver chloride. Calculate the percentage of chlorine in the compound (Answer- 48.29)

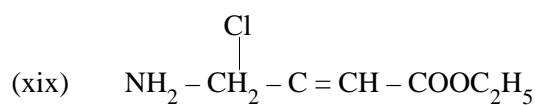
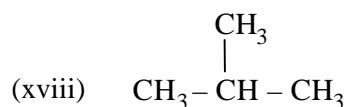
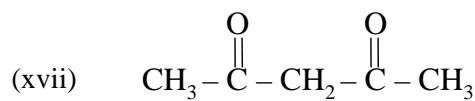
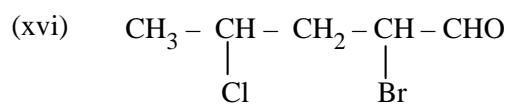
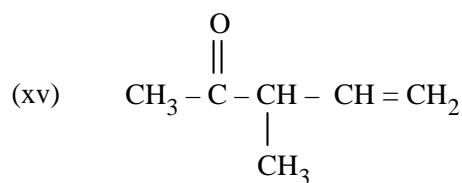
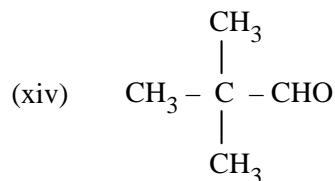
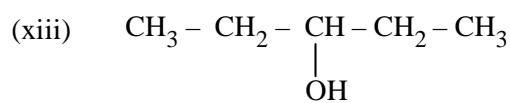
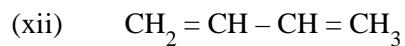
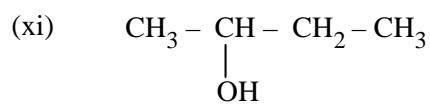
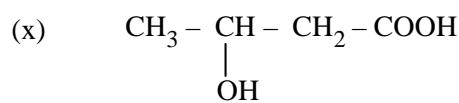
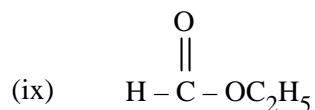
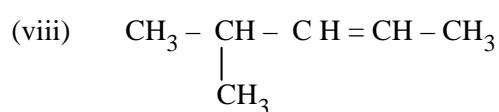
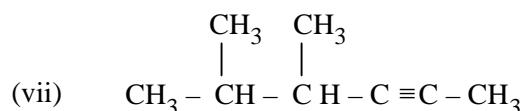
ANSWERS

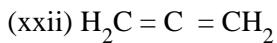
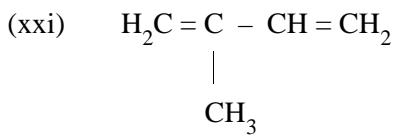
- A.1.** (i) 3, 4 – Diethyl – 2, 5 – dimethylhexane
 (ii) 2 – Chlorobutane
 (iii) 2, 2, 3 – Trimethylpentane
 (iv) (a) 2 – Chloro – 3 – methylbutanoic acid (b) 2 – Bromo – 3 – methylbutanoic acid
 (v) (a) Buta – 1, 3 – diene (b) 2 – Methylbuta – 1, 3 – diene.
 (vi) 4 – Methylpent – 2 – ene.
 (vii) 2 – Ethyl – 3 – methylbut – 1 – ene
 (viii) Butan – 2 – one
 (ix) 3 – Methylbutan – 2 – ol.
 (x) 4 – Methyl – 3 – nitropent – 1 – ene.
 (xi) 4, 5 – Dimethylhex – 2 – yne.
 (xii) 3, 3 – Dimethylbut – 1 – ene.
 (xiii) 3 – Methylbutanal. or 3 – Methylbutan – 1 – al.
 (xiv) 2 – Methylbuta – 1 – al or 2 – Methylbutanal
 (xv) (a) 2 – Chloropropanoic acid (b) 3 – Chlorobutanal
 (xvi) 2 – Methyoxybutane
 (xvii) But – 1 – yne
 (xviii) 3 – Bromopropanoic acid
 (xix) 3 – Methylpent – 1 – ene.
 (xx) Pent – 2 – yne
 (xxi) Ethylpropanoate
 (xxii) (a) Propane – 1, 2, 3 – tricarbonitrile (b) chloroethene
 (xxiii) Propadiene
 (xxiv) 3, 3 – Dimethylpent – 1 – en – 4 – yne
 (xxv) 2 – Methylpentane – 1, 5 – dioic acid or 2 – Methylpentanedioic acid.
 (xxvi) N, N – Dimethylmethanamine.
 (xxvii) 3 – Amino – 5 – methylheptanal.
 (xxviii) Ethyl – 4 – chloro – 2, 2 – dimethylbut – 3 – en – 1 – oate.
 (xxix) 2, 4 – Dimethyl – 3 – hexanamine.
 (xxx) Propane – 1, 2, 3 – tricarboxylic acid.
 (xxxi) 2 – Oxoethanoic acid.

- (xxxii) Ethyl – 3 – formylbutanoate or Ethyl – 3 – methyl – 1 – oxobutanoate.
- (xxxiii) 2 – Amino – 3 – hydroxypropanoic acid.
- (xxxiv) 1, 2 – Pentanediamine.
- (xxxv) 2 – Methyl – 2 – propanamine or *tert* – Butylamine.
- (xxxvi) 3, 3, N, N – Tetramethylbutanamine.
- (xxxvii) 3 – Ethylhex – 2 – ene.
- (xxxviii) 2, 4, 4 – Trimethyl – 3 – (1 – methylethyl) pent – 1 – ene.
- (xxxix) 2 – (2 – Methylpropyl) but – 1 – en – 3 – yne. or
2 – Isobutylbut – 1 – en – 3 – yne
- (xxxx) 2, 4 – Pentanedione.
- (xxxxi) 4 – (Carboxymethyl) – 3 – methylheptanoic acid
- (xxxxii) 4 – Methylpent – 2 – ene
- (xxxxiii) Pentanedioic acid.
- (xxxxiv) 2 – Bromo – 4 – nitropentan – 3 – one
- (xxxxv) 2 – Methylbutan – 1 – ol
- (xxxxvi) 2 – Ethylbut – 2 – enoic acid

2. Structural formula :





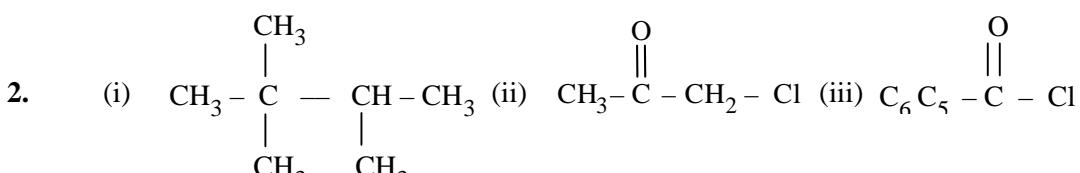


3. (iii) $\text{CH}_3\text{CH}_2\text{NH}_2$
4. Butanol
5. Propanal
6. (a) 5 σ and 2 π bonds. (b) 6 σ and 3 π bonds.
7. Propanal
8. sp
9. Three
10. $\text{CH} \equiv \text{C} -$ or $\text{CH} \equiv \text{C} - \text{CH}_2 -$ or $\text{CH}_3 - \text{C} \equiv \text{C} -$
11. Three σ and 2 π bonds
- B. 6. (i) 3-Ethylhexane (ii) 2, 2, 3-Trimethylhexane

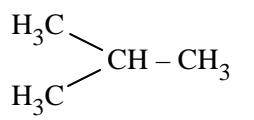
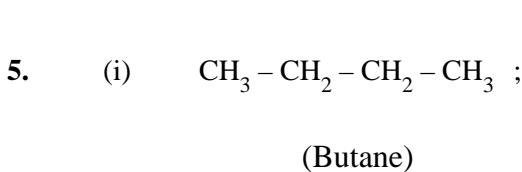
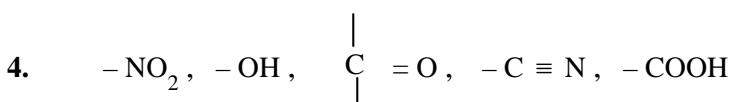
D. MULTIPLE CHOICE

1. (c); 2. (a); 3. (c); 4. (b); 5. (a); 6. (b); 7. (a); 8. (c); 9. (b); 10. (b); 11. (a); 12. (d); 13. (a); 14. (a); 15. (c); 16. (d); 17. (d); 18. (c); 19. (c); 20. (b), 21 (b); 22. (b); 23. (d); 24 (d); 25 (c); 26 (a); 27 (c); 28 (d); 29 (c); 30 (d); 31 (b); 32 (a); 33 (a); 34 (c); 35 (b); 36 (c); 37 (c)

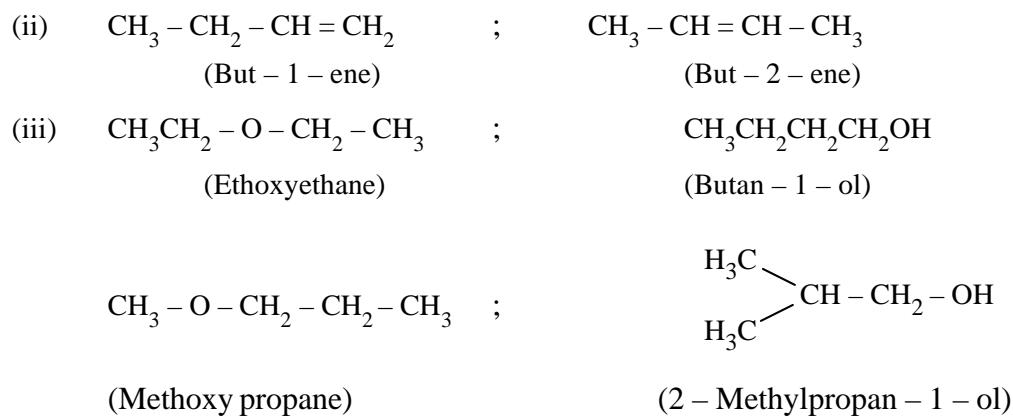
- E. 1. (i) 2-Methylpropanoic acid (ii) Pentan-2-one
 (iii) Ethanoic anhydride (iv) Butanoyl chloride



3. (i) Butan-2-one (ii) 3-Chloropropanoic acid.
 (iii) 4-Ethyl-2-methylhexane.



(2-Methylpropane)



6. (i) 3 – Methylhexane
(ii) 2, 2, 4 – Trimethylpentane
(iii) 4 – Isobutyl – 2, 5 – dimethylheptane
(iv) 6 – Methylhept – 4 – en – 1 – yne.
(v) 4 – Ethyl – 2 – methylheptane
(vi) 3 – Chlorobut – 2 – en – 1 – ol
(vii) 2, 2 – Dimethylpropane
(viii) 2, 2 – Dimethylpent – 2 – ene
(ix) Pent – 2 – yne
(x) 3 – Methylpentane.

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UNIT - XIII

HYDROCARBONS

INTRODUCTION

Hydrocarbons are the simplest organic compounds composed of only carbon and hydrogen. These are widely distributed in nature in form of petroleum, natural gas and coal. Their use in our daily life is not limited to fuels like LPG, CNG and LNG, but the hydrocarbons are extensively used for the manufacture of polymers like polythene, polystyrene, dyes and drugs.

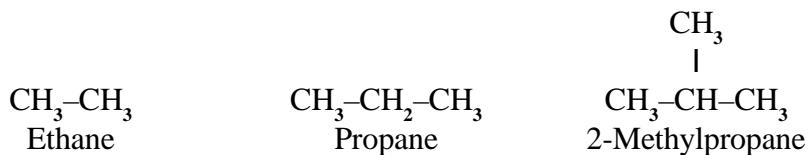
CLASSIFICATION OF HYDROCARBONS

Hydrocarbons can be broadly categorised into two types:

A. Acyclic or open chain or aliphatic hydrocarbons :

These compounds have an open chain of carbon atoms (branched or straight chained) in their molecules which can be further classified into three types depending upon types of carbon-carbon bonds.

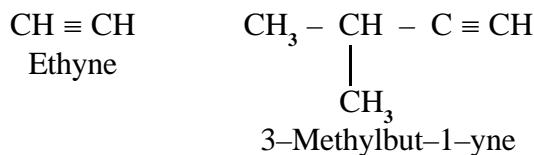
(i) **Alkanes** : Alkanes are the saturated hydrocarbons having only carbon - carbon single bonds. For example,



(ii) **Alkenes** : Alkenes are unsaturated hydrocarbons containing atleast one carbon-carbon double bond.



(iii) **Alkynes** : Alkynes are unsaturated open chain hydrocarbons with atleast one triple bond between two carbon atoms.

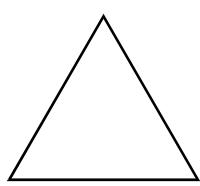


B. Cyclic or closed chain hydrocarbons :

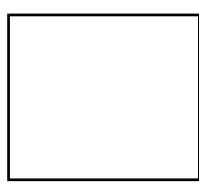
Hydrocarbons containing closed chains or rings of carbon atoms in their molecules are called cyclic hydrocarbons which can be further subdivided into two groups.

(i) Alicyclic hydrocarbons : Cyclic hydrocarbons resembling aliphatic hydrocarbons in their properties are termed as alicyclic hydrocarbons. These are of three types.

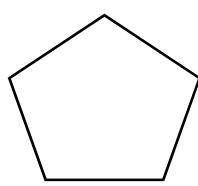
(a) Cycloalkanes : Saturated alicyclic hydrocarbons are called cycloalkanes. For example



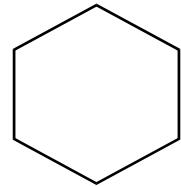
Cyclopropane



Cyclobutane

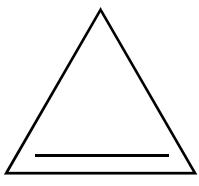


Cyclopentane

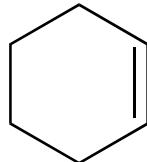


Cyclohexane

(b) Cycloalkenes : Unsaturated alicyclic hydrocarbons atleast one carbon-carbon double bond are termed as cycloalkenes.



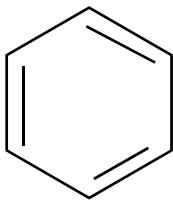
Cyclopropene



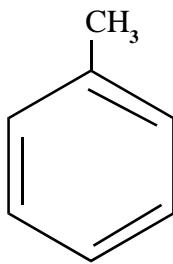
Cyclohexene

(c) Cycloalkyne : Unsaturated alicyclic hydrocarbons containing atleast one carbon-carbon triple bond are called cycloalkynes. However, due to high strain lower members are unstable.

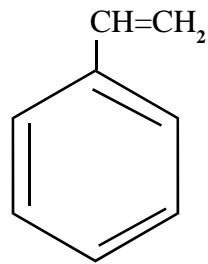
(ii) Aromatic hydrocarbons or Arenes : Hydrocarbons and their alkyl, alkenyl and alkynyl derivatives which contain one or more benzene rings either isolate or fused in their molecules are termed as aromatic hydrocarbons or arenes. For example,



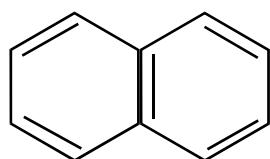
Benzene



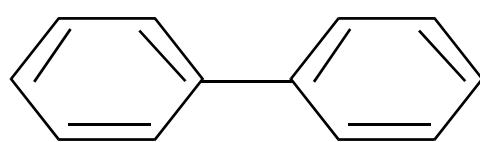
Toluene



Styrene

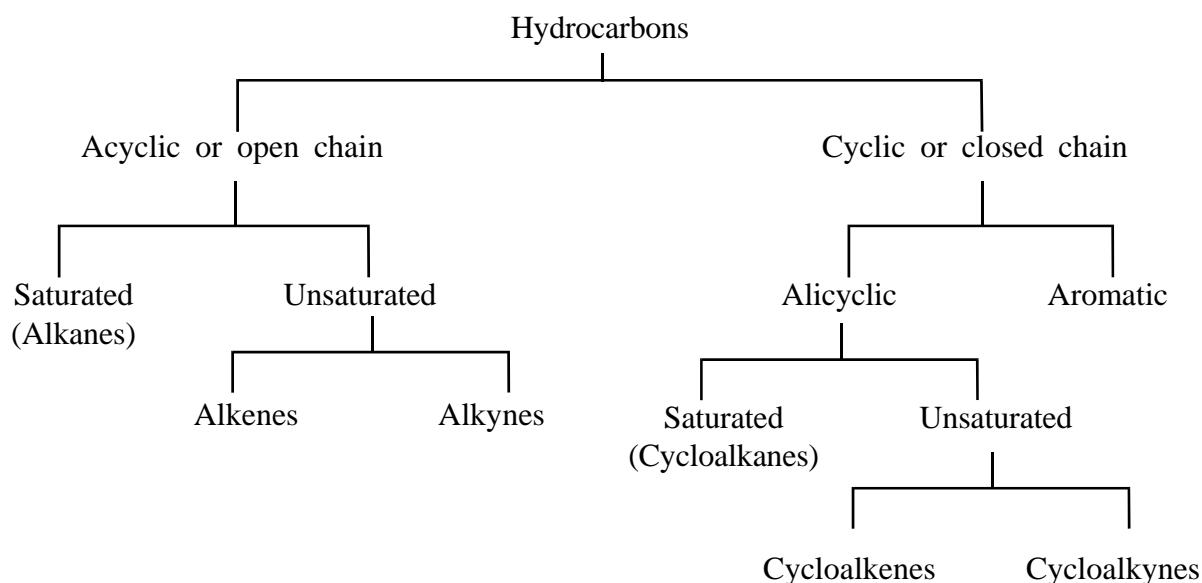


Naphthalene



Diphenyl

The total scheme of classification of hydrocarbons is represented as :



CHAPTER - 17

ALIPHATIC HYDROCARBONS

SATURATED HYDROCARBONS—ALKANES

17.1 SATURATED HYDROCARBONS (PARAFFINS) OR ALKANES

Alkanes are the simplest family of the hydrocarbons. In alkanes, the valencies of carbon atoms are satisfied by single bonds and are almost entirely nonpolar.

The chemistry of the alkane is quite simple. A very few chemicals react with them. This is why they are nicknamed as *paraffins* (Latin : *Parum Affinis* meaning less affinity). They do not contain functional groups.

17.2 GENERAL FORMULA

Alkanes constitute a homologous series of compounds and are represented by the general formula C_nH_{2n+2} , where n is a whole number. In this series one member differs from each adjacent member by one carbon atom and two hydrogen atoms, that is by CH_2 . The simplest member of this family contains only one carbon atom ($n = 1$) and is called **methane**. It has molecular formula CH_4 . The next member ($n = 2$) has the molecular formula C_2H_6 and is called **ethane**. The third member **propane** is C_3H_8 and so on.

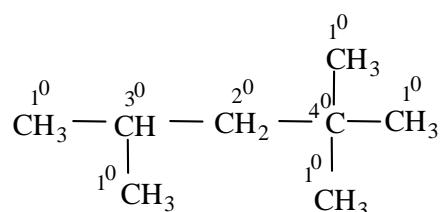
No. of Carbon	C_nH_{2n+2}	Name
$n = 1$	CH_4	Methane
$n = 2$	C_2H_6	Ethane
$n = 3$	C_3H_8	Propane
$n = 4$	C_4H_{10}	Butane
$n = 5$	C_5H_{12}	Pentane
$n = 6$	C_6H_{14}	Hexane and so on

17.3 TYPES OF CARBON ATOM IN ALKANES

The different carbon atoms forming a carbon chain are distinguished as follows.

- (i) A primary (1^0) carbon atom is one which is linked to one or no carbon atom.
 - (ii) A secondary (2^0) carbon atom is one which is linked to two other carbon atom.
 - (iii) A tertiary (3^0) carbon atom is one which is linked to three other carbon atom.
 - (iv) A quaternary (4^0) carbon atom is one which is linked to four carbon atom.

The hydrogen atoms are designated as primary, secondary or tertiary depending upon the carbon atom to which they are attached. Thus a primary carbon atom should contain atleast three hydrogen atoms. The following compounds will illustrate different types of carbon atoms.



The above molecule contains five primary, one secondary, one tertiary and one quaternary carbon atoms.

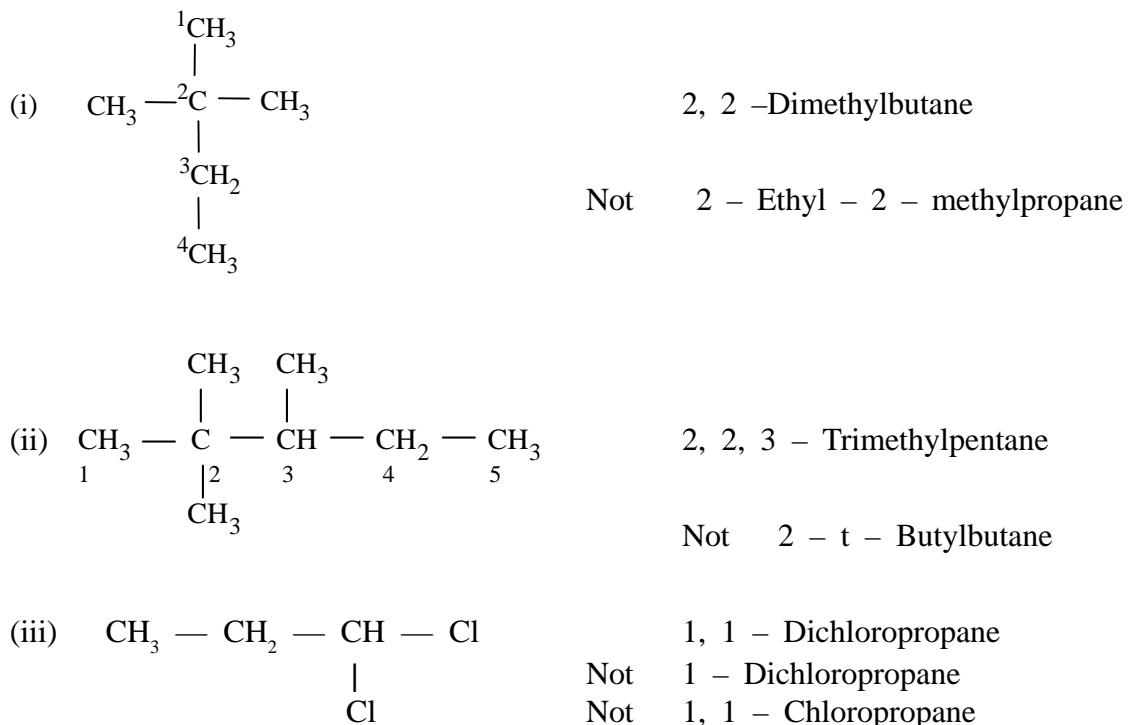
17.4 IUPAC RULES FOR NAMING ALKANES :

The IUPAC rules for the nomenclature of alkanes are as follows.

1. Use the ending –ane for all alkanes.
 2. Select the longest continuous chain of carbon atoms which forms the parent chain.
 3. Attach a prefix to –ane that specifies the number of carbon atoms in the parent chain.
 4. Number the parent chain from an end such that the carbon atom carrying the substituents gets the lowest numeral. The positions of the substituents are indicated by the locants. (The number of carbon atom, locating the position of the substituents in called LOCANT).
 5. If several substituents are present, arrange them alphabetically.

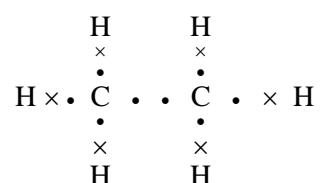
6. Prefix the substituent preceded by the locant to the name of parent hydrocarbon. Two, three and four identical substituents are specified as di-, tri- and tetra- respectively.
7. Separate the locant from the name of the substituent by a hyphen (-). The name of the alkane is written as one word with the name of the substituent and its numeral serving as prefix.

Example :

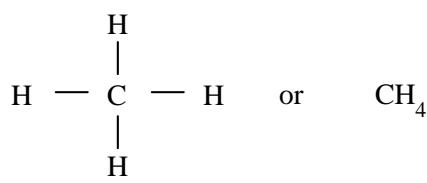


17.5 STRUCTURE OF ALKANES

In alkanes, the carbon atom is always tetravalent and the four valencies are directed towards the four corners of a tetrahedron. The tetrahedral carbon atoms are sp^3 hybridised and form strong σ (sigma) bonds with hydrogens and among themselves.

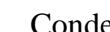


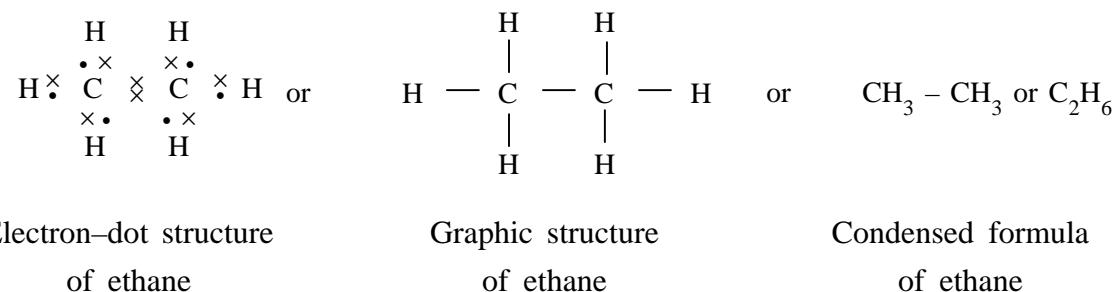
Electron-dot structure
of methane



Graphic structure
of methane

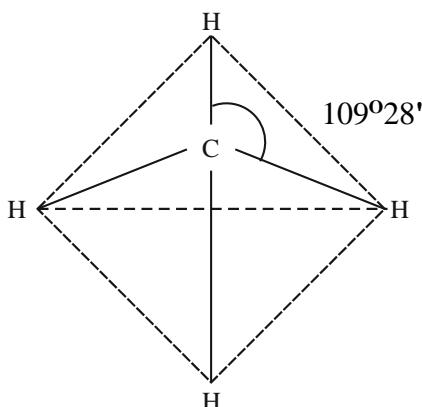
Condensed formula
of methane





Higher members are obtained by replacing hydrogen atoms by carbon atoms.

The covalent bonds are denoted by small line (—) and it must be remembered that each carbon atom must be connected with four such covalent bonds. Thus, methane and ethane can be structurally represented as above. The C – H sigma (σ) bond is formed by the overlapping of sp^3 hybridised orbital of carbon with s – orbital of hydrogen and has the bond length 1.09 \AA^0 . The C – C sigma (σ) bond is formed by the overlapping of sp^3 hybridised orbital of one carbon atom on sp^3 hybridised orbital of another carbon atom and has the bond length 1.54\AA^0 . Thus alkanes have tetrahedral structures with bond angle $109^\circ 28'$.



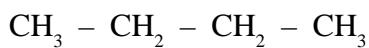
Tetrahedral structure of methane

17.6 ISOMERISM IN ALKANES

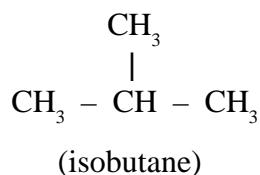
Chain isomerism is exhibited by the alkanes.

Chain isomerism is due to the difference in the structure of the carbon chain. Except the first three members – methane, ethane and propane, other alkanes exhibit this chain isomerism.

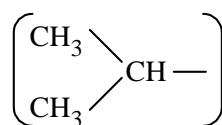
For butane (C_4H_{10}) two possible isomers are



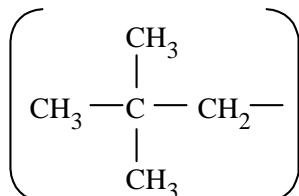
n – Butane



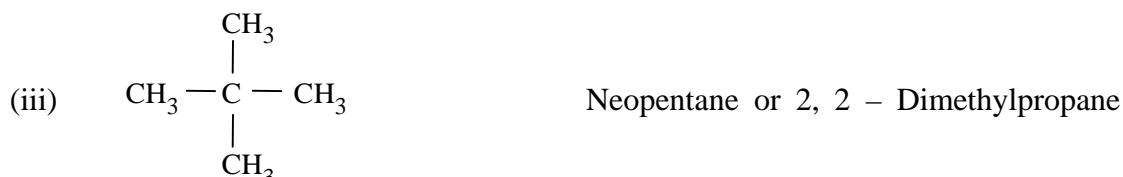
The straight chain paraffins are known as **normal** and usually abbreviated as **n**. The prefix **iso** – is used for branched chain hydrocarbon with two methyl groups at the end

of a straight chain  . The prefix **neo** – is used to denote the hydrocarbon

which contains three methyl groups on the end carbon (quaternary carbon atom) e.g.



. For pentane (C_5H_{12}), three possible isomers are



All higher hydrocarbons show similar chain isomerism and the number of isomers goes on increasing with the increase in the number of carbon atoms. The following table gives the number of isomers for hydrocarbons having different number of carbon atoms.

No. of C-atoms in the Hydrocarbon	4	5	6	7	8	9	10	12	15	20
No. of Isomers possible	2	3	5	9	18	35	75	355	4347	3,66,319

17.7 OCCURRENCE

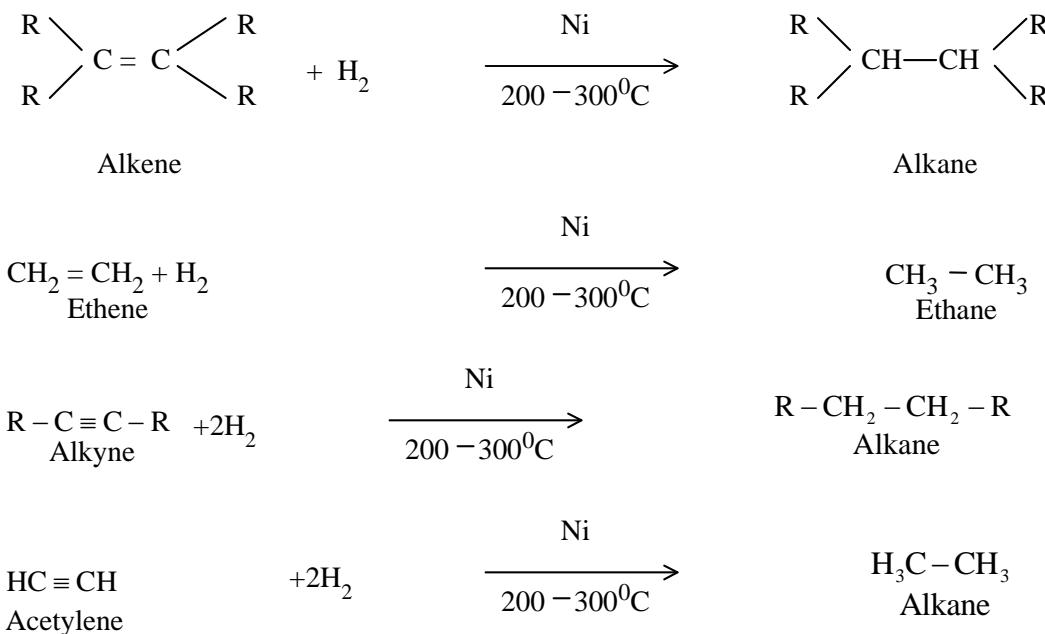
Alkanes are highly widespread in nature. Crude petroleum is a mixture of mostly unlimited quantities of liquid alkanes and higher solid hydrocarbons. Most of the alkanes with lower molecular mass are obtained by the fractional distillation of petroleum and natural gas. Methane, the first member of alkane, is also called **marsh gas** because it is found in marshy places where it is produced by the bacterial decomposition of dead vegetable matter.

17.8 METHODS OF PREPARATION

The alkanes can be prepared by the following general methods.

1. Hydrogenation of alkenes and alkynes

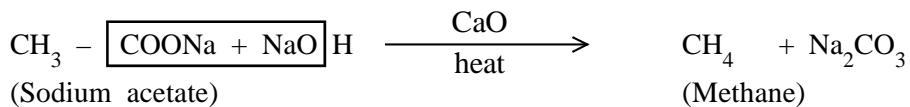
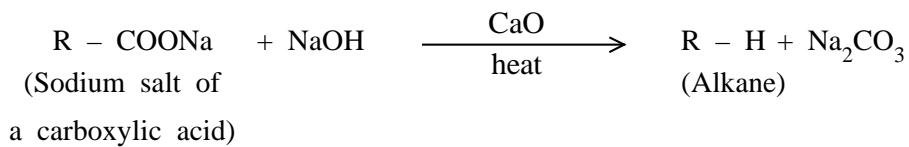
Alkanes are formed by passing a mixture of unsaturated hydrocarbon (alkene or alkyne) and hydrogen over finely divided nickel at $200 - 300^{\circ}\text{C}$. This reaction is known as **Sabatier Senderens reaction**.



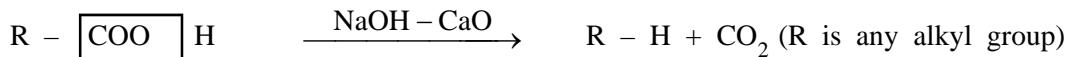
When finely divided Platinum, Palladium or Raney nickel is used as catalyst the above reaction can be carried out at room temperature. Methane can not be prepared by this method. (*why ?*)

2. Decarboxylation of Carboxylic acids

When anhydrous sodium salt of a carboxylic acid is heated strongly with dry sodalime ($\text{NaOH} + \text{CaO}$), an alkane is formed.



The process of elimination of carbon dioxide from a carboxylic acid is known as **decarboxylation**.



The hydrocarbon obtained by this method contains one carbon atom less than the acid from which it is obtained.

Laboratory Method of Preparation of Methane :

In the laboratory methane is prepared by the decarboxylation of sodium acetate with sodalime.

Powdered anhydrous sodium acetate is mixed with two times its mass of dry sodalime. The mixture is heated in a hard glass tube fitted with a delivery tube. The apparatus is arranged as shown in the Fig.17.1 Methane is collected by the downward displacement of water.

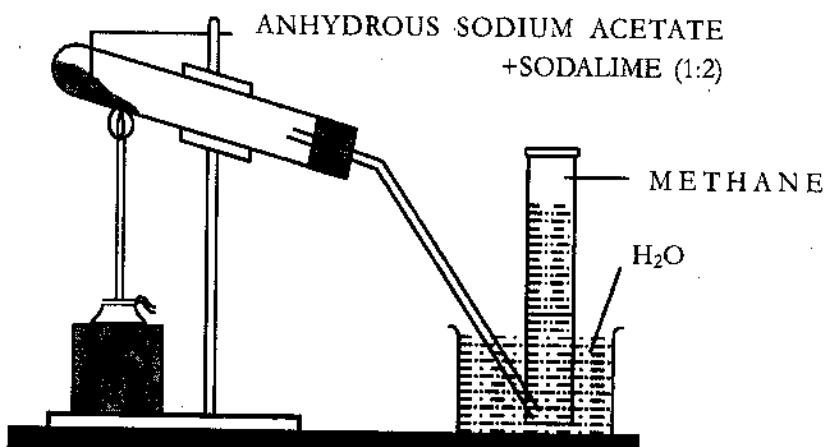
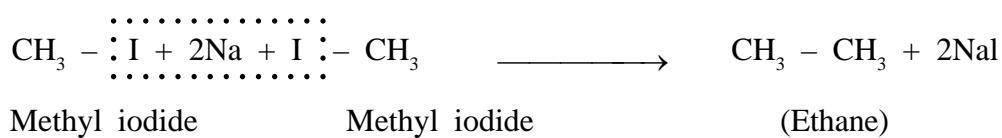


Fig. 17.1 Preparation of methane

3. Wurtz Reaction

When an alkyl halide (mostly) iodide or bromide) is heated with metallic sodium in dry ethereal solution, a higher symmetrical alkane is formed. This reaction is known as **Wurtz reaction**. Two molecules of alkyl halide react with two atoms of sodium forming a hydrocarbon containing double the number of carbon atoms present in the alkyl halide.

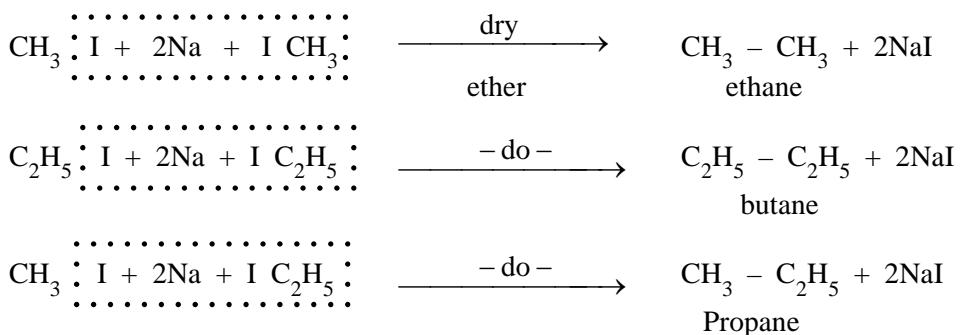


Methane cannot be prepared by this method (*why?*)

Wurtz synthesis is important, because it is used in the preparation of higher hydrocarbon from lower hydrocarbon e.g. methane to ethane. It is not a suitable method for preparing alkanes with odd number of carbon atoms.

When a mixture of two different alkyl halides is taken, a mixture of alkanes is obtained.

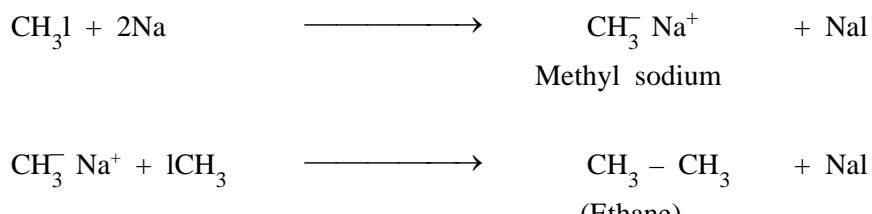
e.g. a mixture of CH_3l and $\text{C}_2\text{H}_5\text{l}$ produces C_2H_6 , C_4H_{10} and C_3H_8



Mechanism : Two mechanisms have been suggested for the Wurtz reaction. Let us start with CH_3I in preparing $\text{CH}_3 - \text{CH}_3$ while explaining this mechanism.

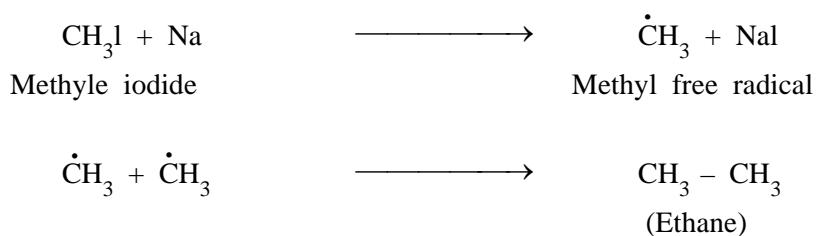
(i) Ionic Mechanism :

According to this mechanism two atoms of sodium react with methyl iodide molecule to produce methyl sodium and sodium iodide. Methyl sodium then reacts with second molecule of methyl iodide to form ethane and sodium iodide.



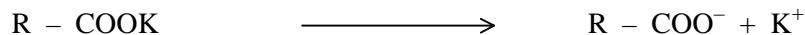
(ii) Free radical Mechanism :

According to this mechanism sodium atom attacks methyl iodide to produce methyl free radical and sodium iodide. Two methyl free radicals then combine to give ethane.

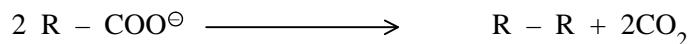


4. Kolbe's synthesis :

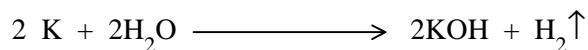
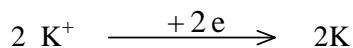
This is also known as **Kolbe's electrolytic method**. When concentrated solution of sodium or potassium salt of a fatty acid is electrolysed, alkane is obtained at the anode and hydrogen gas is liberated at the cathode.



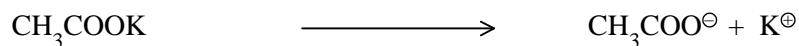
At the Anode :



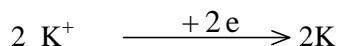
At the Cathode :



For example, a solution of potassium acetate on electrolysis gives ethane at anode and hydrogen at cathode.



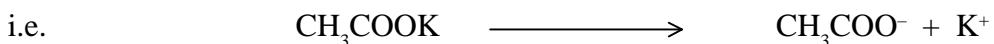
At the Cathode :



Methane can not be prepared by this method.

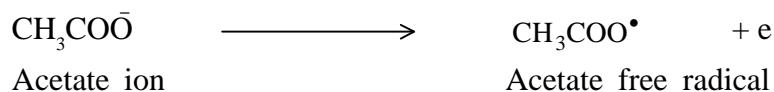
Mechanism :

Several mechanisms have been proposed for the Kolbe's reaction. Out of them free radical mechanism is the most favoured one.

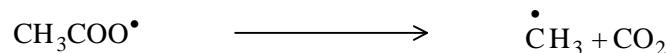


At the Anode :

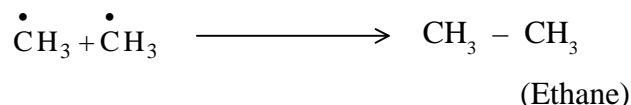
The acetate ion is discharged at the anode to form a free radical.



The acetate free radical then breaks up into the methyl free radical and carbon dioxide.

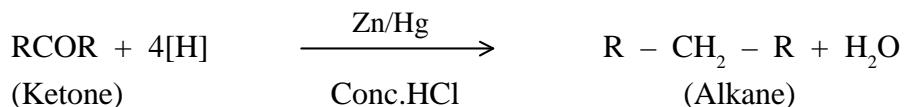
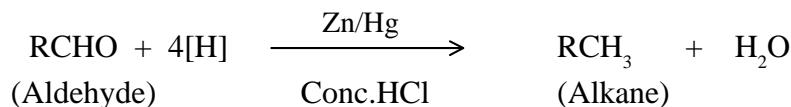


Then two such methyl radicals combine to form a molecule of ethane.



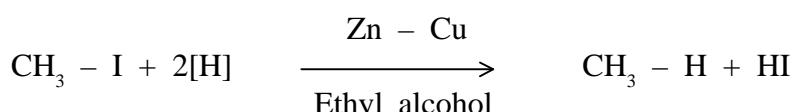
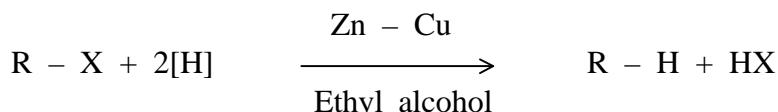
5. Clemmensen's reduction :

Aldehydes and ketones are reduced to alkanes by zinc amalgam and concentrated hydrochloric acid. (Clemmensen's reagent)



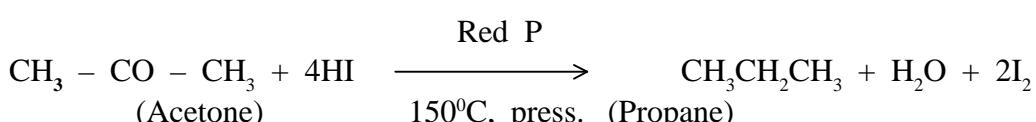
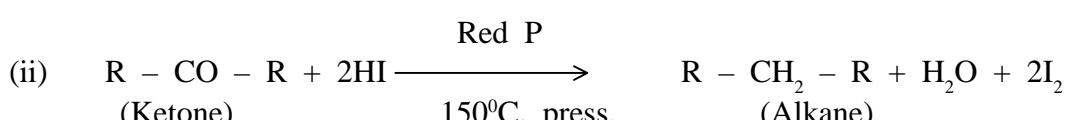
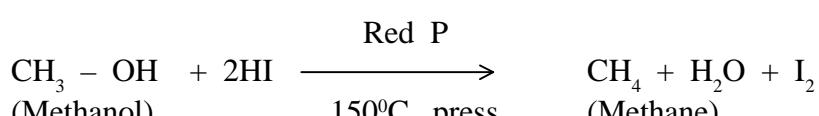
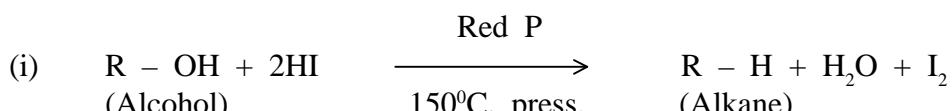
6. Reduction of Alkyl halides :

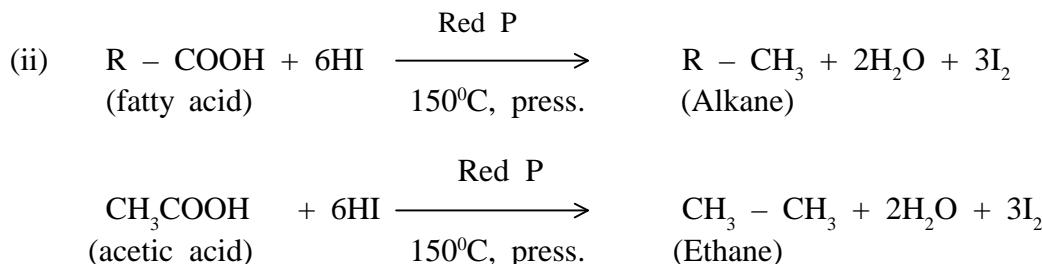
Reduction of alkyl halides by Zn - Cu couple and ethyl alcohol results in the formation of alkanes.



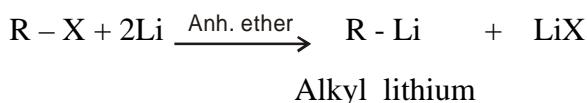
7. Reduction of alcohols, ketones and fatty acids :

Alcohols, ketones and fatty acids when heated with concentrated hydriodic acid in presence of red phosphorus at 150°C under pressure yield alkanes.

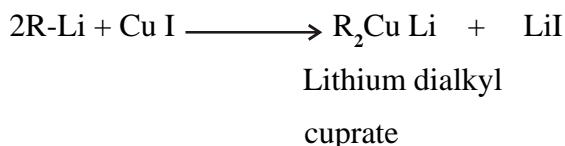




8. Corey - House synthesis - This reaction is very useful for the preparation of unsymmetrical alkanes and higher members of the alkane family. This reaction occurs in two steps. In the first step, the alkyl halide $R - X$ is treated with lithium metal and solvated in anhydrous ether to form alkyl lithium compound, $R-Li$. The starting $R - X$ can be primary, secondary or tert. alkyl halide.



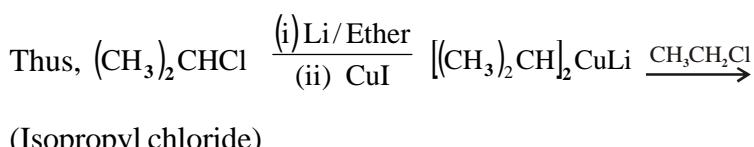
The second step requires the alkyl lithium compound to be treated with cuprous iodide forming lithium dialkyl cuprate compound (known as *Gilman reagent*).



This in turn reacts with the second alkyl halide which couples to the compound.

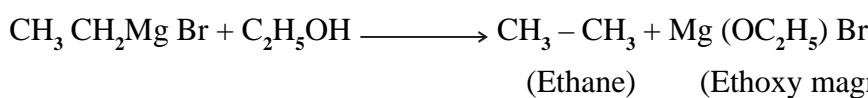
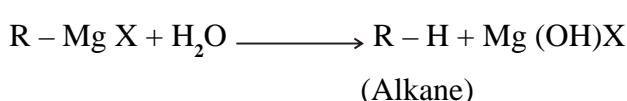


(R and R' groups may be same or different)



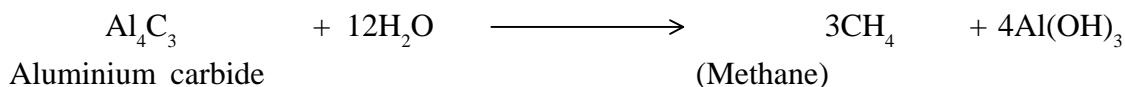
9 Hydrolysis of Grignard Reagent

Alkyl magnesium halides are known as Grignard reagents. When an alkyl magnesium halide in ethereal solution is treated with compounds containing active hydrogen such as water, alcohol, amine etc., an alkane is formed.

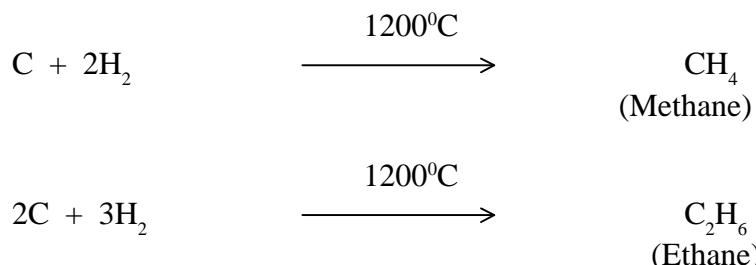


10. Other methods of preparation of methane :

- (a) Methane can be prepared by the action of water on aluminium carbide.



- (b) Lower alkanes, i.e. methane and ethane can be prepared by the direct combination of carbon and hydrogen in an electric arc.

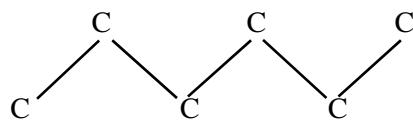


17.9. GENERAL PROPERTIES

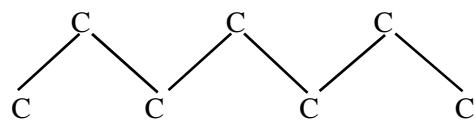
PHYSICAL PROPERTIES :

- (1) **State** – The first four alkanes (i.e. methane, ethane, propane and butane) are colourless gases with petrol like smell, the next thirteen ($C_5 - C_{17}$) are colourless liquids and higher alkanes (C_{18} onward) are colourless solids.
 - (2) **Solubility** – In hydrocarbon both the carbon-carbon and carbon-hydrogen bonds are non-polar, so the hydrocarbon molecules are non-polar in nature and are insoluble in water, whereas they dissolve in non-polar solvents like benzene, carbon tetrachloride etc. Their solubility decreases with the increase in their molecular mass.
 - (3) **Density** – The density of normal alkanes steadily rises for lower members with the increasing chain length, but it reaches a limiting value of about 0.79 with n - hexadecane. Thus alkanes are always lighter than water.
 - (4) **Boiling points** – The boiling point rises regularly as the number of carbon atom in the alkane increases. But branched chain isomers have lower boiling points than the straight chain isomers, which is due to decrease in their surface area.
 - (5) **Melting points** – Unlike boiling point, the melting point of alkanes does not increase regularly with the increase in chain length. The increase in melting point is relatively more in moving from an alkane having odd number of carbon atoms to the next higher alkane, than in moving from an alkane having even number of carbon atoms to the next higher alkanes.

This is because the intermolecular forces in a crystal depend not only on the size of the molecule, but also on how they are packed into crystal. Alkanes having even number carbon atoms have their end carbon atoms on opposite sides, and alkanes having odd number carbon atoms have their end carbon atoms on the same side of the molecule.

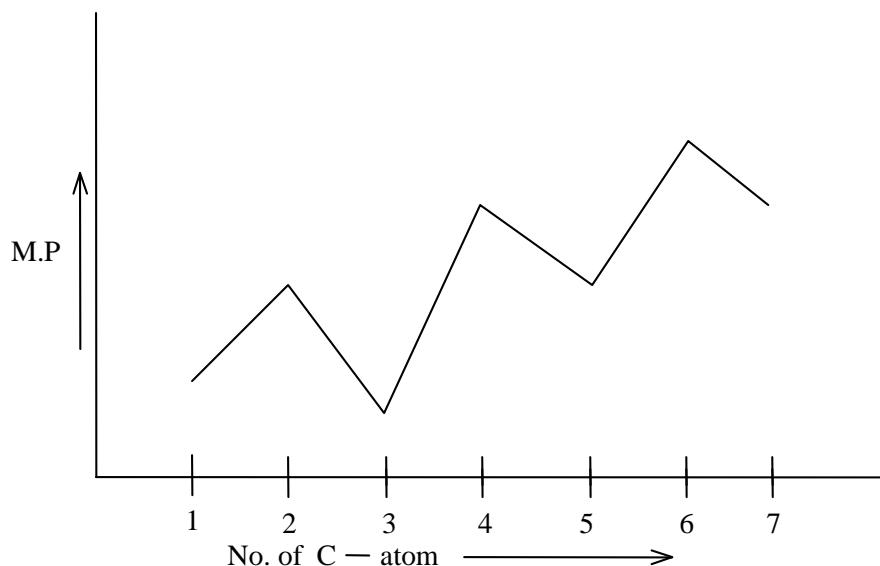


(Even numbered carbon chain)



(Odd numbered carbon chain)

Probably, alkanes with even number of C – atoms fit-well into the crystal lattice, so as to permit greater intermolecular attraction. Therefore, the increase in the melting point with increase in chain length is not uniform.



Physical properties of the alkanes are given in the following table 17.1 and 17.2.

TABLE – 17.1
Physical Properties of the alkanes

No.	IUPAC Name	Structure	Boiling Point °C	Melting Point °C	Density g/ml at 20°C	Heat of Combustion KCal/mole
1.	Methane	CH ₄	– 162	– 183	0.424	210.8
2.	Ethane	CH ₃ CH ₃	– 88	– 172	0.546	368.4
3.	Propane	CH ₃ CH ₂ CH ₃	– 42	– 188	0.501	526.3
4.	Butane	CH ₃ (CH ₂) ₂ CH ₃	0	– 135	0.579	684.0
5.	Pentane	CH ₃ (CH ₂) ₃ CH ₃	^S 36	– 130	0.626	838.3
6.	Hexane	CH ₃ (CH ₂) ₄ CH ₃	69	– 95	0.659	989.3
7.	Heptane	CH ₃ (CH ₂) ₅ CH ₃	98	– 91	0.684	1149.9
8.	Octane	CH ₃ (CH ₂) ₆ CH ₃	126	– 57	0.703	1302.7
9.	Nonane	CH ₃ (CH ₂) ₇ CH ₃	151	– 54	0.718	1463.8
10.	Decane	CH ₃ (CH ₂) ₈ CH ₃	174	– 30	0.730	1610.2
11.	Undecane	CH ₃ (CH ₂) ₉ CH ₃	196	– 26	0.740	1776.3
12.	Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	216	– 10	0.749	1932.6

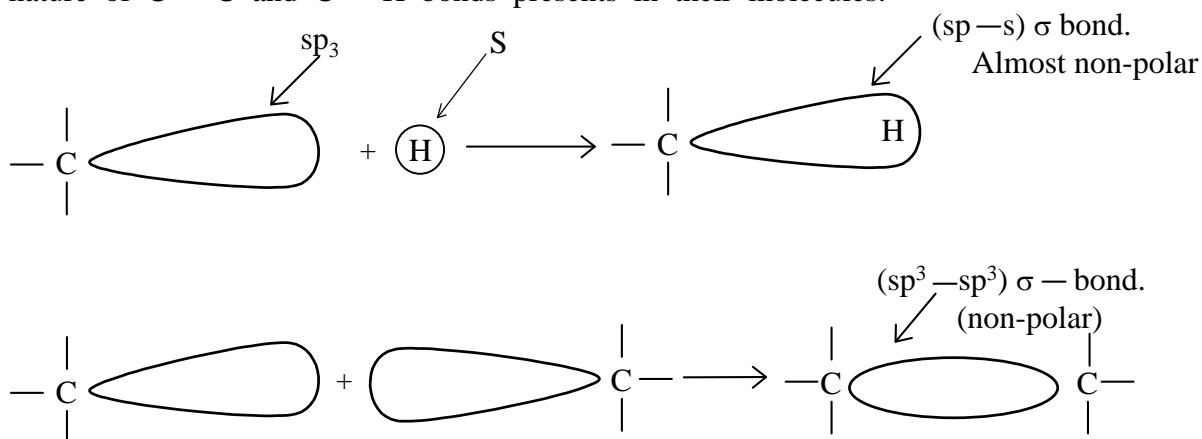
TABLE – 17.2
Physical Properties of hexane isomers.

Isomer	Structure	BP °C	M.P. °C	Density at 20°C
n – Hexane	CH ₃ (CH ₂) ₄ CH ₃	68.7	– 94	0.659
3 – Methylpentane	$\begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ & & \text{CH}_3 & \text{CH}_2 & \text{CHCH}_2 & - & \text{CH}_3 \end{array}$	63.3	– 118	0.664
2 – Methylpentane	$\begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ & & \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CHCH}_3 & \\ & & & & & & \\ & & \text{CH}_3 & & & & \end{array}$	60.3	– 154	0.653
2,3 – Dimethylbutane	$\begin{array}{ccccccc} & \text{CH}_3 & & \text{CH}_3 & & & \\ & & & & & & \\ \text{CH}_3 & - & \text{CH} & - & \text{CH} & - & \text{CH}_3 \end{array}$	58.0	– 129	0.661
2,2 – Dimethylbutane	$\begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & & & & & \\ & & \text{CH}_3 & - & \text{CH}_2 & - & \text{C} & - & \text{CH}_3 \\ & & & & & & & & \\ & & \text{CH}_3 & & & \text{CH}_3 & & & \end{array}$	49.7	– 98	0.649

CHEMICAL PROPERTIES

Alkanes are relatively stable to most of the common reagents at room temperature. They do not react with acids like hydrochloric acid and sulphuric acid, bases like sodium hydroxide or potassium hydroxide, oxidising agents like potassium permanganate or sodium dichromate, reducing agents like stannous chloride and lithium-aluminium hydride and active metals like sodium or potassium.

The relative stability or inactivity of alkanes may be explained by considering the nature of C – C and C – H bonds present in their molecules.



Since the electronegativities of carbon (2.60) and of hydrogen (2.1) do not differ appreciably, the bond electrons in C – H are equally shared between them. Thus C – H bonds in alkanes are almost non-polar and the same is true for C – C bonds. Hence polar and ionic reagents (acids, alkalis etc.) find no reaction sites on alkane molecules to which they can be attracted.

Alkanes mainly undergo two types of reactions :

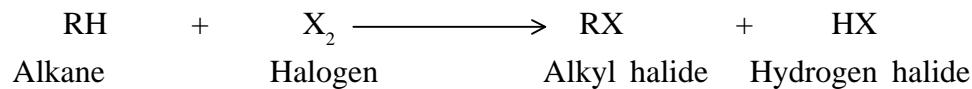
- (A) Substitution reactions
- (B) Thermal and catalytic reactions.
- (A) **Substitution Reactions :**

In substitution reaction, an atom or a group present in a compound is replaced by another without the compound undergoing any change in its structure. The products thus obtained are called substitution products. In the substitution reactions of alkanes the direct replacement of one or more hydrogen atom by halogen atoms or other monovalent groups takes place.

1. Halogenation :

In general, when an alkane, RH reacts with a halogen molecule X_2 , a hydrogen atom of the alkane is replaced by one of the halogen atoms, fluorination)

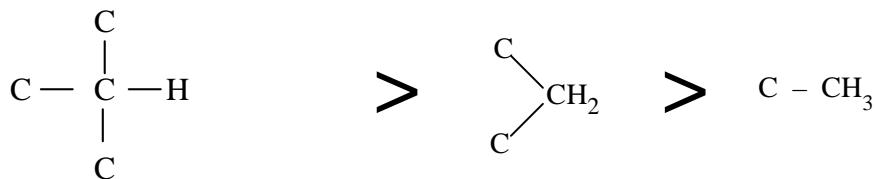
or chlorine (chlorination) or bromine (bromination) or iodine (iodination). The products of this reaction are alkyl halide and hydrogen halide and the reaction by which they are produced is called **halogenation**.



The order of reactivity of halogens is :



The ease of substitution in an alkane is in the following order :

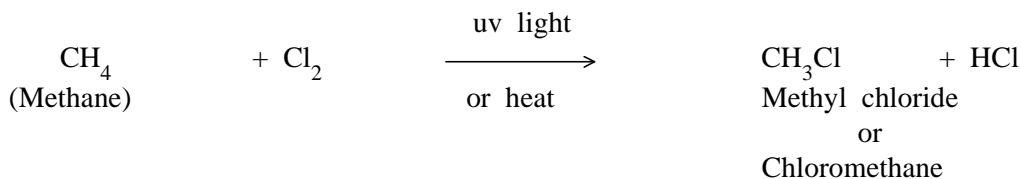


i.e. Tertiary > Secondary > Primary

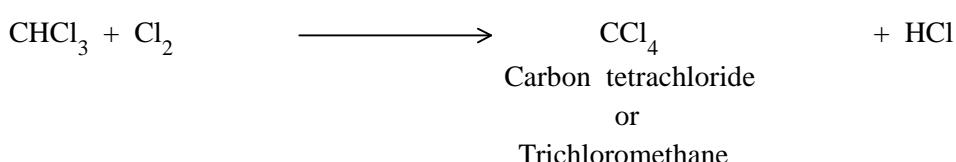
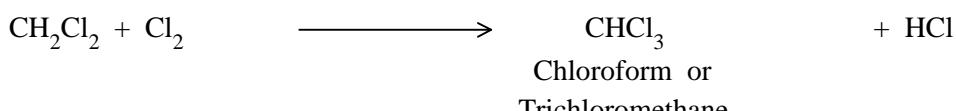
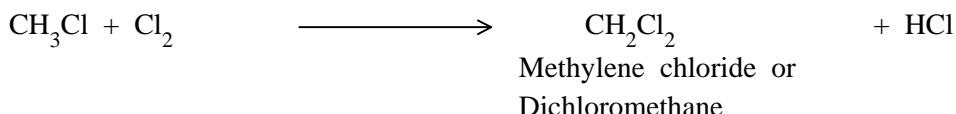
(a) *Chlorination* :

Chlorination may be brought about by light, heat or catalyst and the extent of chlorination depends largely on the amount of chlorine used.

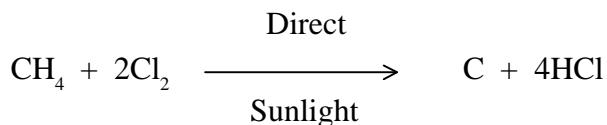
For example, methane reacts with chlorine in the presence of ultraviolet light or at high temperature (300°C) to yield methyl chloride or chloromethane and hydrogen chloride.



The reaction does not stop at this stage and the remaining H – atoms of $\text{CH}_3 - \text{Cl}$ are successively replaced by chlorine atoms.



In the presence of direct sunlight, methane reacts with chlorine with explosion producing carbon.

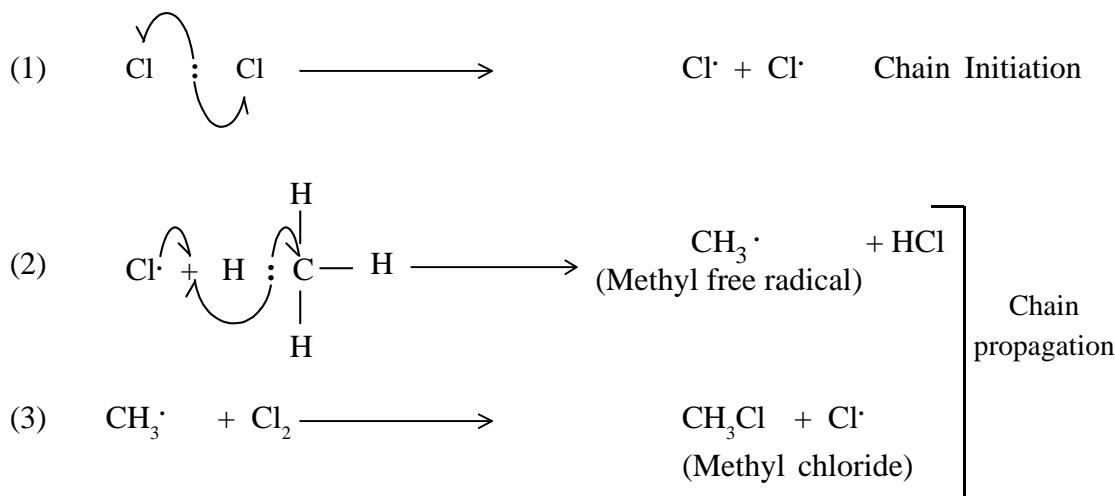


Mechanism of chlorination :

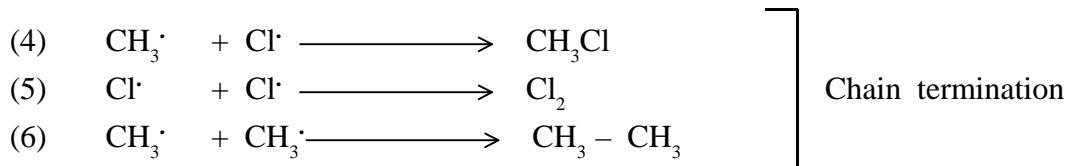
The chlorination of alkanes takes place through the formation of free radicals as intermediates.

An important feature of the mechanism is that the chlorine atom consumed in the first step is replaced by another chlorine atom in the second step. This type of process is called a **chain reaction**.

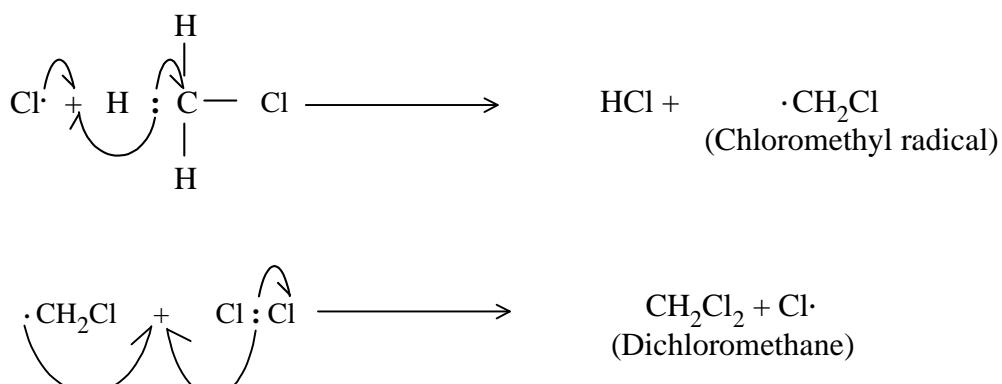
Thus, for the chlorination of methane the following steps have been proposed.



The propagation steps 2 and 3 occur in competition with chain termination steps 4, 5 and 6



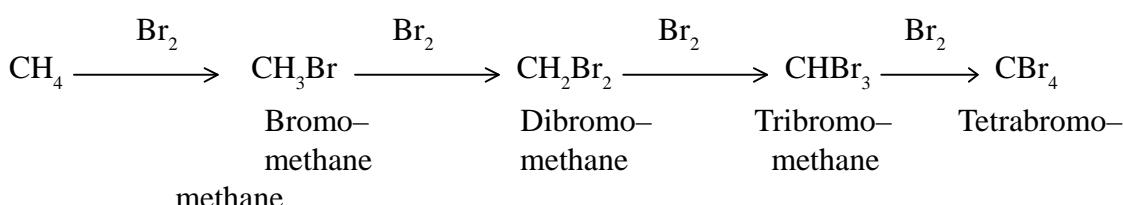
When the concentration of CH_3Cl produced as a result of chain propagation steps increases sufficiently, then it can combine with a chlorine free radical to produce chloromethyl radical and HCl . This radical participates further in chain reaction to form dichloromethane and chlorine free radical which can continue the chain by reacting with another molecule of CH_3Cl



Similarly, trichloromethane and tetrachloromethane are obtained by further chain reactions.

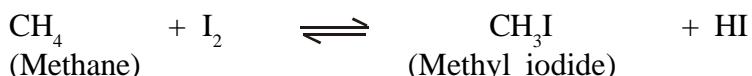
(b) *Bromination* :

Bromination is similar to chlorination, but it is slower. The substitution products obtained are exactly similar. The reaction with methane is given below.

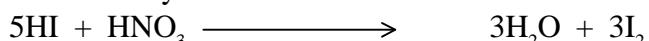


(c) *Iodination* :

Iodine reacts with alkanes reversibly and slowly. The HI formed is a powerful reducing agent and is capable of reducing alkyl iodides to alkanes.



However, alkanes can be iodinated in presence of an oxidising agent such as iodic acid (HIO_3) or nitric acid which destroys HI as it is formed.

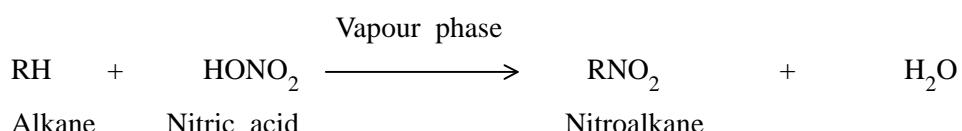


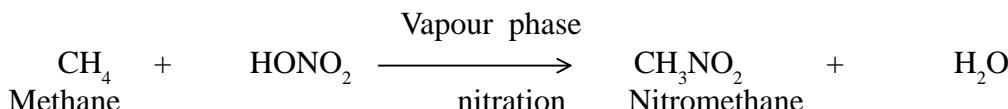
(d) *Fluorination* :

Fluorine is the most reactive of the halogens towards alkanes. Pure fluorine reacts with alkanes explosively under most conditions. Fluorination in alkanes can take place by the action of fluorine diluted with nitrogen.

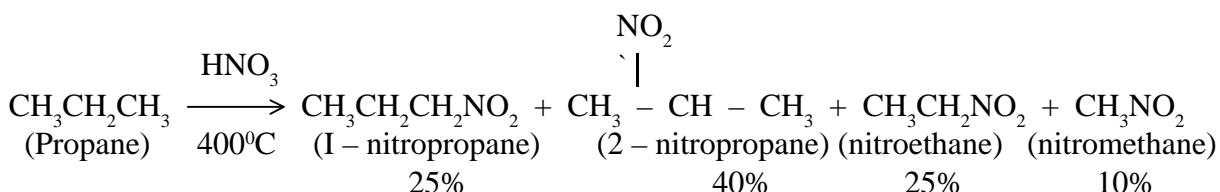
2. Nitration :

Alkanes do not react with nitric acid at ordinary temperature. Under certain conditions, alkanes react with nitric acid forming nitroalkanes. This process is known as **nitration**. Nitration of lower alkanes is carried out in the vapour phase at elevated temperature ($150 - 475^{\circ}\text{C}$)





Higher hydrocarbons can be nitrated in liquid phase and form a mixture of mononitroalkanes, which consists of every possibility of chain fission of alkanes. For example, propane gives a mixture of 1-nitropropane, 2-nitropropane, nitroethane and nitromethane.

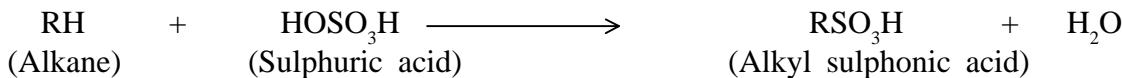


The amount of 1-nitro and 2-nitropropanes indicates that $2^0\text{H} > 1^0\text{H}$ in reactivity.

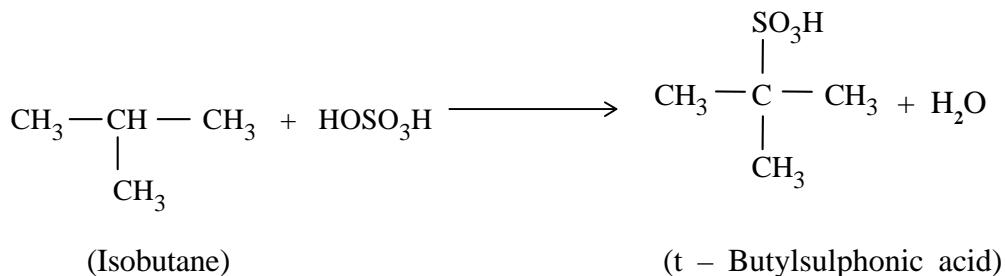
3. Sulphonation :

It is the process of replacing a hydrogen atom by a sulphonic acid group – SO_3H .

Sulphonation of normal alkanes from hexane onwards may be carried out by treating the alkanes with fuming sulphuric acid $\text{H}_2\text{S}_2\text{O}_7$ (i.e. $\text{H}_2\text{SO}_4 + \text{SO}_3$). Lower hydrocarbons are not sulphonated.



Replacement of tertiary hydrogen atom easily takes place by sulphonic acid group.
For example,



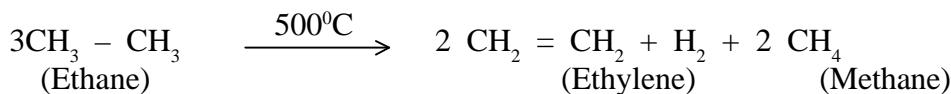
B. Thermal and catalytic reaction :

(1) Thermal decomposition, pyrolysis or cracking :

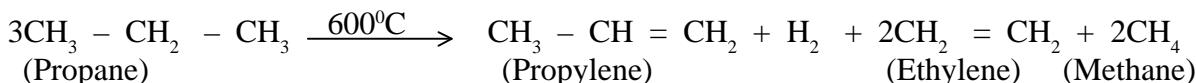
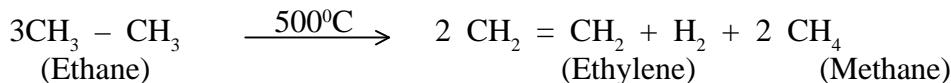
Thermal decompositon of alkanes to produce lower hydrocarbons (saturated or unsaturated) is known as **pyrolysis** or **cracking**. When alkanes are heated at high temperature in the **absence of air**, cracking occurs.



- (i) Ethane when passed through a hot metal tube (500°C) in the absence of air, it breaks to yield a mixture of methane, ethylene and hydrogen.

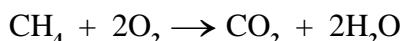


- (ii) Cracking of propane at 600°C , gives a mixture of ethylene, methane and hydrogen.



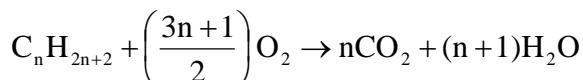
When cracking is carried out in the presence of a catalyst (finely divided silica-alumina), the process is called **catalytic cracking**.

(2) Oxidation : (a) Combustion : The process in which alkanes readily burn on heating in the presence of air or oxygen producing CO_2 and H_2O is called combustion.



Since this is an exothermic reaction, alkanes which are the constituents of LPG, Diesel, Kerosine oil are widely used as fuels.

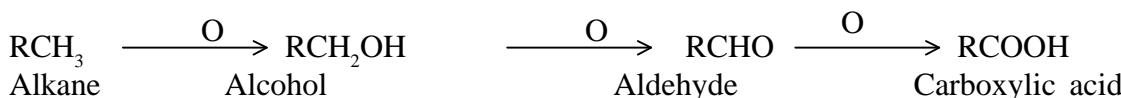
General combustion reaction can be expressed as



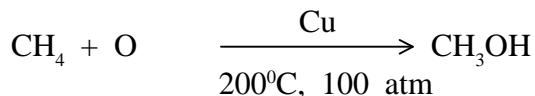
During incomplete combustion of alkanes with limited supply of air or oxygen, CO is produced along with unburnt carbon in the form of carbon black or soot which is used in the manufacture of ink, paints and polishes.



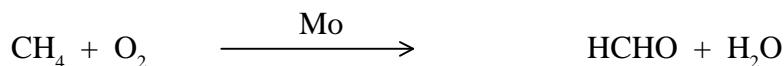
- (a) *Catalytic oxidation* : Controlled oxidation of alkanes gives different products depending upon the conditions. The reaction takes place with oxygen at high pressure in presence of a catalyst.



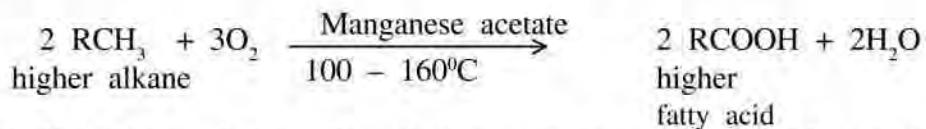
- (i) When a mixture of methane and oxygen in the ratio 9 : 1 is passed through a copper tube at 200°C and 100 atmospheric pressure, methyl alcohol is formed.



- (ii) When methane mixed with oxygen is passed over molybdenum, it is oxidised to formaldehyde.

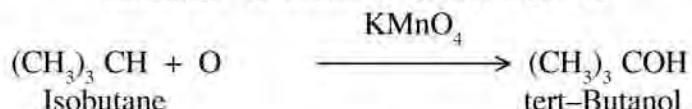


(iii) Higher alkanes are catalytically oxidised to higher fatty acids.



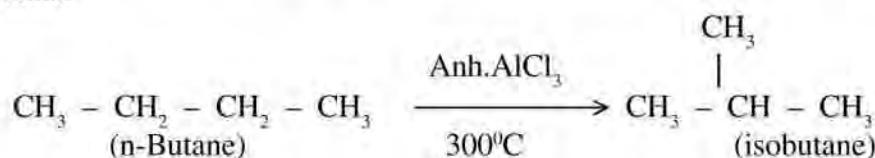
(b) *Chemical oxidation* : Potassium permanganate readily oxidises tertiary hydrogen atom to a hydroxyl group.

e.g. Isobutane is oxidised to tert-butanol.

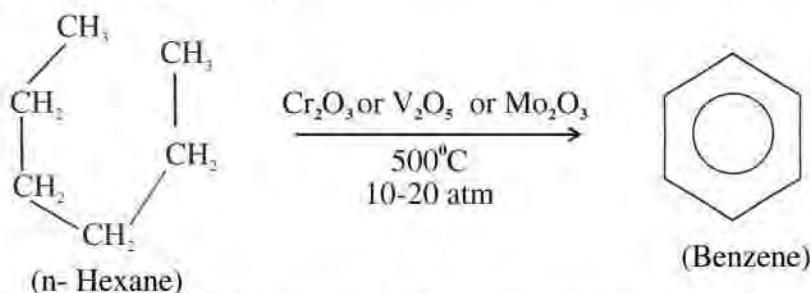


(3) Isomerisation :

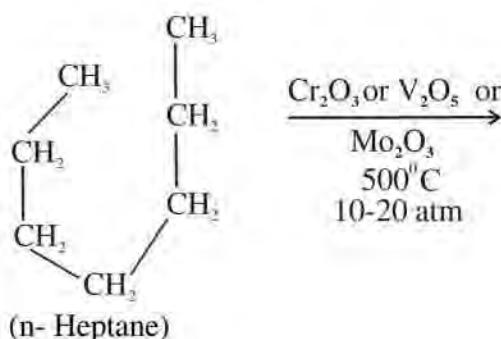
Isomerisation means conversion of one isomer into another isomer in the presence of some catalyst. When n-butane is heated with anhydrous AlCl_3 it is converted into isobutane.



(4) **Aromatisation** : n-Alkanes having six or more carbon atoms on heating to 500°C at 10-20 atmospheric pressure in presence of oxides of V, Mo or Cr supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as **aromatisation or reforming**.



Toluene, the methyl derivative of benzene can be prepared from n-heptane under similar conditions.



CONFORMATION OF ALKANES

Alkanes contain carbon-carbon sigma (σ) bonds. The electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C – C bond. Thus, ethane which contains such a C - C sigma bond maintains a full degree of overlap while its two ends rotate. Hence the energetic barrier to rotation about sigma bond is generally very low. The different spatial arrangements formed by rotation about a single bond are called *conformations or conformers or rotamers*.

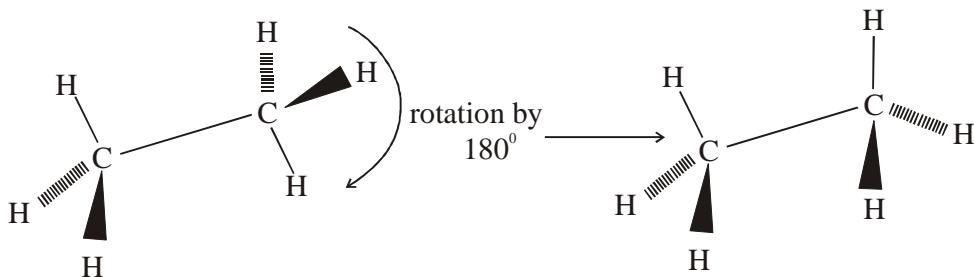


Fig. : 17.2 Free rotation about C – C bond in ethane

Visualising Conformation : Several methods are available for visualising conformation. One of these methods uses wedges to denote bonds that are extending out from the plane of the page towards the reader and dashes to indicate bonds that are going into the plane of the page away from the reader. This notation is generally used to represent the tetrahedral geometry of sp^3 hybridised carbon.

Conformations of Ethane

Ethane molecule (C_2H_6) contains C – C single bond and each carbon atom is attached to three hydrogen atoms. Keeping one carbon atom stationary, one can rotate the other carbon atom around the C – C axis. This rotation results in infinite number of spatial arrangements of hydrogen atoms attached to one C-atom with respect to hydrogen atoms attached to the other C-atom. These are called **conformational isomers** or **conformers** or **rotamers**. Out of several conformers there are two extreme cases. One in which the H-atoms attached to two C-atoms are as close as possible is called **eclipsed conformation** and the other in which such H-atoms are as far apart as possible is called **staggered conformation**. Any other intermediate conformation is called a **skew conformation**. Eclipsed and staggered conformations can be represented by **Sawhorse** and **Newman** projections.

1. Sawhorse Projection

Here, the molecule is viewed along the molecular axis. On the paper, it is projected by drawing the central C – C bond as a long straight line diagonally from upper right side to lower left side. The upper end is the rear C and the lower end is the front C-atom. The lines are inclined at an angle of 120° to each other. Eclipsed and staggered conformation are shown below (fig17.3)

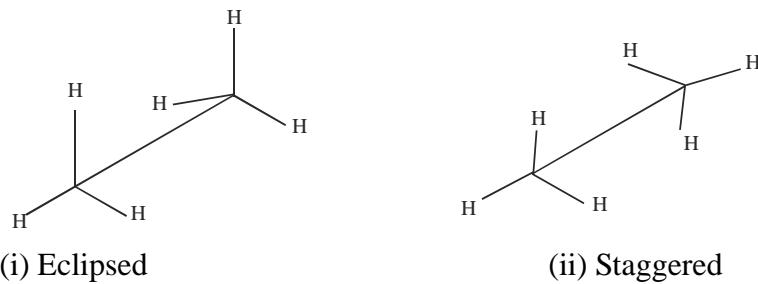


Fig : 17.3 Sawhorse projections of ethane

2. Newman Projection

A Newman projection can be used to specify the conformation of a particular bond with clarity and detail. Newman projection represents the head-on look down the bond of interest. The circle in the projection represents the rear C-atom with three hydrogen atoms attached to it by the shorter lines at an angle of 120° to each other. The front carbon atom is represented by a point at the centre of the circle from which three lines are drawn at an angle of 120° referring to three hydrogen atoms.

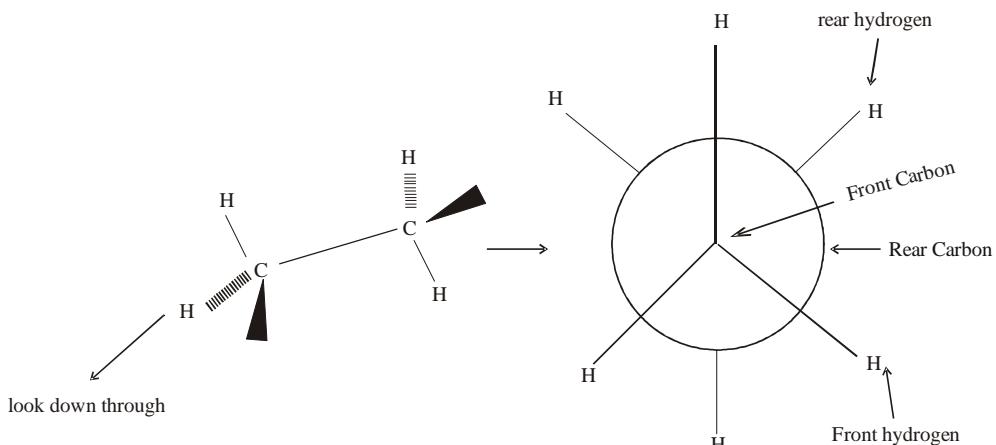


Fig : 17.4 How to draw Newman projection

Newman projection can be characterised by the angle formed between the bonds on the front atom and bonds on the rear atom. Such angles are termed as **dihedral angle**. The full 3D shape of any molecule can be described by its bond length, bond angle and dihedral angle.

In the eclipsed conformation, the C – H bonds in the front and back carbons are aligned with each other with dihedral angle of 0 degree. In the staggered conformation, the C – H bonds on the rear C lie between those on the front C with dihedral angle of 60 degrees.

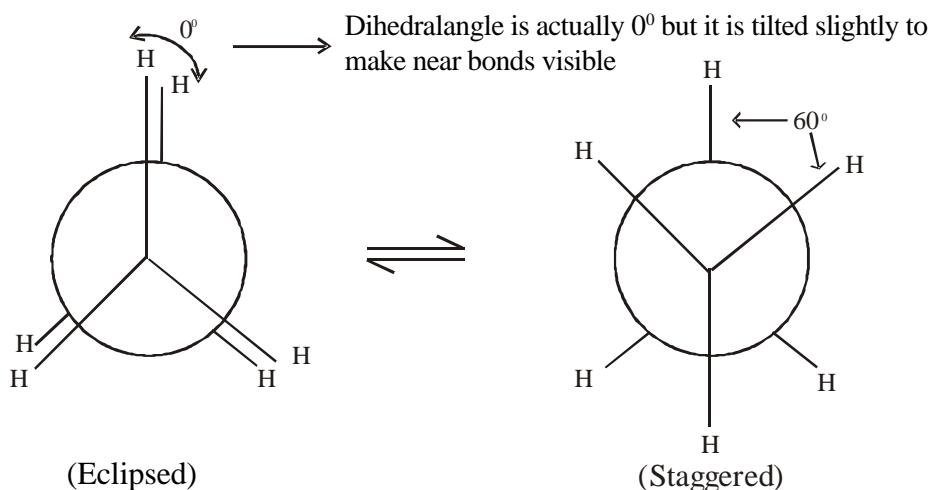


Fig. 17.5 Eclipsed and staggered conformations of Ethane

Energetically, not all conformations are equally formed. The eclipsed conformation of ethane is less stable than staggered one by 3 kcals / mol. The staggered conformation is most stable of all possible conformations of ethane, since the angle between C – H bonds of the front and rear carbon one maximised at 60° . In the eclipsed form, the electron densities on the C – H bonds are closer together than they are in the staggered form. When the C – H bonds are brought into a dihedral angle of 0 degree, the electron clouds experience repulsion, which raises the energy of the molecule. The eclipsed conformation of ethane has 3 such C – H eclipsing interaction, so we can infer that each eclipsed C – H costs roughly 1 kcal/mol.

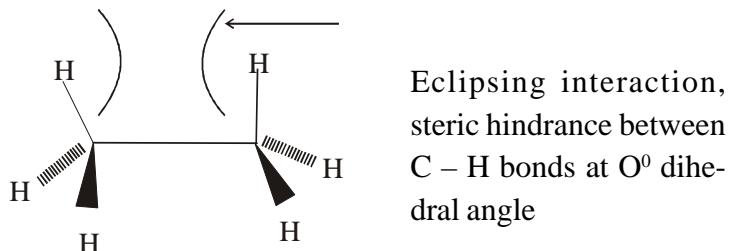


Fig. 17.6 Eclipsing interaction in ethane

Eclipsing interactions are the examples of a general phenomenon called **steric hindrance**, which occurs whenever bulky portions of a molecule repel other molecule or other part of the same molecule. Because such hindrance causes resistance to rotation, it is also called **torsional strain**. The 3 kcal / mol needed to overcome the resistance is the **torsional energy**. This energy is very small and at room temperature, the collisions of ethane molecules supply sufficient kinetic energy to overcome this energy barrier. Due to this rapid rotation it is impossible to isolate any particular conformer. Therefore, conformers are not true isomers because of rapid interconversion.

The variation of energy of the conformations of ethane with rotation about C–C single bond is shown in Fig. 17.7.

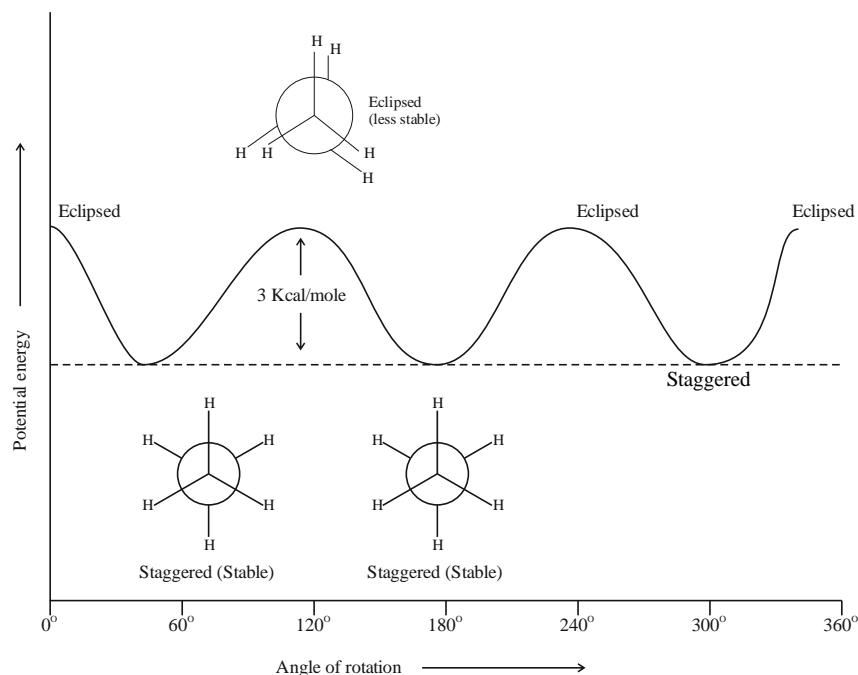
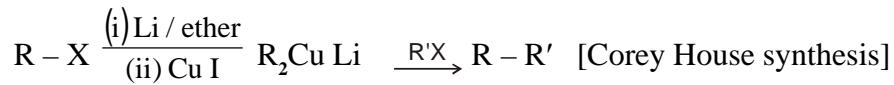
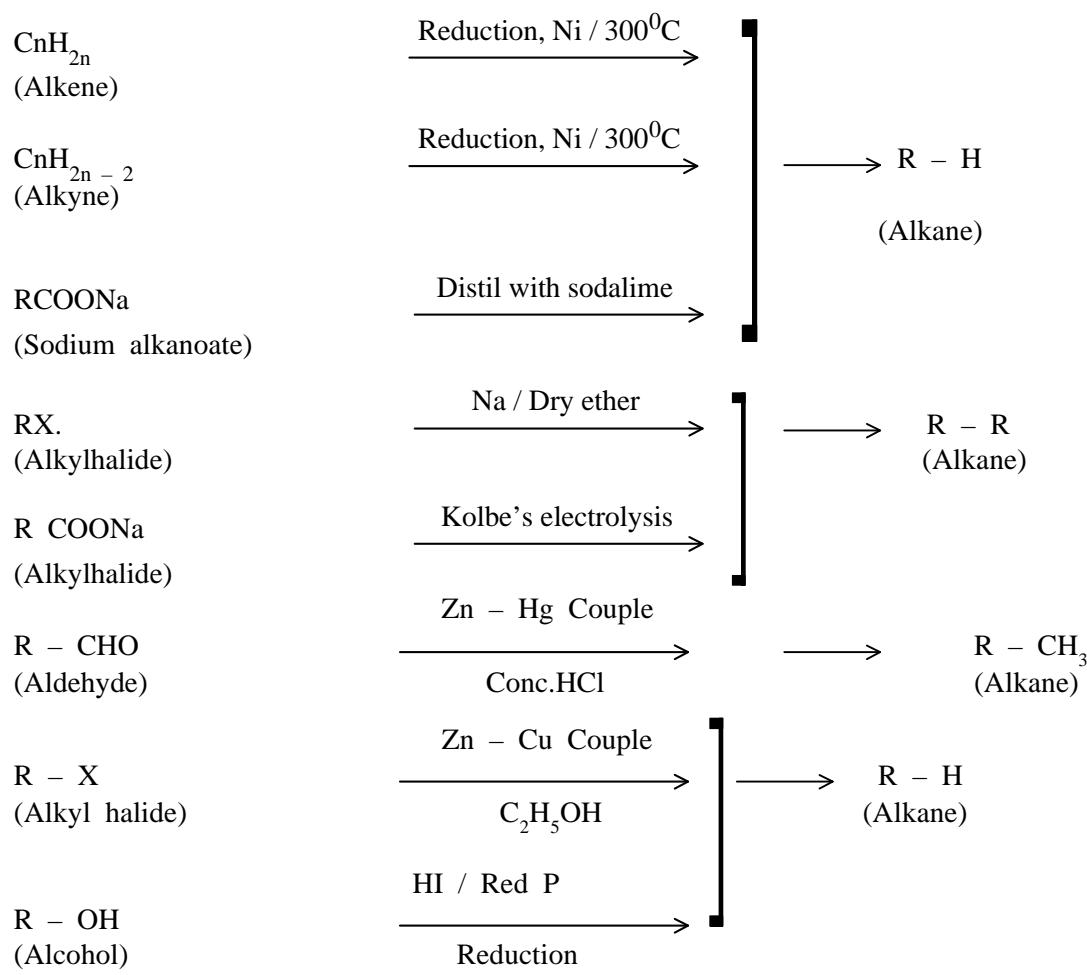


Fig. 17.7 Variation of energy during rotation about C–C single bond in ethane molecule.

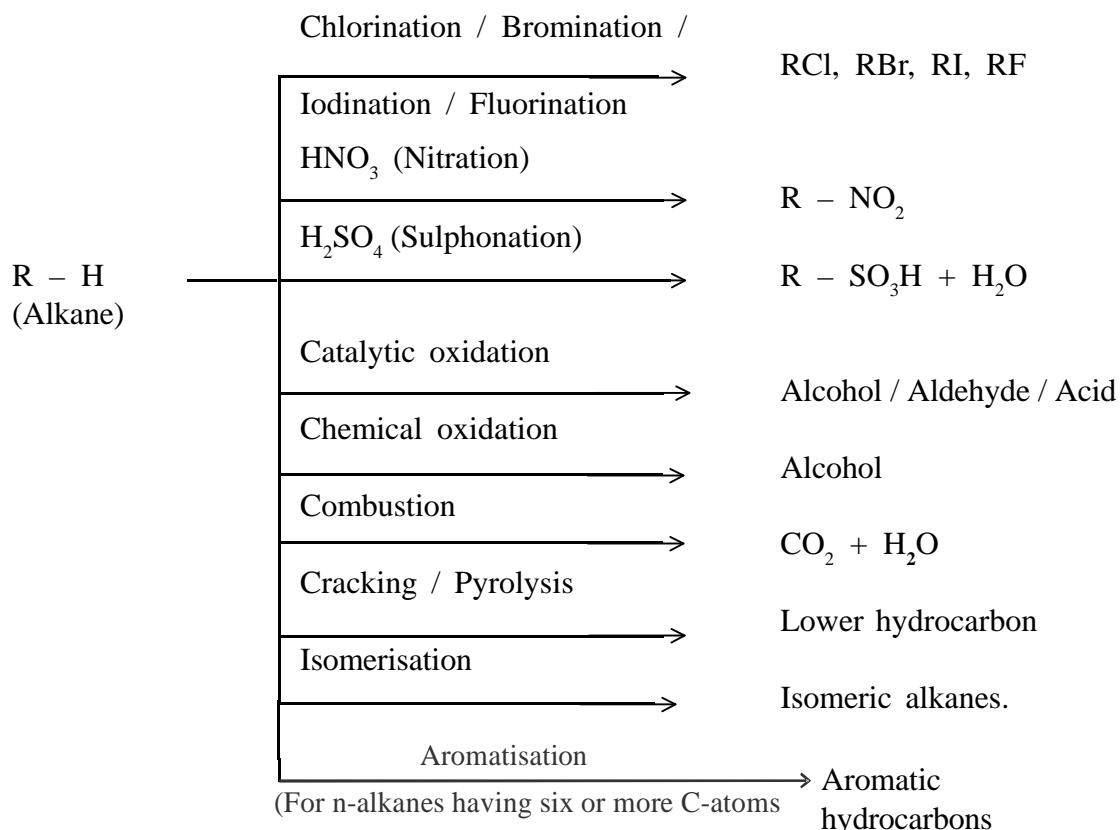
CHAPTER (17) AT A GLANCE

Preparation of alkanes :

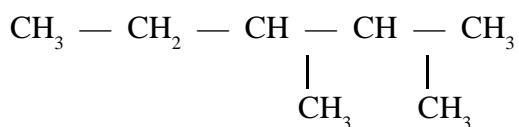


(Alkyl halide) (Alkane)



Chemical properties of alkanes :**QUESTIONS****A. SHORT QUESTIONS : (One mark each)**

1. How many isomers are possible for a compound of molecular formula C_4H_{10} ?
2. Marsh gas mainly contains _____ (H_2S , CO , C_2H_2 , CH_4)
3. What is the angle between any two bonds in methane ?
4. Give the IUPAC name of

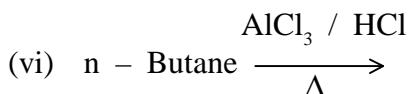
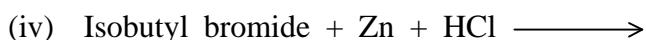
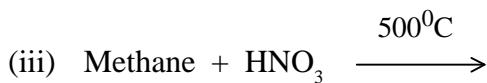
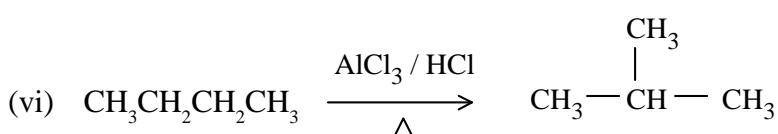
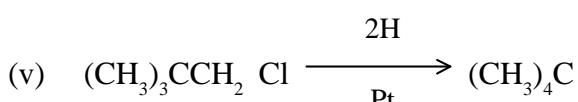
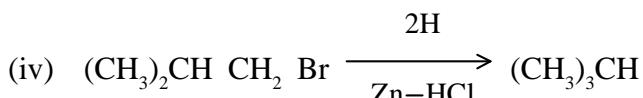
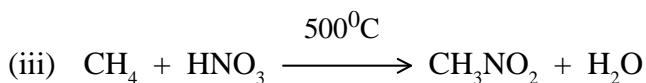
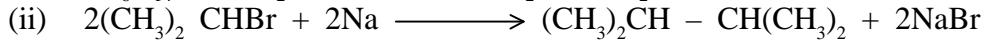
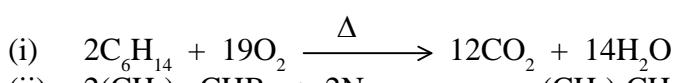
**B. SHORT QUESTIONS : (Two marks each)**

1. How do you get ethane from acetylene ?
2. How can you convert methane to ethane ?

3. Write a short note on 'Wurtz reaction'.
4. What happens when sodium propionate is heated it sodalime ?
5. What happens when ethane reacts with nitric acid at 400°C ?
6. What is Wurtz reaction ? Give an example of it.
7. State with equation what happens when aqueous solution of sodium acetate is electrolysed.
8. What happens when ethyl iodide is heated with sodium in dry ethereal solution? Give equation.
9. Two moles of sodium acetate will produce how many moles of methane and how many grams of methane ?

C. OTHER SHORT QUESTIONS :

1. Complete the reaction
 - (a) $\text{CH}_4 + 2\text{F}_2 \longrightarrow$
 - (b) $\text{Al}_4\text{C}_3 + \text{H}_2\text{O} \longrightarrow$
2. A hydrocarbon having the formula $\text{C}_n\text{H}_{2n+2}$ diffuses twice as fast as SO_2 at the same temperature. Calculate the value of n. [Ans. n = 1]
3. Name the alkanes which are obtained when a mixture of methyl iodide and ethyl iodide is treated with metallic sodium and dry ether. Explain the formation of alkanes with equations.
4. There are five isomers of C_6H_{14} . Write their structures and IUPAC names.
5. Identify A and B.
 - (i) $\text{A} + \text{H}_2\text{O} \longrightarrow \text{CH}_4 + \text{B}$
 - (ii) $\text{A} + \text{Na} \xrightarrow{\text{Ether}} \text{C}_2\text{H}_6 + \text{B.}$
 - (iii) $\text{CH}_3\text{COONa} + \text{A} \xrightarrow{\text{Heat}} \text{CH}_4 + \text{B.}$
 - (iv) $\text{CH}_3\text{COOH} \xrightarrow{\text{KOH}} \text{A} \xrightarrow{\text{Kolbe's reaction}} \text{B.}$
 - (v) $\text{CH}_3\text{Br} \xrightarrow[\text{and alcohol}]{\text{Zn-Cu Couple}} \text{A} \xrightarrow{\text{Cl}_2} \text{B.}$
6. Balance and complete the following equation :
 - (i) Hexane + $\text{O}_2 \xrightarrow{\Delta}$

**ANSWERS**

7. Fill in the blanks :

(i) Ethane can be prepared by the hydrolysis of _____.

(ii) Ethane can be prepared by the hydrogenation of _____.

(iii) Hydrogen iodide reduces _____ to alkane in the presence of _____.

(iv) n - Hexane has _____ boiling point than neohexane.

(v) Neopentane has _____. number of quaternary hydrogen atoms.

(vi) A saturated alkyl group has the general formula _____.

(vii) The common name of tribromomethane is _____.

Answers :

- (i) C_2H_5MgX (ii) Ethene (iii) alkyl halide, red phosphorous.
 (iv) higher (v) nil (vi) C_nH_{2n+1} (vii) Bromoform.
8. How would you carry out the following conversions ?
 (i) Methane to Ethane and vice versa.
 (ii) Ethane to Propane and vice versa.

D. LONG QUESTIONS :

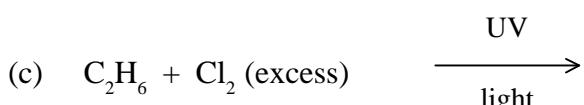
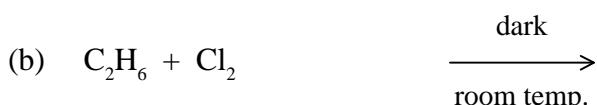
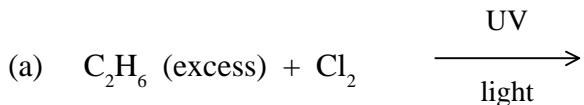
1. Write notes on :
 - (a) Wurtz reaction.
 - (b) Kolbe's reaction.
 - (c) Substitution reaction in alkanes.
 - (d) Pyrolysis.
 - (e) Sabatier and Senderens reaction.
 - (f) Combustion
2. Describe any three methods for the preparation of aliphatic saturated hydrocarbons and their general chemical reactions.
3. How methane can be prepared ? What are the chief properties of these compounds ? Explain the statement "Methane is a saturated hydrocarbon."
4. How does methane react with halogens ? Give the order of reactivity of halogens with alkanes and the order of reactivity of alkanes with halogens.
5. Describe a method for the preparation of ethane. From ethane how would you obtain methane and vice versa ?
6. Explain the following with suitable examples.
 - (a) Isomerisation of alkanes.
 - (b) Chain isomerism in alkanes
 - (c) Cracking of alkanes.
 - (d) Substitution reactions of alkanes.

E. MULTIPLE CHOICE QUESTION :

1. Which of the following compound is likely to have the lowest boiling point ?

(a) n – Butane	(b) Ethane
(c) n – Pentane	(d) Propane
2. Marsh gas mainly contains.

(a) C_2H_2	(b) CH_4
(c) H_2S	(d) CO



11. When sodium acetate is heated with sodalime _____ is formed.

 - (a) Methane (b) Ethane
 - (c) Ethylene (d) Acetaldehyde

12. Which of the following is most stable.

 - (a) CH_3^+ (b) $(\text{CH}_3)_2\text{CH}^+$
 - (c) $(\text{CH}_3)_3\text{C}^+$ (d) CH_3CH_2^+

[Hint : The stability of carboonium ion is in the order tert > sec > prim]

13. The reactivity of hydrogen atom in an alkane towards substitution by bromine is

 - (a) $1^\circ\text{H} > 2^\circ\text{H} > 3^\circ\text{H}$ (b) $1^\circ\text{H} < 2^\circ\text{H} < 3^\circ\text{H}$
 - (c) $1^\circ\text{H} > 2^\circ\text{H} < 3^\circ\text{H}$ (b) $1^\circ\text{H} < 2^\circ\text{H} > 3^\circ\text{H}$

14. Isomerization in alkane may be brought about by using

 - (a) Al_2O_3 (b) Fe_2O_3
 - (c) AlCl_3 and HCl (b) Conc. H_2SO_4

15. The major product obtained in the photobromination of 2-methyl butane is

 - (a) 1-bromo-2-methylbutane (b) 1-bromo-3-methylbutane
 - (c) 2-bromo-3-methylbutane (d) 2-bromo-2-methylbutane

16. Electrolysis of concentrated solution of sodium salt of propanoic acid produce hydrocarbon

 - (a) Methane (b) Ethane
 - (c) Propane (d) Butane

ANSWERS

- | | | | |
|---------|---------|---------|---------|
| 1. (b) | 2. (b) | 3. (b) | 4. (a) |
| 5. (b) | 6. (c) | 7. (a) | 8. (d) |
| 9. (a) | 10. (b) | 11. (a) | 12. (c) |
| 13. (b) | 14. (c) | 15. (d) | 16. (d) |

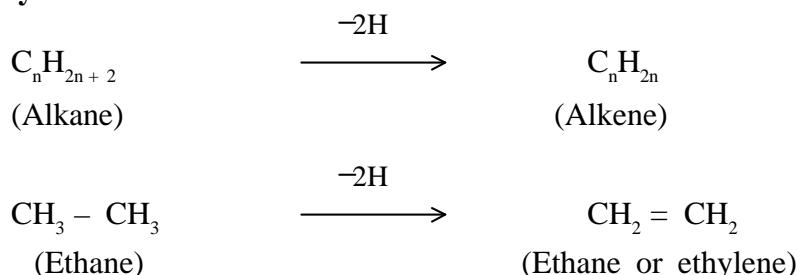


CHAPTER - 18

UNSATURATED HYDROCARBONS - ALKENES

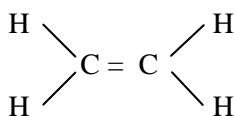
18.1 **ALKENES (OLEFINS)**

Alkenes are hydrocarbons containing carbon to carbon double bond(s) ($C = C$) in their molecules. They have the general formula C_nH_{2n} , where n is the number of carbon atoms. Alkenes contain two hydrogen atoms less than the corresponding alkanes and are thus designated as **unsaturated hydrocarbons**.

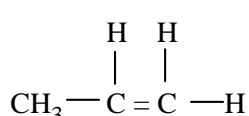


These hydrocarbons are called *olefins*. The name '*olefin*' arose from the fact that the ethylene was called '*olefiant gas*' (oil forming gas), since it forms oily liquid when treated with chlorine. The carbon to carbon double bond ($C = C$) in an alkene constitutes the functional group and largely determines its chemical behaviour. The double bond is commonly referred to as the **olefinic or ethylenic bond**.

Since there can be no alkene with one carbon, the first member of the series has the molecular formula C_2H_4 ($n = 2$) and is commonly known as ethylene. The second member of this family has the molecular formula C_3H_6 ($n = 3$) and is commonly known as propylene. These may be represented by the following structures.

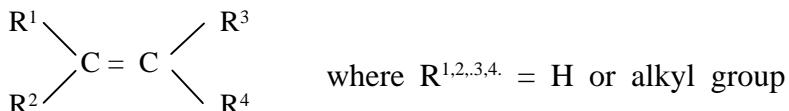


Ethylene (C_2H_4)



Propylene (C_3H_6)

In general alkene may be represented by the formula



18.2 NOMENCLATURE OF ALKENES

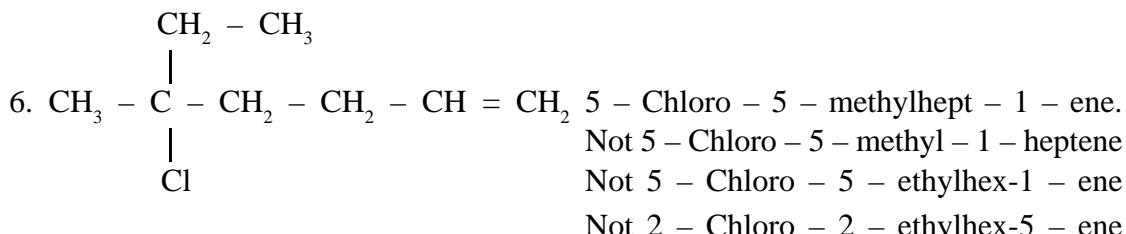
According to the IUPAC system of nomenclature, the suffix for the class of olefins is *-ene*.

While naming the alkene the following rules are followed.

1. Use the ending *ene* for alkenes.
2. Choose the parent chain containing the double bond, as the longest chain of carbon.
3. Number the parent chain from the end that gives the lowest possible number to the carbon involved in the double bond.
4. Attach the numerical prefix to *- ene* that specifies the position of the double bond, preceded by the parent hydrocarbon part.
5. Use the suffix *diene*, *triene* if the alkene contain two or three double bonds respectively.
6. Use the number of first carbon involved in each double bond as its locant.
7. Indicate the side chains or substituents as in the case of alkanes.

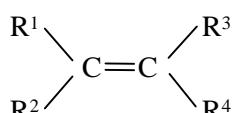
Examples :

1. $\text{CH}_2 = \text{CH}_2$ Ethene or Ethylene.
2. $\text{CH}_3 - \text{CH} = \text{CH}_2$ Propene or Propylene
3. $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} = \text{CH}_2 \end{array}$ 2 – Methylpropene
Not 2 – Methyl prop-1-ene.
4. $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$ But – 1 – ene
Not 1 – Butene or 3 – Butene
5. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3$ Hex – 2 – ene
Not 2 – Hexene
Not 4 – Hexene.



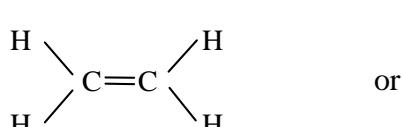
18.3 STRUCTURE OF ALKENE

Alkenes can be represented by the general structural formula

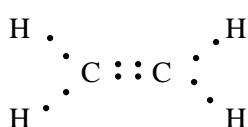


where R = Alkyl group (same or different) or H atoms.

The simplest member ethylene can be represented as



All the atoms lie in one plane.



(Lewis electron-dot structure)

The simplest alkene, ethylene (C_2H_4) contains one carbon-carbon double bond, which consists of a sigma (σ) bond and a pi (π) bond. The strong sigma (σ) bond is formed by the end-on overlap of the sp^2 – orbitals of two carbon atoms and the weak pi (π) bond, by the side-wise overlap of their $2p_z$ orbital. The s-orbital of hydrogen atoms overlaps on sp^2 orbitals of carbon atoms forming sigma (σ) bonds.

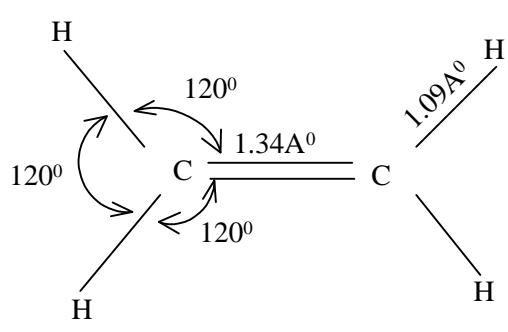
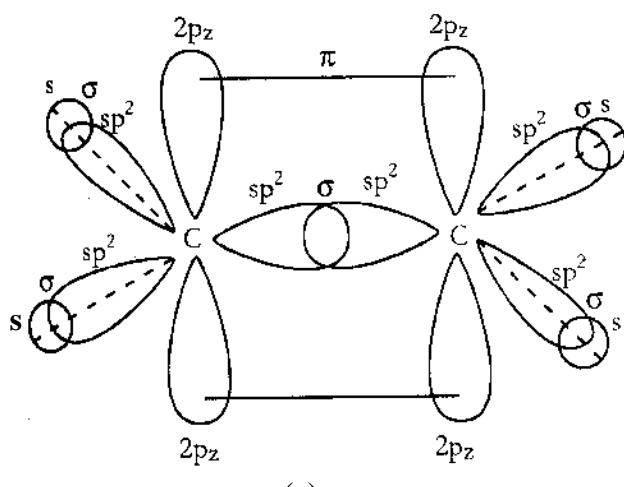


Fig. 18.1 : (a) End-on overlap of two sp^2 orbitals forming a sigma bond, lateral overlap of two $2p_z$ orbitals forming a pi (π) bond.

End-on overlap of s-orbitals of hydrogen on sp^2 orbitals of carbon forming sigma (σ) bond

(b) Planar representation of ethylene molecule.

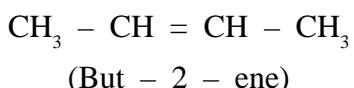
The H – C – C and H – C – H bond angles are 120° and the C – H bond length is 1.09A^0 , whereas C – C bond length is 1.34A^0 as compared to C – C bond length 1.54A^0 in ethane. The bond strength of a carbon double bond is found to be 147 kcal / mole (σ bond = 83kcal, π bond = 64 kcal) which is more than carbon carbon single bond. Because of the higher bond strength the two nuclei are pulled closer and the bond length is shorter by about 0.2A^0 than the carbon-carbon single bond.



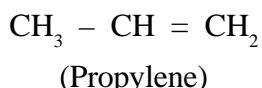
The alkenes are more reactive than alkanes because of the high electron density of π - electron cloud, which makes the double bond a **nucleophile**. Due to lateral overlap, the pi-bond is weak and pi-electron pair is more mobile and available easily for electron seeking reagents (**electrophiles**). The energy required to break a π -bond is only 70% of that required for breaking a σ - bond. Hence the double bond, instead of being a source of strength is really a vulnerable point of attack by outside reagents.

Symmetrical and Unsymmetrical alkenes :

Alkenes are said to be **symmetrical** if the atoms and groups attached on all the carbon atoms of the carbon to carbon double bond are same, such as in but – 2 – ene.



Alkenes are said to be **unsymmetrical**, if one carbon of C = C is substituted with atoms and groups different from those in other carbon, such as in propylene.



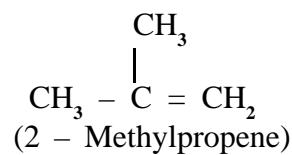
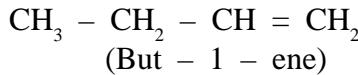
18.4 ISOMERISM

The presence of double bonds in alkenes increases the possibility of isomerism. Alkenes exhibit three types of isomerism.

1. Chain isomerism :

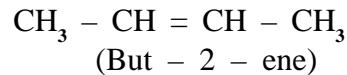
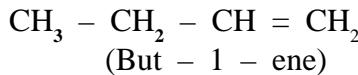
Alkenes having the same molecular formula but differing in the structure of the parent chain due to branching are chain isomers.

Example :



2. Position isomerism :

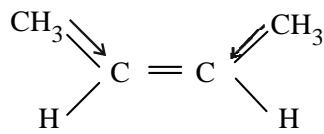
Alkenes having same molecular formula, but differing in the position of double bond in the same chain are position isomers.



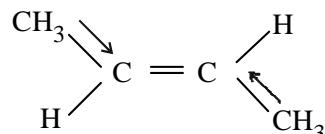
3. Geometrical isomerism :

In alkenes there is no free rotation about the carbon carbon double bond. If two different atoms or groups are attached to the double bonded carbon atoms, two isomers are possible, which differ only in the spatial arrangement of these groups or atoms about the double bond. These are referred to as geometrical isomers and designated as *cis*-and *trans*-isomers.

When the two similar groups lie on the same side of the double bond, the isomer is called *cis*- and when they lie on the opposite side of the double bond, the isomer is called *trans*-isomer. Thus two geometrical isomers are possible for but - 2 - ene. The molecule in which two methyl groups are on the same side of C = C is the *cis* but - 2 - ene and the molecule in which two methyl groups are on opposite sides of double bond, is the *trans* isomer.



cis But - 2 - ene ($\mu=0.33\text{D}$)



trans But - 2 - ene ($\mu=0$)

The two isomers differ in their physical and chemical properties and can be distinguished from each other. For example, *trans* but-2 ene is non-polar whereas the *cis*-but-2-ene is polar having dipole moment 0.33 Debye.

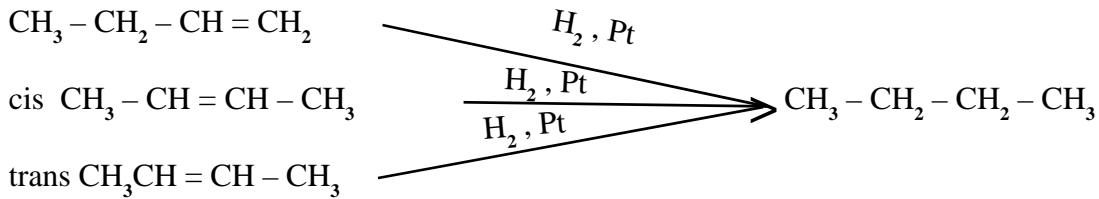
18.5 STABILITY OF ALKENES

The stability of alkenes may be explained on the basis of heat of hydrogenation of alkenes. Heat of hydrogenation is the energy difference between the starting alkene and the product alkane. The table No. shows the heat of hydrogenation of a few alkenes.

Table 18.1 Heat of hydrogenation of some alkenes

Name	Structure	$-\Delta H, \text{Kcal/mole}$
Ethene	$\text{CH}_2 = \text{CH}_2$	32.8
Propene	$\text{CH}_3 - \text{CH} = \text{CH}_2$	30.1
1-Butene	$\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2$	30.3
<i>cis</i> -2-butene	$\text{cis} - \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$	28.6
<i>trans</i> -2-butene	$\text{trans} \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$	27.6
1, 3 butadiene	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$	57.1

Consider 3 alkenes which can be reduced to butane.



The greater the value of heat of hydrogenation, the higher is the energy of the starting alkene and less is the stability. So, from the table it can be concluded that out of 3 butenes trans 2-butene is the most stable and 1-butene is the least stable.

Conclusion

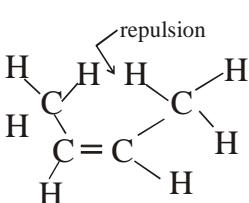
- Alkenes with more alkyl groups on the pi bond carbons are more stable. This is due to inductive effect of alkyl groups which release electron density towards sp^2 hybridised carbons.



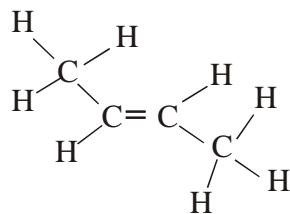
Increase in stability \rightarrow

This can also be explained on the basis of hyperconjugation.

- Conjugated dienes are more stable than dienes with same number of isolated double bonds. This is due to delocalisation of pi-electron density.
- Trans-alkenes are more stable than cis alkenes. This is because of fewer steric repulsions in trans - isomer.



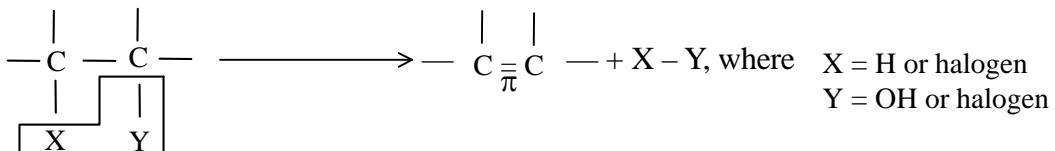
less stable (cis)



more stable (trans)

18.6 METHODS OF PREPARATION

The preparation of alkene involves the elimination of an atom or group of atoms from adjacent carbons and subsequent formation of a carbon – carbon double bond.



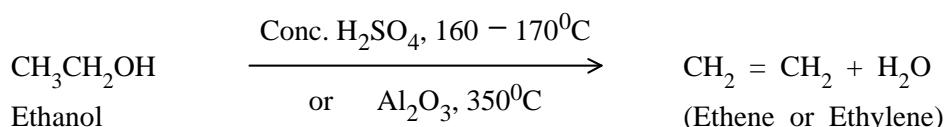
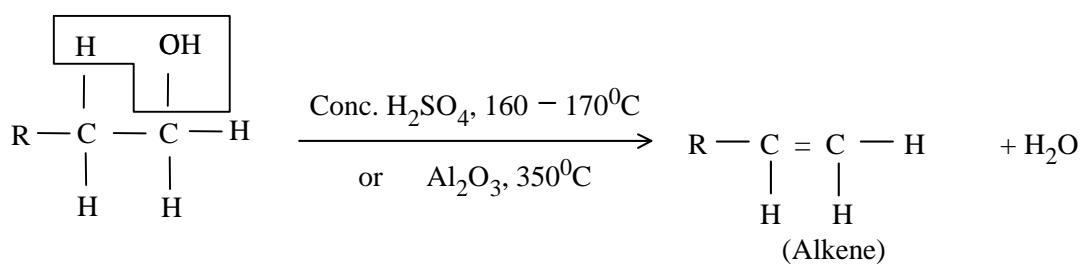
Two atoms or groups attach to vicinal carbon atoms are removed with the simultaneous formation of a π – bond. There is also a redistribution of hybridisation of C – atoms from sp^3 to sp^2 . It is brought about by different routes.

These are

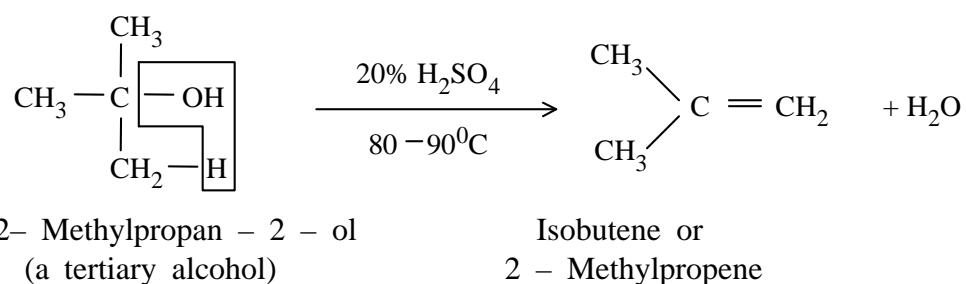
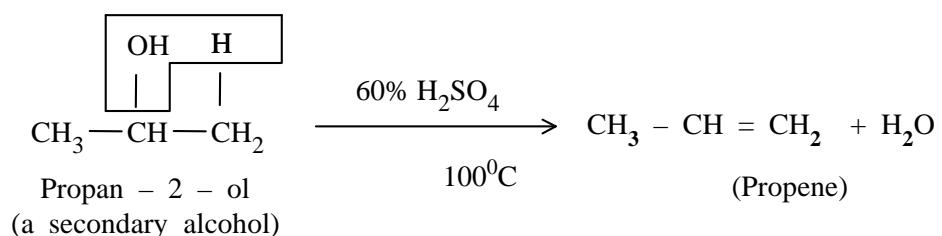
(1) Dehydration of alcohols :

- (a) When a primary alcohol is heated with concentrated sulphuric acid at 160 – 170°C, a molecule of water is eliminated and an alkene is formed. In place of concentrated sulphuric acid, other dehydrating agents like glacial phosphoric acid, phosphorus pentoxide, anhydrous zinc chloride or alumina can be used.

When vapours of alcohol are passed over heated alumina (Al_2O_3) at 350°C , dehydration takes place and alkene is formed.



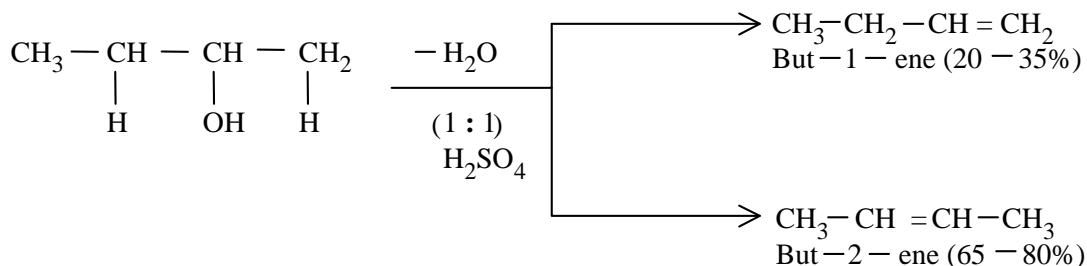
- (b) Dehydration of secondary and tertiary alcohols is best carried out using dilute sulphuric acid at lower temperature.



The ease of dehydration of alcohols is in the following order.

Tertiary alcohol > Secondary alcohol > Primary alcohol.

- (c) With unsymmetrical secondary and tertiary alcohol, dehydration may occur in two ways. e.g.



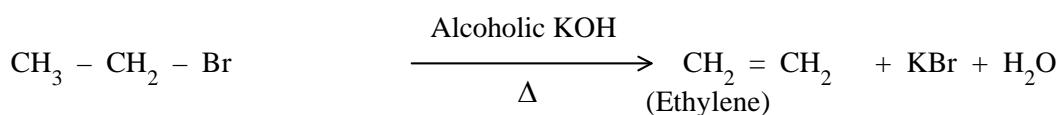
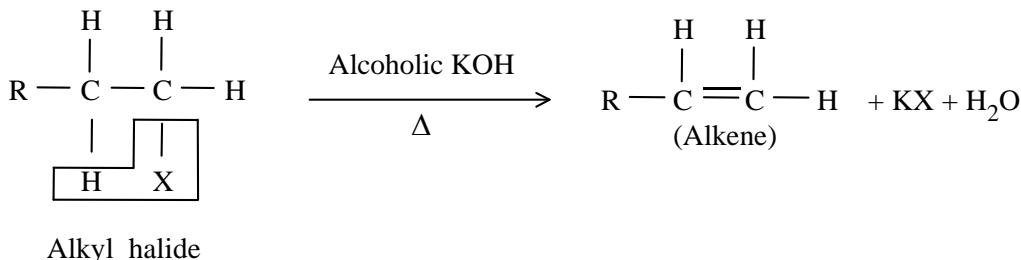
Experiments show that hydrogen attached to the adjacent carbon atoms having least number of hydrogen atoms is eliminated most easily.

Thus in the above reaction, the major product is but-2-ene (65 – 80%)

This elimination occurs in accordance with **Saytzeff's rule** for the dehydration of alcohols. According to this rule, "always the most alkyl substituted olefin is formed as the major product during the dehydration of alcohols" as more substituted the alkene, greater is its stability.

(2) Dehydrohalogenation of alkyl halides :

When an alkyl halide is refluxed with alcoholic KOH (solution of KOH in ethyl alcohol) solution, a halogen atom (X) and a hydrogen atom (H) from two adjacent carbon atoms are eliminated in the form of halogen hydacid (HX) and result in the formation of an alkene.



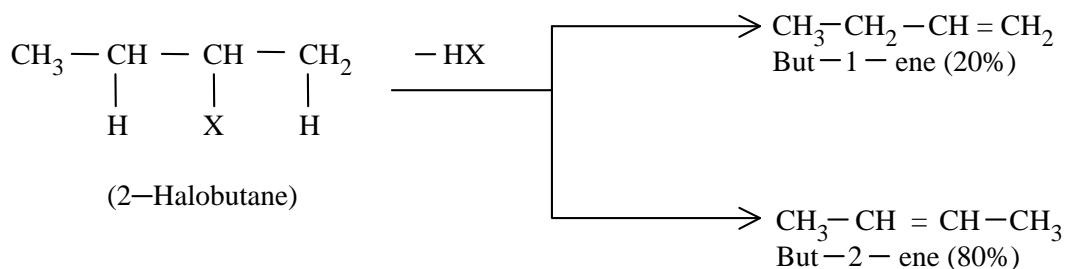
The reactivity of alkyl halides is in the following order.

Alkyl iodide > Alkyl bromide > Alkyl chloride

The case of dehydrohalogenation of alkyl halides is in the following order.

Tertiary > Secondary > Primary

With unsymmetrical secondary and tertiary alkyl halides, dehydrohalogenation may occur in two ways. e.g.



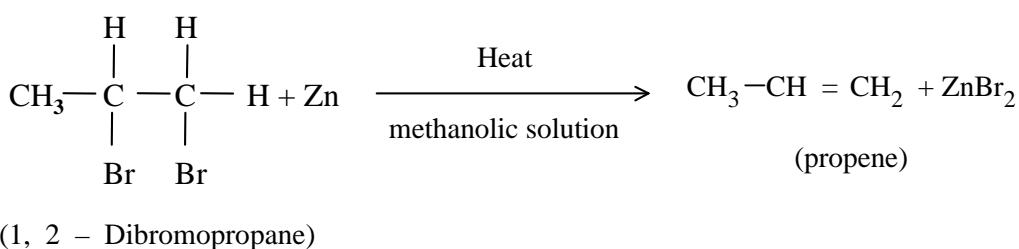
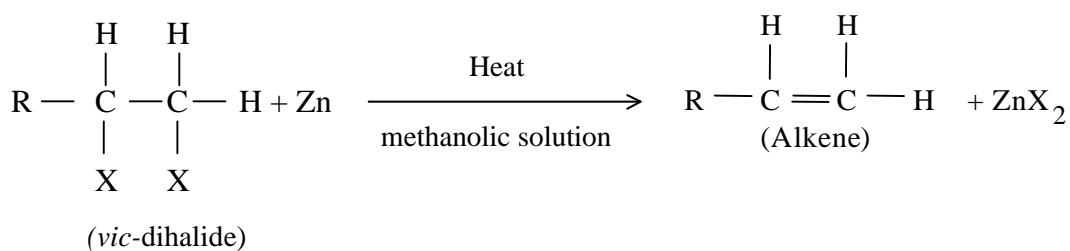
According to Saytzeff's rule the major product is the most alkyl substituted alkene.

but - 2 - ene is the major product here.

(3) Dehalogenation of vicinal dihalides :

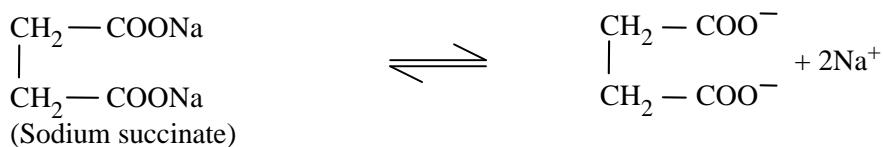
Dehalogenation involves the removal of a halogen molecule from the reactant molecule.

Compound having two halogen atoms on adjacent carbon atoms is called a *vicinal* dihalide or *vic* – dihalide. Compound having two halogen atoms on the same carbon atom is called a *geminal* dihalide or *gem*-dihalide.

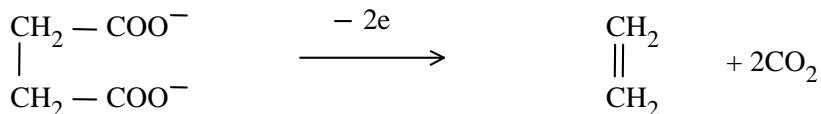


(4) Electrolysis of dibasic acids :

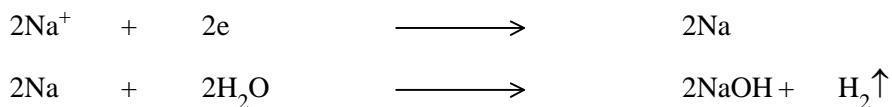
When sodium or potassium salt of a dibasic acid (for example, succinic acid) is electrolysed, alkene is liberated at the anode.



At the Anode :



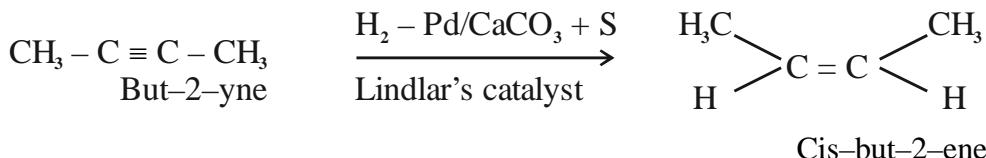
At the Cathode :



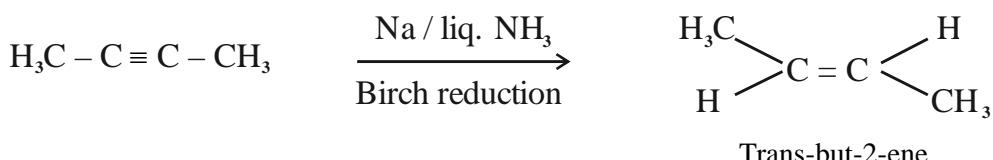
(5) Partial Reduction of Alkynes :

Alkynes on partial reduction either by **Lindlar's catalyst** or by **Birch reduction** result in cis - or trans - alkenes depending on the nature of the catalyst used.

(i) Catalytic reduction of alkynes in the presence of palladium supported over CaCO_3 , or BaSO_4 and partially poisoned by addition of PbCO_3 , S or quinoline (**Lindlar's catalyst**) gives cis-alkenes.



(ii) If alkynes are reduced with sodium in liquid ammonia (Birch reduction), trans-alkenes are the major products.



18.7 PROPERTIES

Physical Properties :

The physical properties of alkenes are similar to those of corresponding alkanes.

- (1) **State :** Lower members ethene, propene and butene are gases. Members containing upto 18 carbon atoms are colourless liquids and beyond this, higher members are colourless solids.
- (2) **Solubility :** They are insoluble in water but are soluble in organic solvents such as ether, alcohol, chloroform, benzene etc. Alkenes with lower molecular mass are slightly more soluble in water because of polarizability of the π – electrons.

- (3) **Density** : They are lighter than water and just like alkanes, have limiting density of rather less than 0.8.
- (4) **Melting and Boiling point** : The melting and boiling point of alkenes show a regular gradation with the rise in molecular mass. Further, branched-chain alkenes have lower boiling points than straight-chain alkenes.
- (5) **Odour** : Alkenes possess characteristic odour. The lower members act as general anaesthetics.

Table – 18.2
Properties of some alkenes

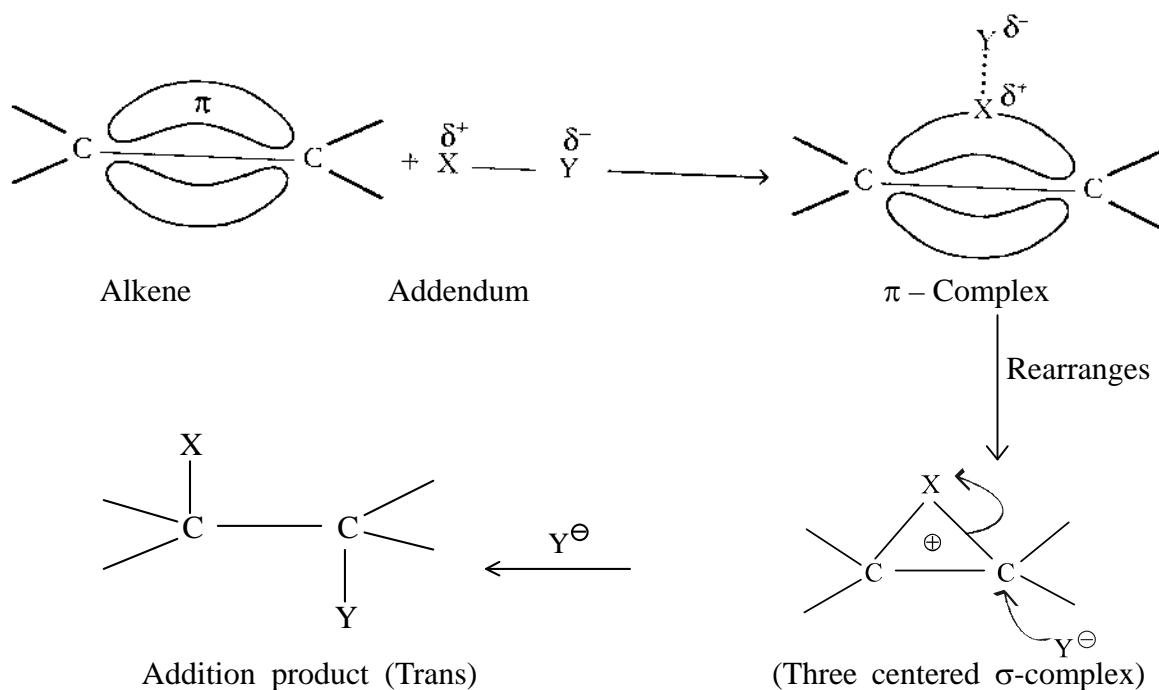
IUPAC Name	Structure	Boiling Point °C	Melting Point °C	Density (g / ml) at 10°C
Ethene	$\text{CH}_2 = \text{CH}_2$	– 103.8	– 169	0.566
Propene	$\text{CH}_3 = \text{CH} - \text{CH}_3$	– 47.7	– 185	0.609
But – 1 – ene	$\text{CH}_3 = \text{CH} - \text{CH}_2 - \text{CH}_3$	– 6.5	– 185	0.625
Pent – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_2 - \text{CH}_3$	30	– 165	0.641
Hex – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_3 - \text{CH}_3$	64	– 140	0.676
Hept – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_4 - \text{CH}_3$	94	– 119	0.697
Oct – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_5 - \text{CH}_3$	121	– 102	0.715
Non – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_6 - \text{CH}_3$	147	– 81	0.729
Dec – 1 – ene	$\text{CH}_2 = \text{CH} - (\text{CH}_2)_7 - \text{CH}_3$	171	– 66	0.741

Chemical Properties :

The carbon carbon double bond in an alkene is an unsaturated group and can undergo a wide variety of addition reactions. Double bond contains a σ bond and a π – bond. The π – bond is weaker than σ – bond. During addition reaction the π – bond breaks and the sigma bond remains intact. In such a process the π – bond is replaced by two new sigma bonds.

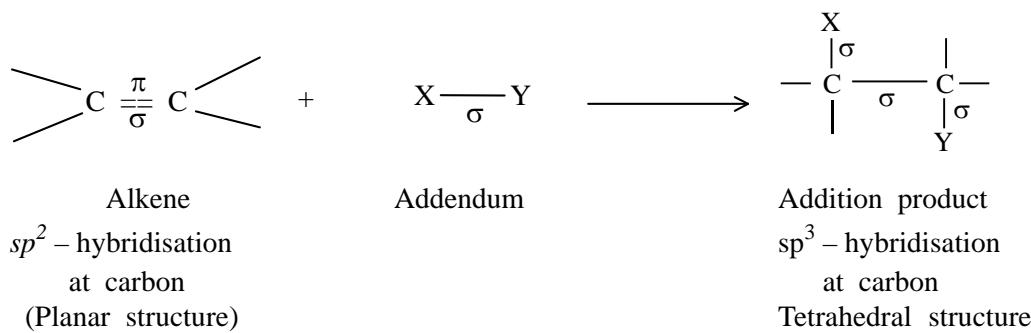
Also the π – bond in alkene acts as a source of electrons. Hence electrophiles, which are positively charged species and can accept electrons, would be attracted by the π – electron cloud while nucleophiles with completed shell structure will be repelled. Therefore, the characteristic reaction of alkenes are the **electrophilic addition reactions**.

The mechanism of addition of X – Y to an alkene is given below. If Y is more electronegative than X, the addendum can be represented as $\begin{matrix} \delta^+ & \delta^- \\ X & -Y \end{matrix}$. Thus,



Here the positive end of addendum attached to the π - electron cloud gives positive charge to the π - complex, leaving the nucleophile Y^\ominus . Then the π - complex rearranges to a carbocation which reacts with the nucleophile Y^\ominus to form the addition product.

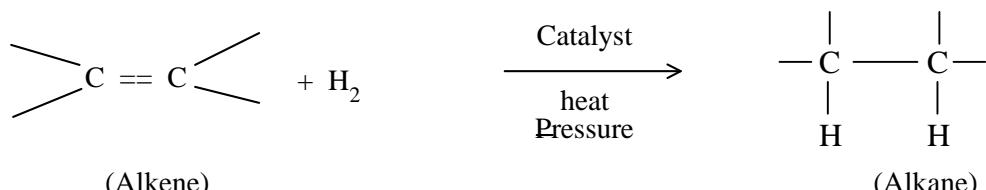
In this process, the hybridisation of carbon changes from the planar arrangement of alkene (sp^2 hybridisation) to a tetrahedral structure (sp^3 hybridisation).



The carbon – carbon double bond adds H_2 , Cl_2 , Br_2 , HX , HOX , H_2SO_4 and H_2O and is attacked by strong oxidising agents including ozone.

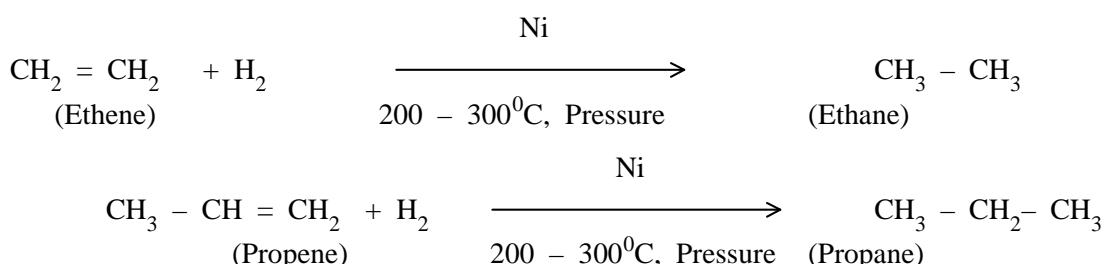
(1) *Addition of hydrogen :*

In the presence of powdered metal catalyst and under pressure and heat, hydrogen adds to double bond of alkene forming the corresponding alkane. The process is known as **catalytic hydrogenation**.



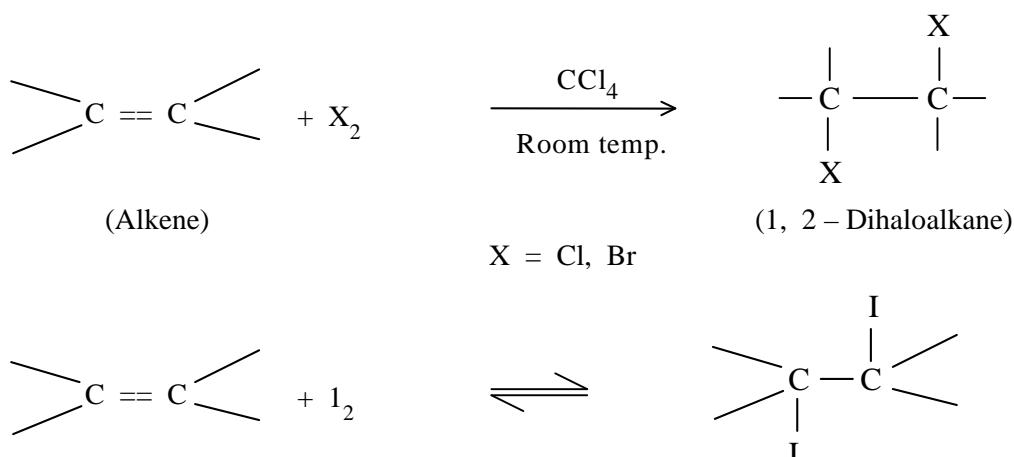
Hydrogenation of alkenes can be effected by passing the vapour of alkene and hydrogen over finely divided nickel at $200 - 300^{\circ}\text{C}$ and pressure of 50 – 100 atmosphere. With the more active catalyst like Pt, Pd or Raney Ni addition occurs at room temperature and atmospheric pressure.

Examples :

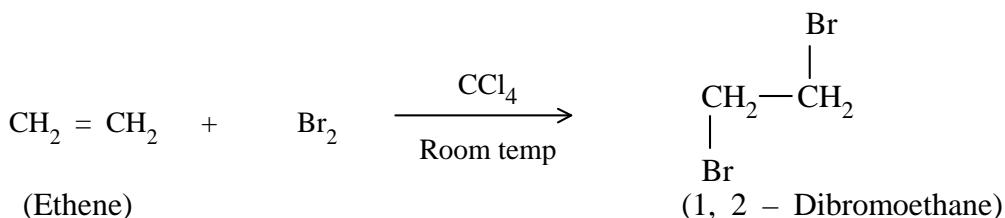


(2) *Addition of chlorine or bromine :*

When an alkene is treated with chlorine or bromine in an inert solvent like carbon tetrachloride, halogens add rapidly to the carbon carbon double bond to form dihaloalkanes. Iodine reacts very slowly with alkenes, the di-iodide being unstable regenerate alkene.



Example :

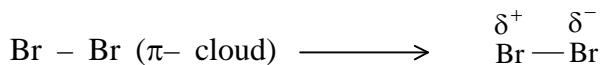


[**Note :** The reaction with bromine is used as a test for unsaturation. When an alkene is treated with a 5% solution of bromine in carbon tetrachloride, the reddish brown colour of bromine is immediately discharged]

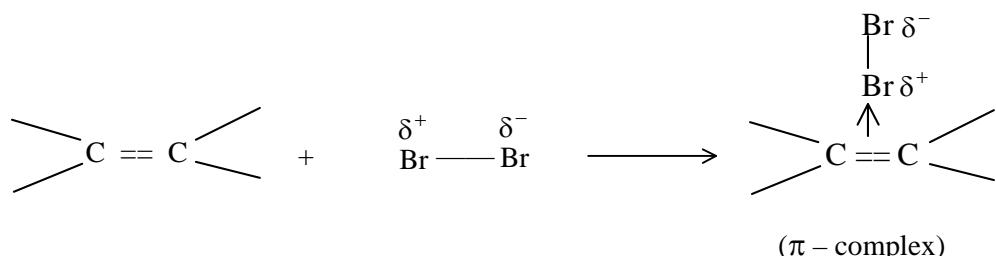
Mechanism :

The addition of halogens (say Br_2) to alkene forming 1, 2 – dihaloalkanes takes place through the following steps.

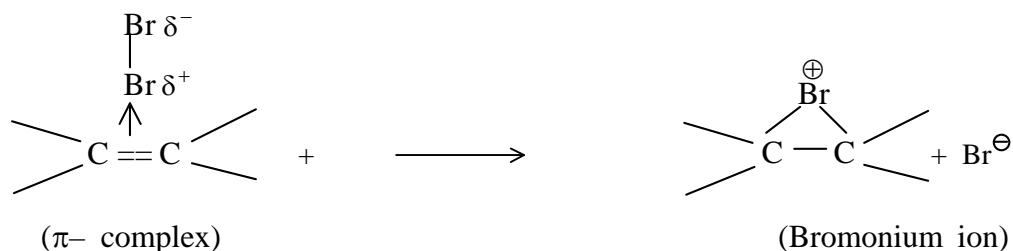
- (i) When bromine molecule comes in the proximity of an alkene, the negative π -electron cloud of the alkene causes polarisation of the bromine molecule.



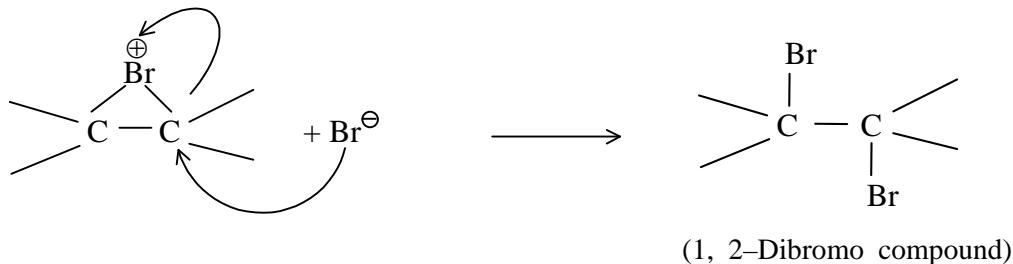
- (ii) The positive end of the polarised molecule is then attracted near the π – electron cloud to form a low stability π – complex.



- (iii) The positively charged bromine atom is then attracted by both carbons of the double bond and then the $\text{Br} - \text{Br}$ bond breaks. The negatively charged bromine leaves as Br^- and bromonium ion is formed.



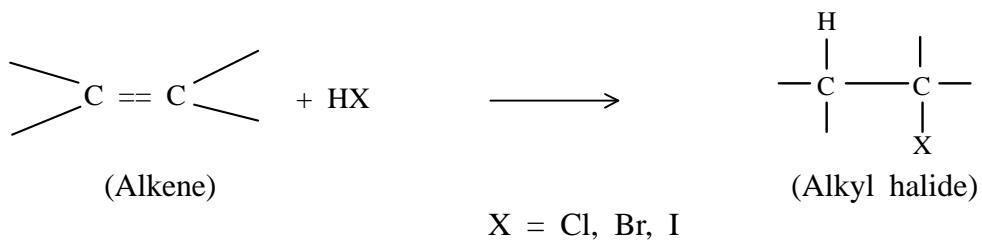
- (iv) Nucleophilic attack of bromide ion (Br^-) yields dibromo compounds.



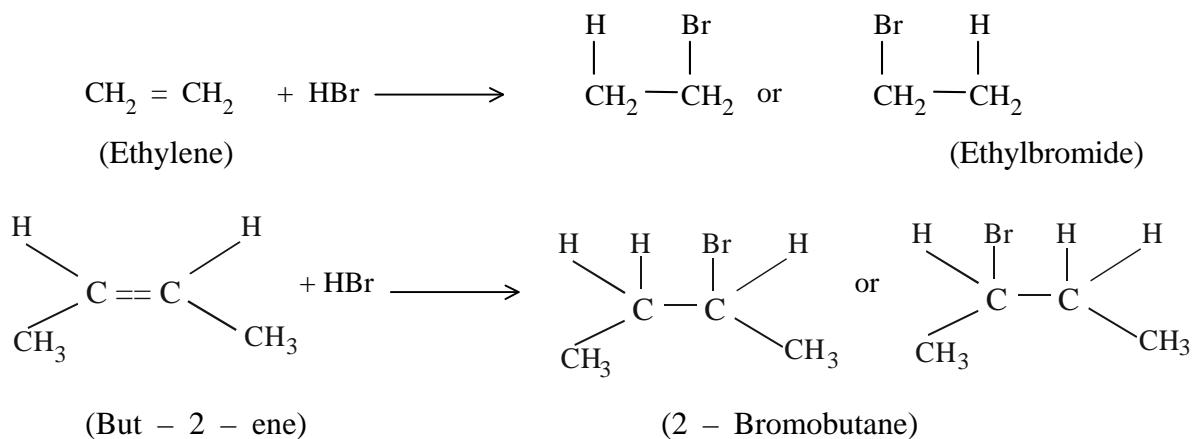
(3) Addition of hydrogen halide :

When alkenes are treated with halogen acids HX (HCl , HBr , HI) alkyl halides or haloalkanes are formed and the reaction is known as **hydrohalogenation**.

The order of reactivity of hydrogen halides is $\text{HI} > \text{HBr} > \text{HCl}$

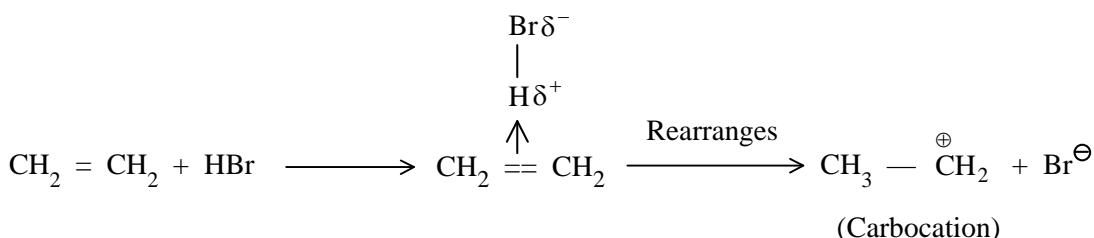
**Addition to symmetrical alkenes :**

The addition of hydrogen halide to a symmetrical alkene gives only one product because it does not matter as to which carbon of the double bond the halogen is attached.

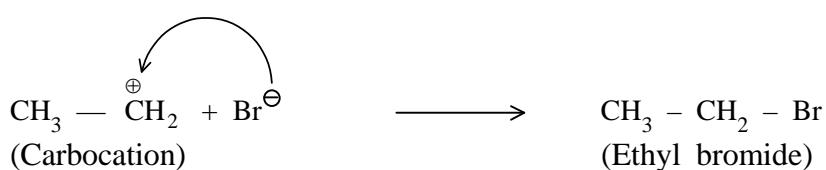
Example :**Mechanism :**

Hydrohalogenation of symmetrical alkene follows carbocation mechanism, as given below.

Step - I Hydrogen halide forms a π - complex which rearranges to give carbocation.



Step - II Nucleophilic attack of Br^\ominus to the carbocation results in the formation of alkyl halide.

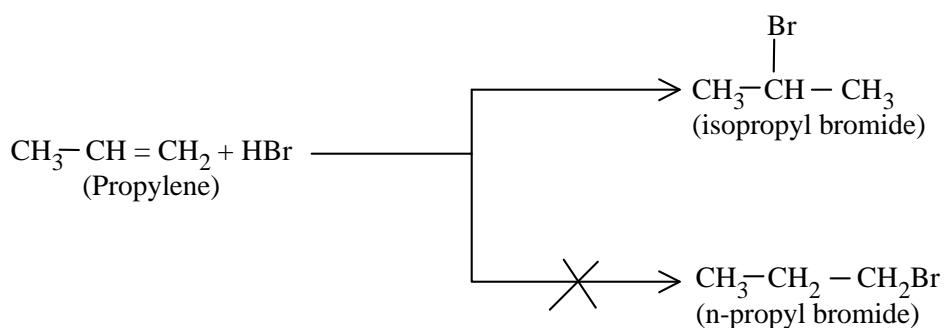


Since only one type of carbocation is possible from a symmetrical alkene, only one product is formed.

Addition to unsymmetrical alkene :

When hydrogen halide is treated with an unsymmetrical alkene, two addition products are possible as the halogen atom is placed on one or the other carbon of the double bond.

Thus, propylene reacting with HBr, can form n - propyl bromide or isopropyl bromide.



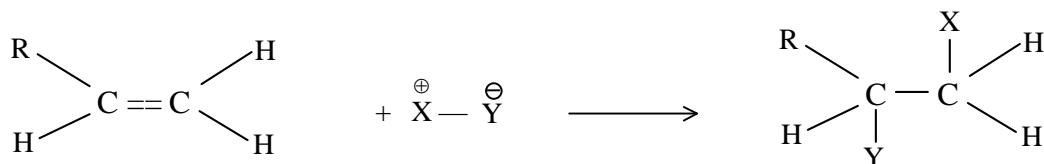
But experimentally, it has been found that, isopropyl bromide is obtained predominantly.

Such a direction of addition of an unsymmetrical reagent to an unsymmetrical alkene was first observed by Vladimer Markownikoff (1870), a Russian Chemist and his work is honoured till today by a rule named after him – **Markownikoff's rule**.

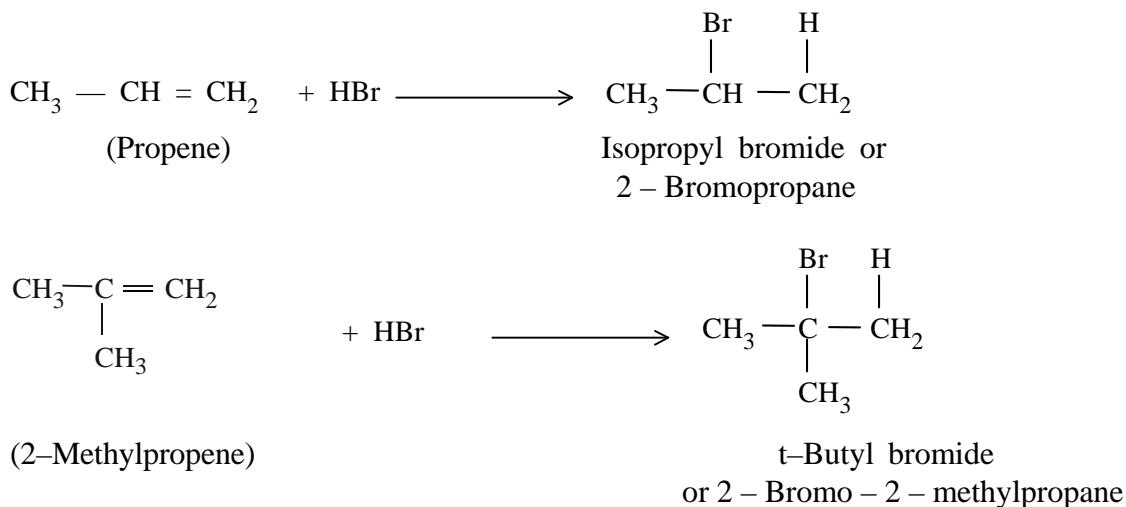
Markownikoff's rule :

The rule states the negative part of the addendum (molecule to be added) goes to that carbon atom which contains least number of hydrogen atoms during the addition across a carbon-carbon double bond of an unsymmetrical olefin.

In otherwords, when an unsymmetrical reagent (X^+Y^-) adds to an unsymmetrical alkene, the positive portion of the reagent (X^+) adds to that carbon of the double bond, which has greater number of hydrogen atoms.



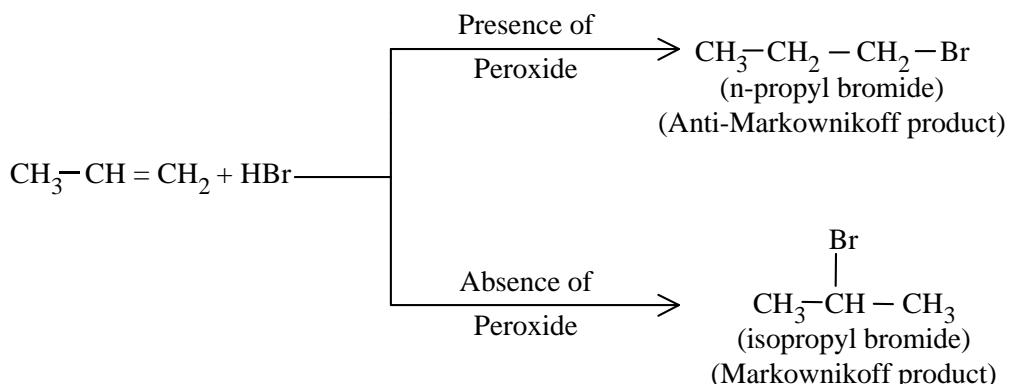
Thus hydrogen bromide will add to propene to give isopropyl bromide and to 2-Methylpropene to give t-butyl bromide as the major product.



Anti-Markownikoff's Rule : (*Kharasch Peroxide effect*)

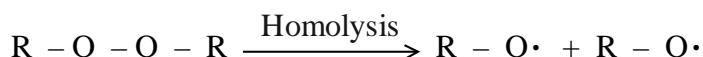
Kharasch & Mayo (1933) observed that the addition of HBr to unsymmetrical alkene, in the presence of organic peroxide (R – O – O – R) takes place opposite to that predicted by Markownikoff. This phenomenon of anti-Markownikoff addition caused in presence of peroxide, is called **Kharasch peroxide effect**.

Thus, when propylene reacts with HBr in the presence of a peroxide, the product is mainly n-propyl bromide, whereas in the absence of peroxide, the main product is isopropyl bromide.

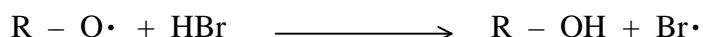


The addition of HBr, in the presence of peroxide is a free radical chain reaction.

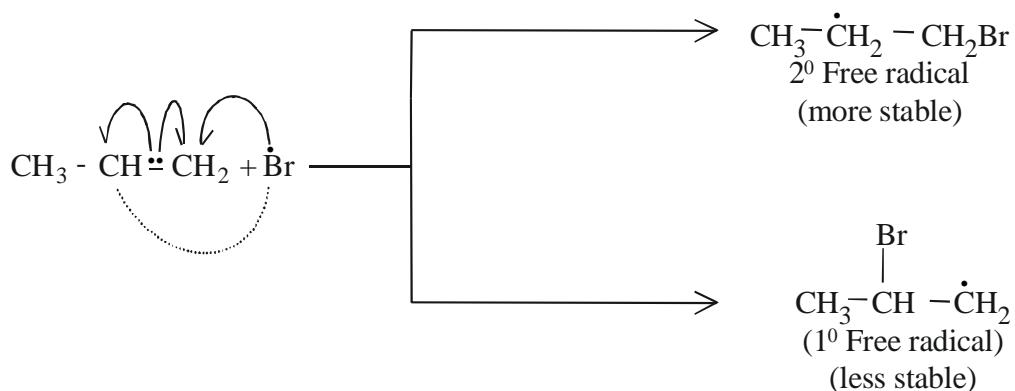
- (a) R – O – O – R decomposes to give radicals



- (b) R – O· radical reacts with HBr to form free bromine radical.

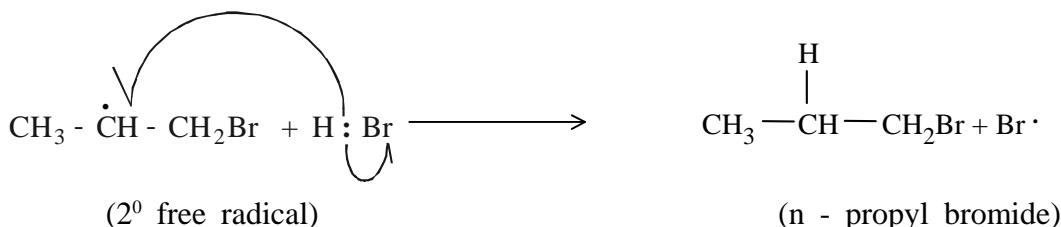


- (c) The bromine radical then attacks the alkene giving two possible bromoalkyl free radicals.



Since the order of stability of free radical is $3^0 > 2^0 > 1^0$, the 2^0 free radical is formed predominantly.

- (d) The more stable radical (2^0 free radical) reacts with HBr forming anti-Markownikoff product and another bromine free radical which propagates the chain reaction.



HCl and HI do not give anti-Markownikoff products in the presence of peroxide, because

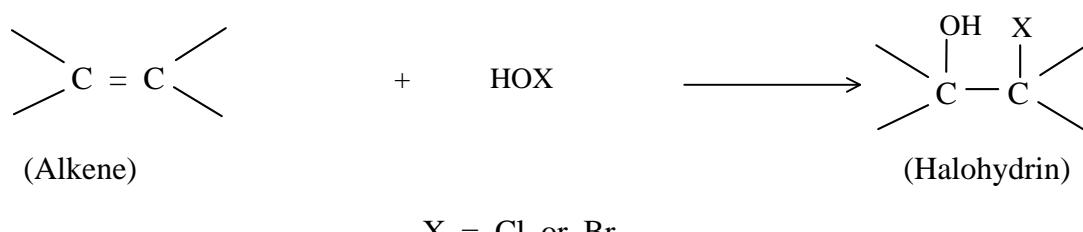
- (i) the H – Cl bond is stronger than H – Br bond. It is not broken by alkoxy free radicals obtained from peroxide.

(ii) The H – I bond is weaker than H – Br. It is broken by alkoxy free radical obtained from peroxide, but the iodine atoms so formed readily combine with each other giving iodine molecule rather than attacking the double bond of alkene.

(4) *Addition of Hypohalous acids (HOX) :*

(4) *Addition of Hypohalous acids (HOX) :*

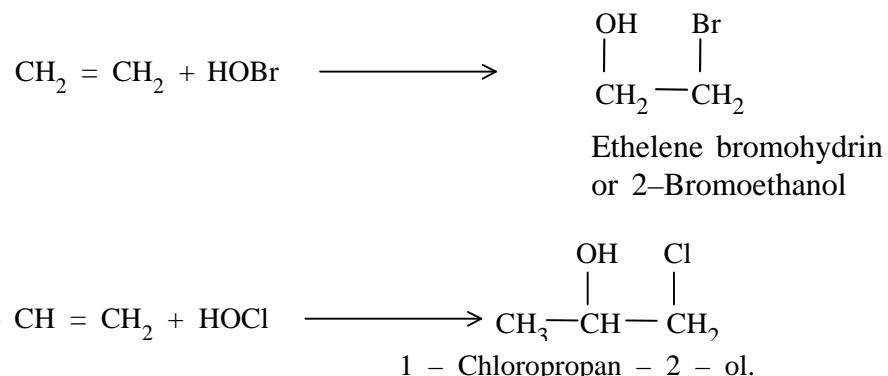
Alkenes when treated with hypohalous acid form halohydrins.



In hypohalous acid, the OH group behaves as the negative part of the adding species ($\text{HO}^- \text{X}^+$).

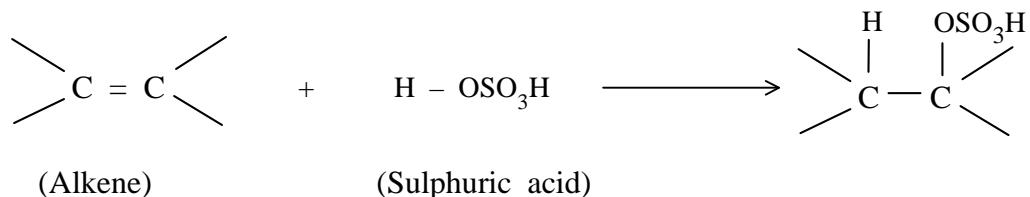
The addition follows Markownikoff's rule

Examples :



(5) *Addition of sulphuric acid :*

Alkenes when treated with cold conc. H_2SO_4 at room temperature, form alkyl hydrogen sulphates.

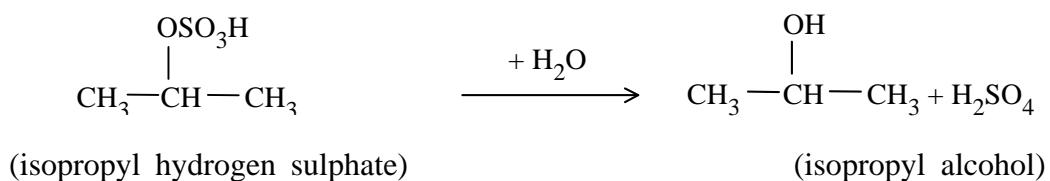


With unsymmetrical alkenes, the addition of sulphuric acid follows Markownikoff's rule.

For example :



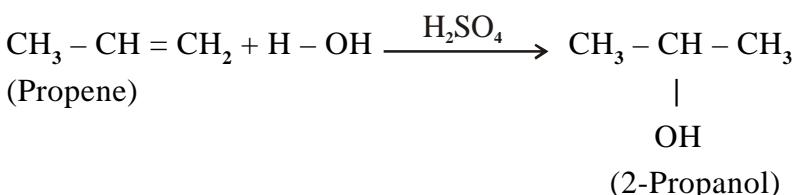
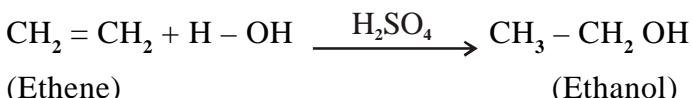
The resulting alkyl hydrogen sulphate upon hydrolysis give respective alcohols.



(6) Addition of Water (Hydration)

Alkenes undergo acid-catalysed addition of water to give alcohols. Ethanol is industrially prepared by the method.

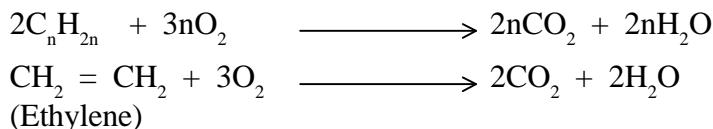
Sulphuric acid is commonly used as catalyst. The addition obeys Markownikoff's rule.



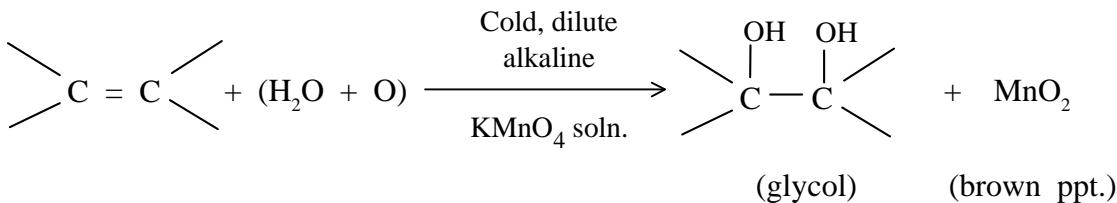
(7) *Oxidation* :

Alkenes are easily oxidised than alkanes. The products of oxidation depend upon the nature of oxidising agent.

- (i) *Combustion* : Alkenes burn in air with luminous flame to form carbon dioxide and water.

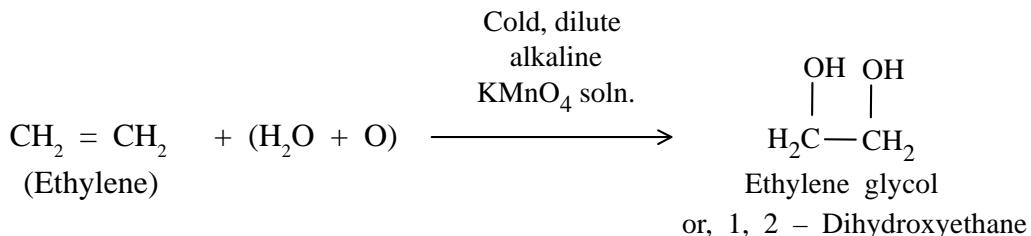


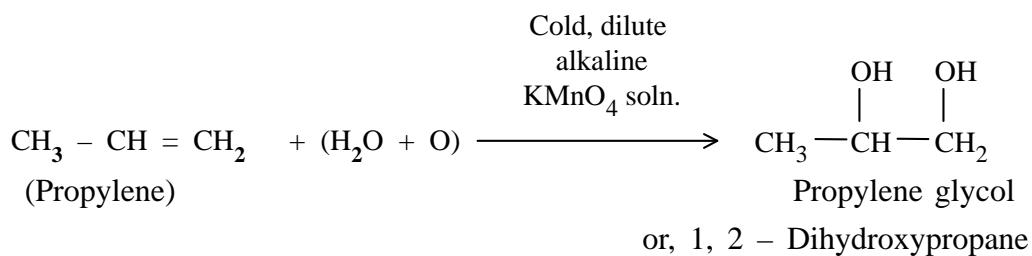
- (ii) **Hydroxylation** : Alkenes when treated with cold dilute aqueous or alkaline solution of potassium permanganate (**Baeyer's reagent**) add two hydroxyl groups across the double bond to form 1, 2 – dihydroxy compounds, known as glycol. The pink colour of KMnO_4 is discharged and a brown precipitate of MnO_2 is formed.



The reaction is known as **hydroxylation** of alkenes.

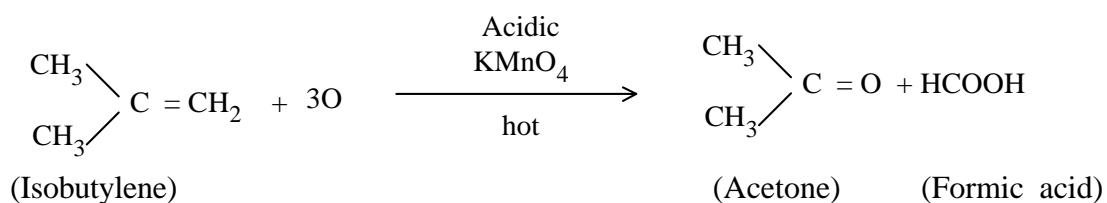
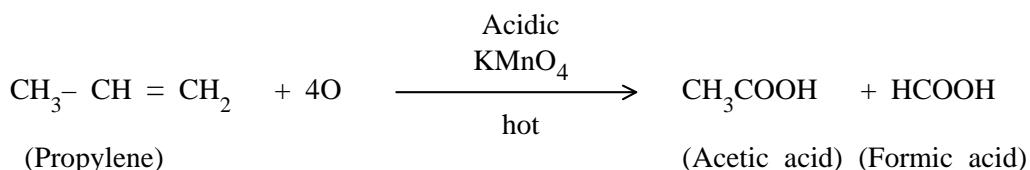
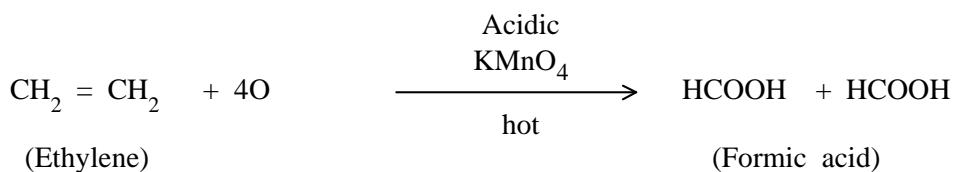
For example :



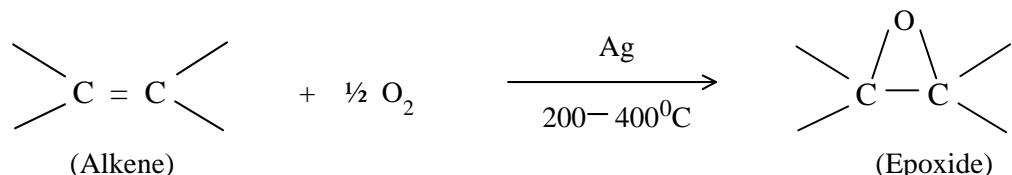


(iii) *Chemical oxidation* : With strong oxidising agents like warm acidified potassium permanganate or aqueous chromic acid, the double bond is ruptured and the products are aldehyde, ketone and acid depending upon the nature of alkene.

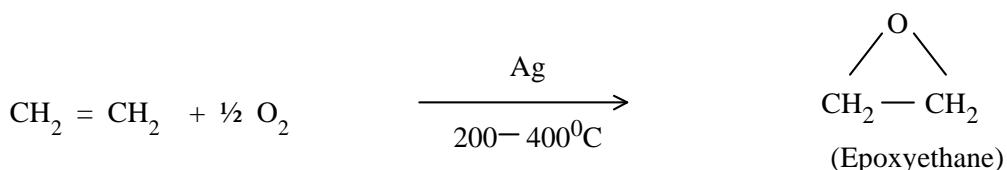
Example :



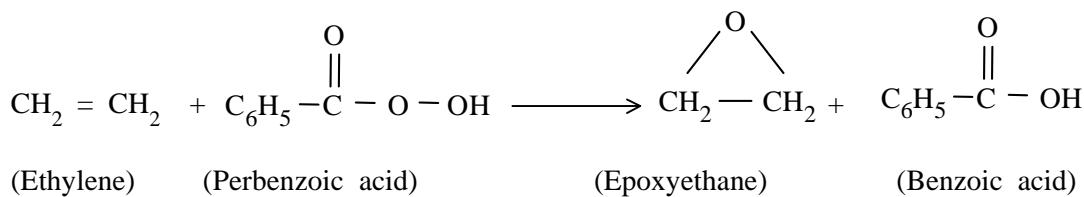
(iv) **Epoxidation** : Lower alkenes react with oxygen at $200 - 400^{\circ}\text{C}$ in the presence of silver as catalyst forming epoxides.



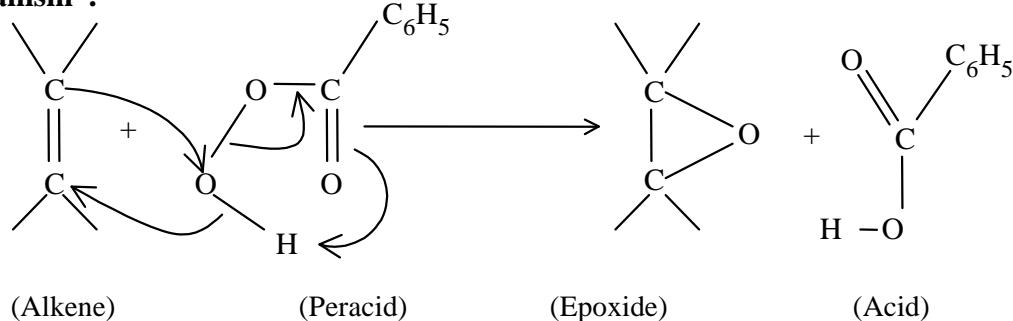
The oxidation reaction of alkene giving epoxides is *epoxidation*. Thus,



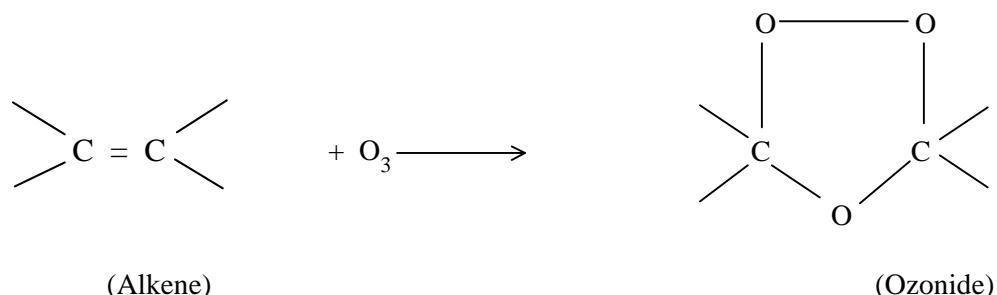
The better method of epoxidation is by the treatment of alkene by peracids such as perbenzoic acid, trifluoroperacetic acid.



Mechanism :

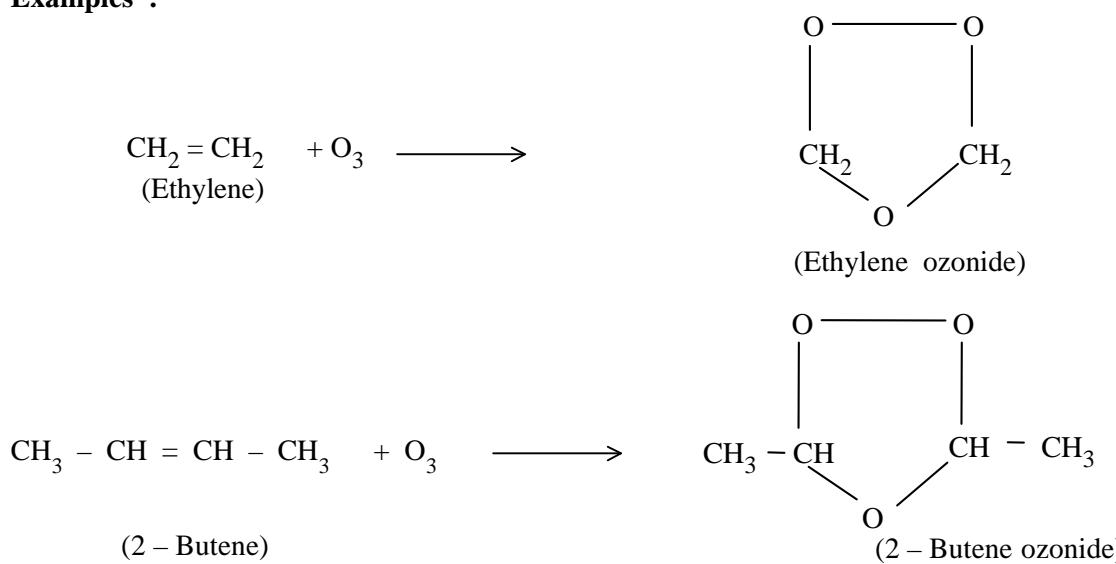


- (v) **Ozonolysis** : When ozone gas is bubbled into a solution of an alkene in an inert solvent (CHCl_3 or CCl_4) at low temperature, an addition compound known as **ozonide**, is formed.

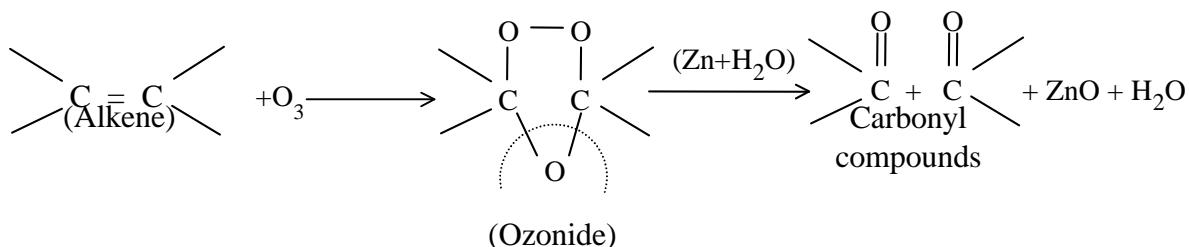


The reaction is known as **ozonisation** of alkenes. Ozonisation breaks both π and σ bonds of alkene.

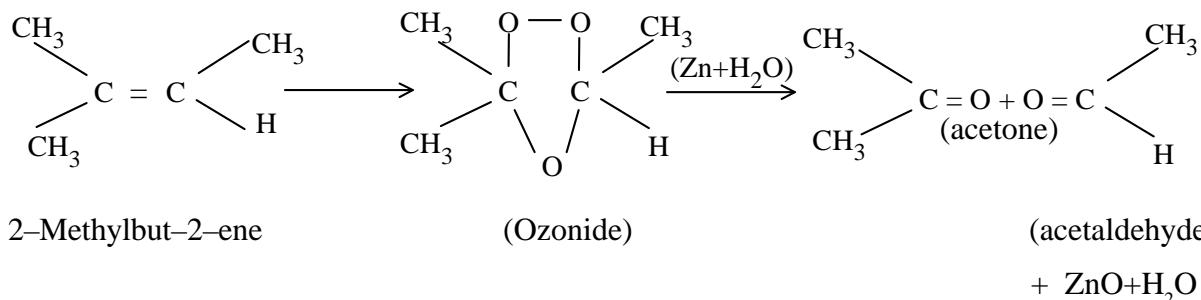
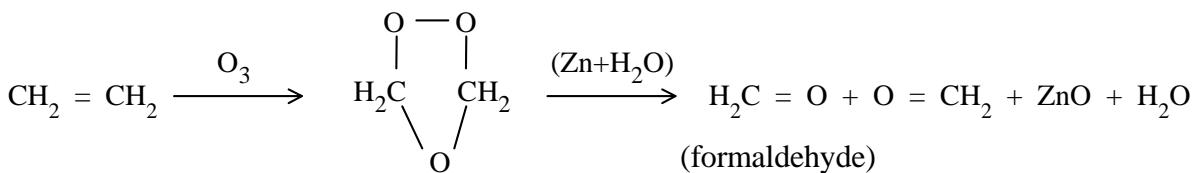
Examples :



Ozonides are unstable and when treated with reducing agents like zinc and water are cleaved at the position of double bond to give two carbonyl fragments. The cleavage of alkenes by the action of ozone and subsequent hydrolysis is known as **ozonolysis**. The products of ozonolysis are aldehydes, ketones or an aldehyde and a ketone depending on the nature of the alkenes. This reaction is highly helpful in detecting the position of the double bond in alkenes or other unsaturated compounds.

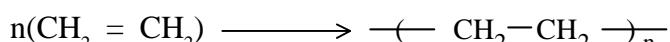
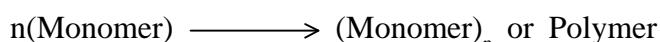


Examples :



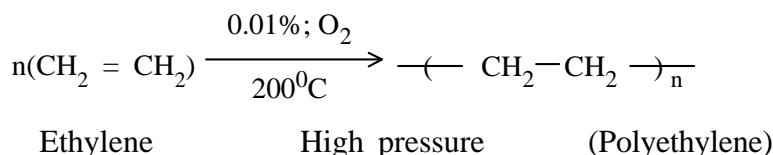
(8) *Polymerisation :*

A polymer is a long chain molecule with repeating structural units. The repeating structural units are generally known as **monomer** and the process of formation of polymers is known as **polymerisation**. Examples are polyethylene, polypropylene etc.



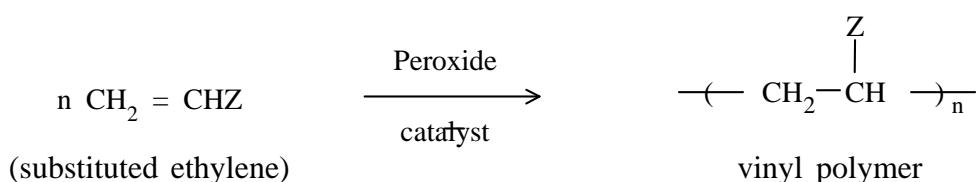
This type of polymerisation shown by alkenes without any loss of atoms is known as **addition polymerisation**. The alkene serves as monomer.

Polyethylene is manufactured by heating ethylene to about 200°C under high pressure (1500 – 2000 atm) in the presence of very small amount of oxygen.

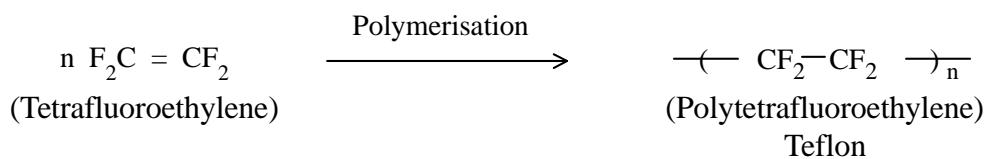
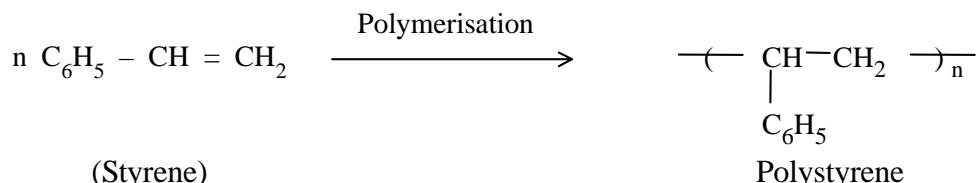
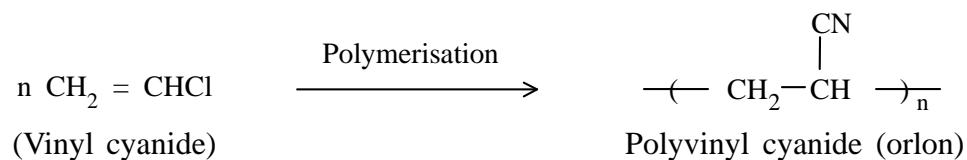
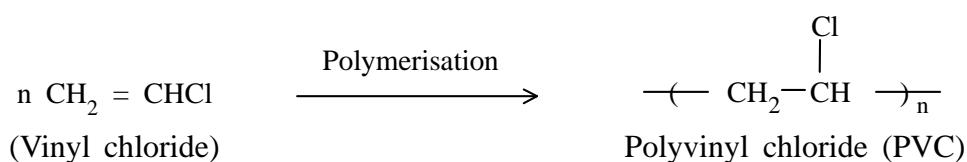


It is widely used for making wire, bottles, tubing, toys and packing materials.

Substituted ethylenes $\text{CH}_2 = \text{CHZ}$ ($Z = \text{Cl}, \text{CN}, \text{C}_6\text{H}_5$ etc) also undergo polymerisation to form a wide variety of commercially important synthetic polymers.



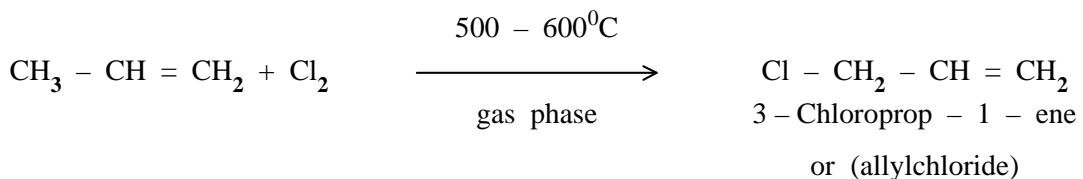
When Z = Cl, CN and C_6H_5 the polymers are known as polyvinyl chloride (PVC), polyvinyl cyanide (orlon) and polystyrene respectively.



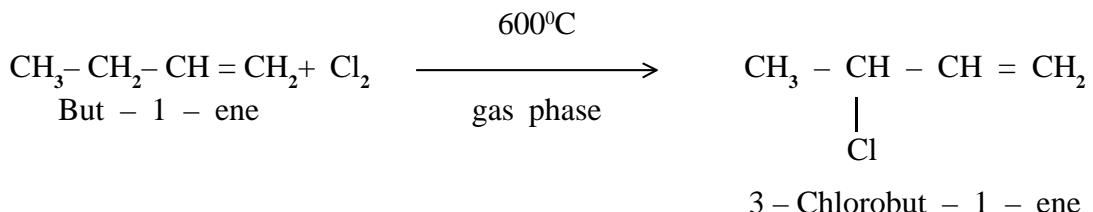
Teflon is used as electrical insulator and for making gaskets, valve seals and other lining on nonstick kitchenware.

(9) Substitution reaction in Alkenes :

All alkenes contain carbon carbon double bond and all except ethylene, also contain a saturated alkyl group as a part of the molecule. The alkyl groups of alkenes undergo substitution reaction at high temperature. Thus propylene reacts with chlorine at a temperature of $500^{\circ} - 600^{\circ}\text{C}$ to yield allyl chloride. Bromine behaves similarly.



When the alkyl group has more than one carbon atom, substitution occurs at the α carbon atom (allylic carbon atom). Thus,

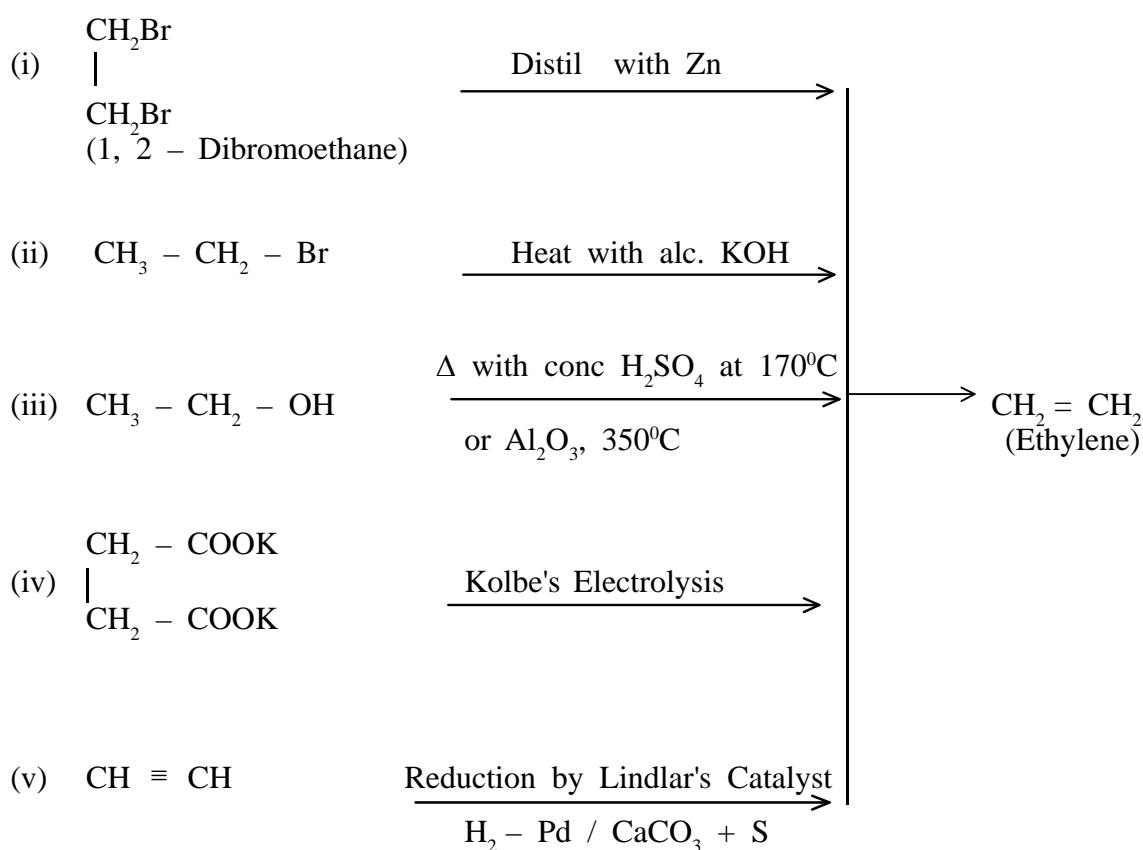


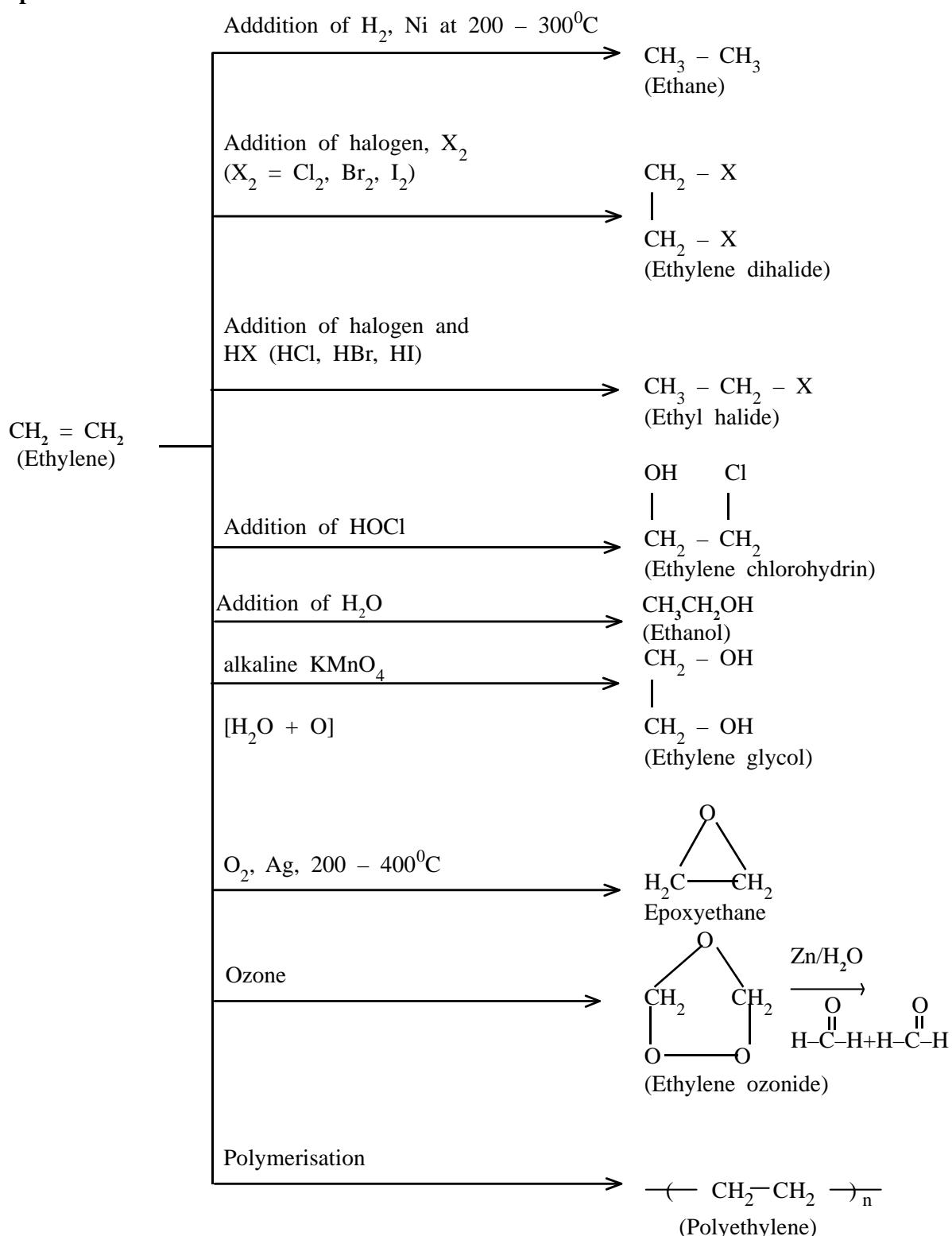
CHAPTER (18) AT A GLANCE

ALKENE

General molecular formula – C_nH_{2n}

Preparation of Ethylene :

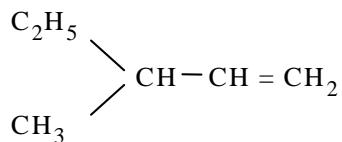


Properties :

QUESTIONS

(A) Short questions (One mark each)

1. What type of compounds undergo addition reaction ?
2. Ethylene reacts with dilute KMnO_4 to give _____.
3. Write down the structural formula of but – 2 – ene.
4. A double bond is composed of _____ sigma & one _____ bone.
5. Shape of ethylene molecule is _____.
6. Write the IUPAC name of the compound.



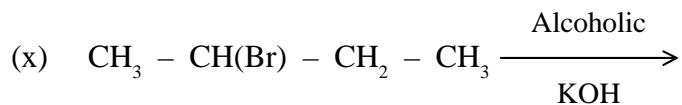
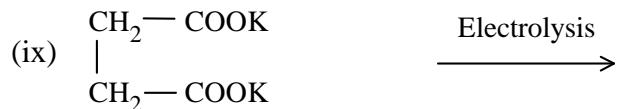
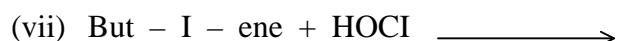
7. Which metal is used as catalyst in the hydrogenation of unsaturated hydrocarbons ?
8. What is the polymerised product of ethylene.
9. How many olefins are obtained when a mixture of 1-chloropropane and 2-chloropropane is heated with alcoholic KOH solution ? Name it/them.

(B) Short questions (Two marks each)

1. What happens when propene is treated with hydrogen gas in the presence of finely divided platinum as catalyst. Give equation.
2. State Markownikoff's rule.
3. What happens when ethylene reacts with ozone ?
4. What happens when sodium succinate solution is subjected to electrolysis ?
5. Write with equation what happens when propene and HBr react.
6. Which alkene is formed when an aqueous solution of sodium ethanoate is electrolysed ?
7. How is ethylene obtained from ethyl alcohol ? Give equation.
8. What is Kharasch Effect ? Discuss with example.
9. How can you detect unsaturation in an organic compound ? Give equation for the test.
10. How many isomers can be obtained from the molecular formula of dichloroethene ? Write their structures. Which of the isomer will have zero dipole moment ?
11. An unsaturated hydrocarbon having the molecular formula C_5H_8 gives two molecules one of formaldehyde and one molecule of 2-oxopropanal on ozonolysis. Write the structure of the hydrocarbon.
12. What happens when 2-bromobutane is treated with alc. KOH ?

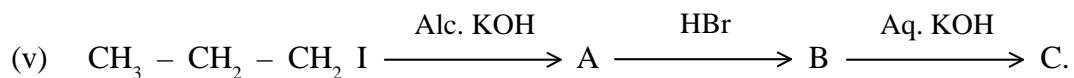
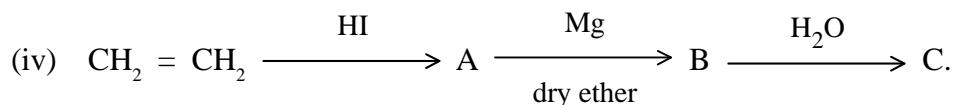
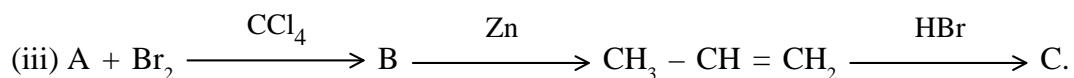
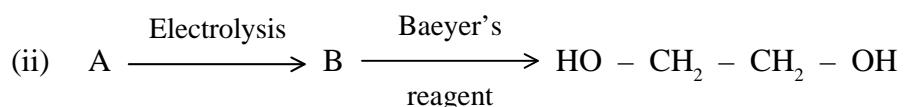
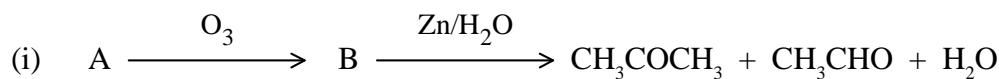
(C) Other short and objective Question :

1. Complete the following reactions.



[* Hint : In (IV) and (VI) normal addition product as per Markownikoff's rule will be obtained].

2. Identify the compounds A, B and C.



3. How would you carry out the following conversions ?
 - (i) Ethyl alcohol to ethylene and vice versa.
 - (ii) Ethane to ethylene and vice versa.
 - (iii) Ethyl bromide to ethylene and vice versa.
4. Explain the following.
 - (i) π – bond is weaker than sigma bond.
 - (ii) Ethane is insoluble in conc. H_2SO_4 , but ethene dissolves readily.
 - (iii) In the series HI, HBr, HCl, HI is easily added to the carbon carbon double bond.
 - (iv) But-1-ene reacts with hydrogen bromide in the presence of peroxide to give 1 – bromobutane but not 2 – bromobutane.
5. Fill in the blanks :
 - (i) Ethylene is prepared by the electrolysis of _____ .
 - (ii) An alkene has the general formula _____ .
 - (iii) Propylene can be obtained from methyl acetylene by _____ .
 - (iv) An alkene decolourises the _____ colour of _____ solution in CCl_4 .
 - (v) Hydration of _____ will give butan-2-ol.
 - (vi) But-2-ene exhibit both _____ and _____ isomerism.
 - (vii) Baeyer's reagent reacts with alkene to form _____ .
 - (viii) The reduction of $RC \equiv CR$ to $RCH = CHR$ with Na / liquid NH_3 produces _____ isomer.
 - (ix) The dehydration of alcohols producing alkenes is catalysed by _____ .

Answers :

- [(i) Potassium succinate, (ii) C_nH_{2n} , (iii) partial hydrogenation, (iv) red, bromine, (v) but-2-ene, (vi) position and geometrical, (vii) glycol, (viii) trans (ix) acid
6. Write the structural formula and IUPAC names for all isomeric pentenes C_5H_{10} . Include cis and trans isomers.
 7. Explain what is meant by sp^2 - hybridisation at carbon.

(D) Long Questions :

1. How ethylene is prepared from ethyl alcohol ? Explain it with equation. How does ethylene react with (a) HOCl (b) alkaline $KMnO_4$ (c) Ozone and treatment with water ?
2. Give a method for ascertaining the position of a double bond in a molecule.
3. Write notes on

(a) Markownikoff's rule.	(b) Ozonolysis
(c) Peroxide effect.	(d) Epoxidation
(e) Saytzeff rule	(f) Polymerisation
4. Discuss the structure of ethylene molecule. Describe two methods of preparation of alkenes.

5. What are alkenes ? Give the general methods of preparation of alkenes.
6. How ethylene is prepared from ethyl chloride ? How can you convert ethylene into (a) Ethane (b) Acetylene (c) Ethyl alcohol (d) Ethyl bromide ?
7. How are alkenes prepared from
 - (a) alkyl halides (b) alcohols

What happens when propene reacts with the following substances

 - (a) HOCl (b) alkaline KMnO_4 (c) Ozone
8. How is ethene prepared from (a) ethyl alcohol (b) Sodium Succinate ? What happens when ethene reacts with the following substances ?
 - (a) HOBr (b) Ozone (c) Alkaline KMnO_4 .

(E) Multiple choice questions :

1. Propene belongs to
 - (a) Paraffins (b) Alkynes (c) Olefins (d) Alkanes
2. Alkene is formed by the dehydration of an
 - (a) Alcohol (b) Acid (c) Aldehyde (d) Amide
3. Which one of the following decolourises dilute alkaline solution of KMnO_4 .
 - (a) ethane (b) ethylene (c) methane (d) CCl_4
4. Which one of the following gases is produced when potassium succinate is electrolysed ?
 - (a) ethane (b) ethylene (c) acetylene (d) propane
5. The product obtained after the hydrolysis of ethylene ozonide is
 - (a) CH_3CHO (b) $\text{CH} \equiv \text{CH}$ (c) HCHO (d) C_2H_6 .
6. The reaction of HCl with ethylene is an example of
 - (a) Substitution (b) Polymerisation (c) Condensation (d) Addition
7. The middle carbon atom in $\text{CH}_2 = \text{C} = \text{CH}_2$ has the hybridisation
 - (a) sp (b) sp^2 (c) sp^3 (d) dsp^2
8. In the addition of haloacids to alkenes, Kharasch peroxide effect was shown only by
 - (a) HF (b) HCl (c) HBr (d) HI
9. Addition of a molecule of HBr to but - 1 - ene in the presence of peroxide gives.

(a) n - Butane	(b) 1 - Bromobutane
(c) 2 - Bromobutane	(d) 1,2 - Dibromobutane
10. 2 - Chlorobutane when treated with alcoholic KOH gives

(a) 2 - Butanol	(b) 2 - Butene
(c) 4 - Butene	(d) none of above
11. Out of the following alkenes, the one which shows geometrical isomerism is

(a) 1 - Butene	(b) 2 - Butene
(c) Ethene	(d) Propene

ANSWERS

1. (c) 2. (a) 3. (b) 4. (b) 5. (c) 6. (d)
7. (a) 8. (c) 9. (b) 10. (b) 11. (b) 12. (d)
13. (c) 14. (a) 15. (d) 16. (d) 17. (d) 18. (b)

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CHAPTER - 19

UNSATURATED HYDROCARBONS-ALKYNES

Alkynes are unsaturated hydrocarbons with carbon-carbon triple bond ($C \equiv C$). They have the general formula C_nH_{2n-2} . The simplest member of this family, acetylene has the molecular formula C_2H_2 . Alkynes have two hydrogen atoms less than the corresponding alkenes. They are also known as 'acetylenes' after the name of the first member, acetylene. The triple bond, $-C\equiv C-$, in an alkyne constitutes the functional group and largely determines the chemical behaviour.

19.1 NOMENCLATURE

In the IUPAC system, this class have the suffix-*yne*. They are named after the corresponding alkane by replacing the suffix *-ane* by *-yne*. The IUPAC system of naming the alkyne follows the following rules.

- (i) the rules for numbering the carbon atoms are the same as for alkenes.
- (ii) hydrocarbons with two triple bonds are called alkadiynes.
- (iii) hydrocarbons with both double and triple bond are called alkenynes.

In numbering alkenynes, the double bond is given preference over the triple bond, provided it does not violate the lowest set of locants rule

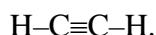
$H-C\equiv C-H$	$CH_3-C\equiv C-CH_3$
(Ethyne)	(But-2-yne)
$CH_3-C\equiv C-H$	$HC\equiv C-C\equiv CH$
(Propyne)	(Butadiyne)
$CH_3-CH_2-C\equiv CH$	$CH_3-CH=CH-C\equiv CH$
(But-1-yne)	(Pent-3-en-1-yne).
	(Not Pent - 2 - en - 4 - yne)

19.2 STRUCTURE OF ALKYNE

Alkynes can be represented by the general formula



where R may be alkyl group or H. The simplest member, acetylene can be represented as



In the formation of acetylene molecule *sp*- hybridised carbon atoms are used.

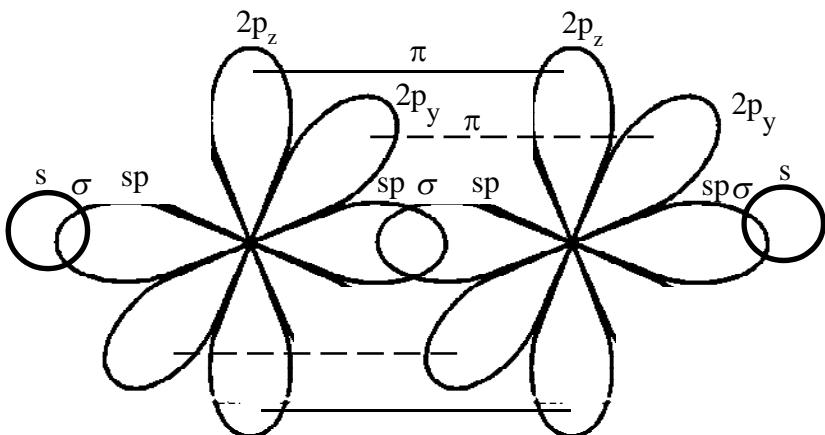


Fig. 19.1 Orbital structure of acetylene

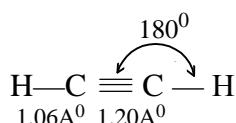
Acetylene is a linear molecule. The carbon-carbon triple bond consists of one sigma (σ) and two pi (π) bonds. (Fig.18.1)

The C–C–H bond angle is 180° .

The C–C bond length is 1.20 \AA^0 .

The C–H bond length is 1.06 \AA^0 .

The bond length and bond angle in acetylene molecule are shown below.

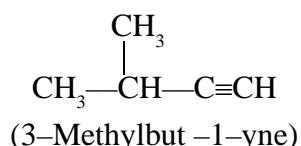
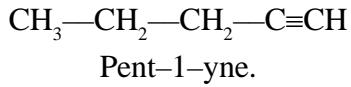


19.3 ISOMERISM

Alkyne being a linear molecule, do not exhibit *cis-trans* isomerism. Acetylene and methylacetylene do not exhibit isomerism. However, the following types of isomerism are shown by higher alkynes.

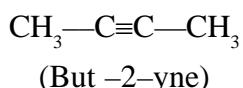
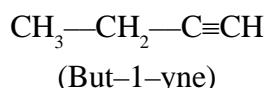
(i) Chain Isomerism :

Alkynes differ in the structure of parent chain.



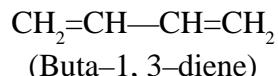
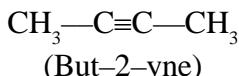
(ii) Position Isomerism :

Alkynes differ in the position of the triple bond



(iii) Functional isomerism

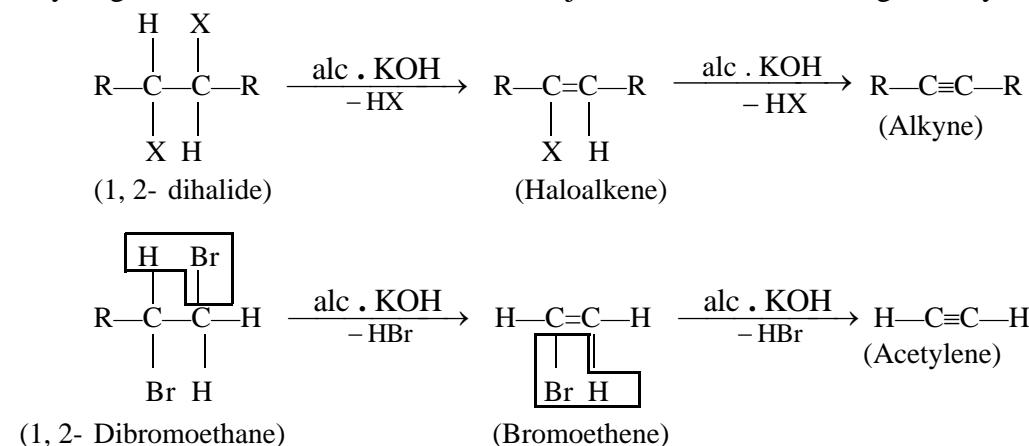
Alkynes are isomeric with alkadienes.



19.4 METHODS OF PREPARATION

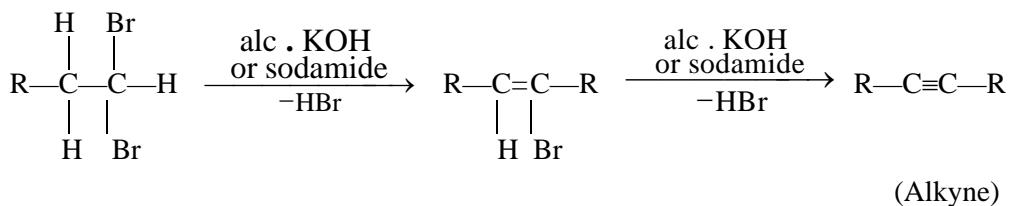
1. Dehydrohalogenation of vicinal dihalides :

When vicinal or 1,2- dihalo compounds are treated with alcoholic KOH, two molecules of hydrogen halides are eliminated from adjacent carbon atoms to give alkynes.



2. Dehydrohalogenation of gem- dihalides :

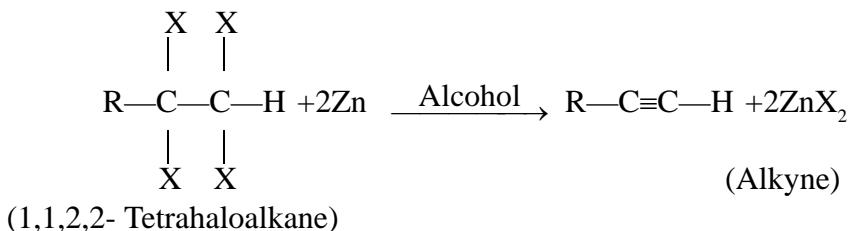
Gem- or 1,1- dihalides when treated with alcoholic KOH or sodamide double dehydrohalogenation takes place forming alkynes.

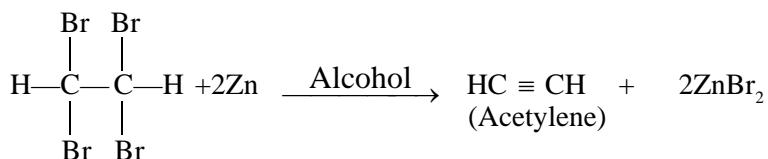


When R=H, we get H-C≡C-H (acetylene).

3. Dehalogenation of tetrahalides :

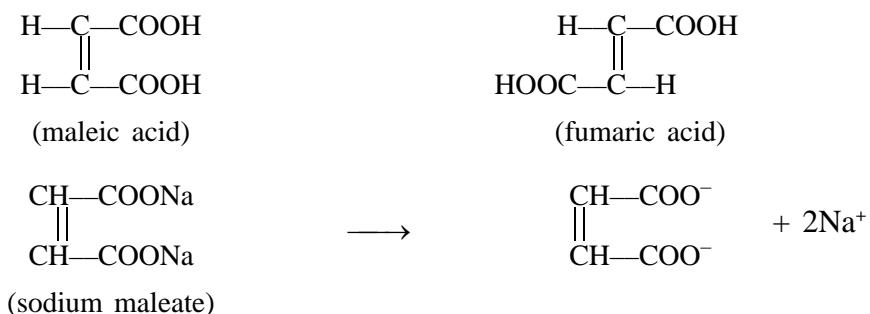
Tetrahalides in which the four halogen atoms are attached to two adjacent carbon atoms, when treated with zinc dust in ethanol yield alkynes.



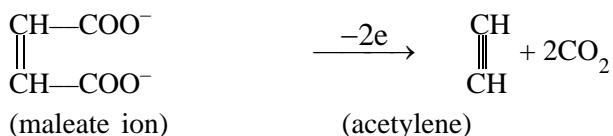


4. Kolbe's electrolytic method :

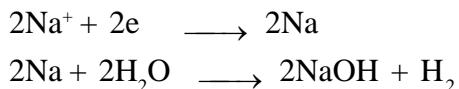
When a concentrated solution of sodium or potassium salt of maleic or fumaric acid is electrolysed, acetylene is obtained at the anode.



At the Anode



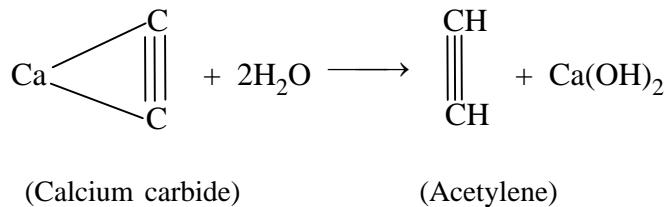
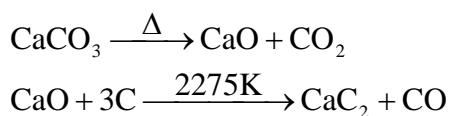
At the Cathode



5. Laboratory method of preparation of acetylene :

In the laboratory acetylene is prepared by the action of water on calcium carbide (CaC_2)

Calcium carbide required for this purpose is manufactured by heating lime stone with coke in an electric furnace.



Acetylene thus obtained is contaminated with impurities like NH_3 , H_2S , PH_3 , AsH_3 etc. The gas is purified by bubbling it through acidified copper sulphate solution, which absorbs NH_3 , PH_3 , H_2S , and AsH_3 except acetylene. Acetylene is collected by the downward displacement of water.

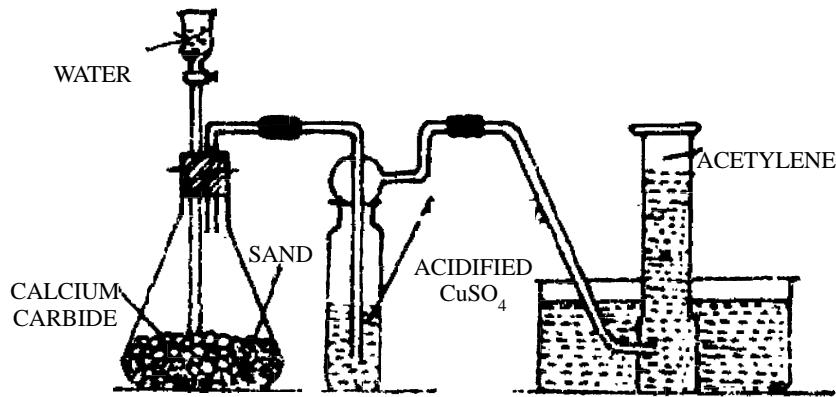
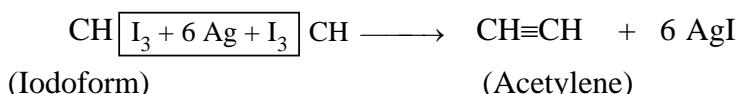


Fig. 19.2 Preparation of Acetylene

The apparatus consists of conical flask fitted with a dropping funnel and a delivery tube. The end of this delivery tube is dipped in acidified CuSO_4 solution. A mixture of CaC_2 and sand is taken in the conical flask and water is added from the dropping funnel. The gas after bubbling through CuSO_4 solution, is collected by the downward displacement of water.

6. From Iodoform :

Iodoform when heated with silver powder, pure acetylene is formed.



7. Synthesis :

Berthelot (1860) synthesised acetylene by striking an electric arc between two carbon electrodes in an atmosphere of hydrogen inside a silica tube. The yield is only 7%.



19.5 **PROPERTIES**

(A) Physical Properties :

- State :** The first three members ($\text{C}_2 \rightarrow \text{C}_4$) are gases, next fourteen (C_5 to C_{18}) are liquids and the higher alkynes ($\text{C}_{19} \rightarrow$) are solids.
- Colour and odour :** All alkynes are colourless and odourless except acetylene which has characteristic garlic odour.
- Solubility :** Alkynes are compounds of low polarity and hence they are slightly soluble in water. Alkynes are soluble in organic solvents like ether, benzene, carbon tetrachloride etc.
- Melting point, boiling point and density :** The melting point, boiling point and density of alkynes are slightly higher than the corresponding alkanes. These properties regularly increase with the increase in molecular mass. Again, branched chain alkynes have lower melting points than their corresponding straight chain isomers.

(B) Chemical properties :

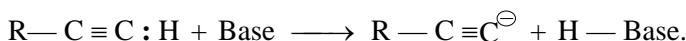
The chemical properties of alkynes are mainly due to the

(i) Presence of electrons :

Alkynes are characterised by the presence of triple bond (i.e. one sigma and two pi-bonds). Due to the presence of pi bonds, which contain loosely held pi electrons, alkynes undergo electrophilic addition reactions like alkenes. However, the addition reactions of alkynes differ from those of alkenes in the aspect that, $\text{C}\equiv\text{C}$ is less reactive than $\text{C}=\text{C}$.

(ii) Presence of acidic hydrogen atoms :

Hydrogen atom attached to carbon – carbon triple bond can be easily removed by a strong base and hence acetylenes are considered as weak acids.

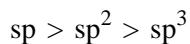


As we move from ethane to ethylene and then to acetylene, there is a gradual increase in s-character.

Hydrocarbon	 $\text{H}-\text{C}(\text{H})-\text{C}(\text{H})-\text{H}$	 $\text{H}-\text{C}(\text{H})=\text{C}(\text{H})-\text{H}$	 $\text{H}-\text{C}\equiv\text{C}-\text{H}$
Type of hybridisation	sp^3	sp^2	sp
s-character in C	25%	33.3%	50%

Due to more s-character of the sp-hybrid carbon in alkyne, the electron pair constituting the C—H bond is closer to the carbon nucleus than in an alkene and alkane.

We know that higher the electronegativity of an atom greater is the ability to hold bonding electrons to it. The electronegativity of the three types of carbon atom is

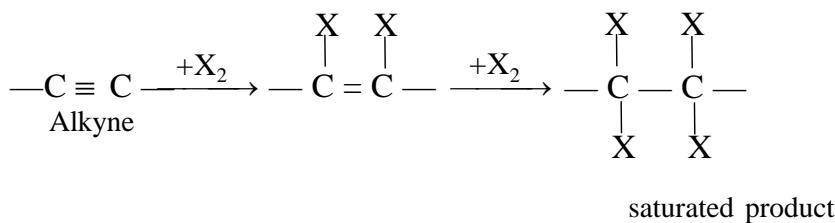


Hence, hydrogen atom in an alkyne will tend to be more positive and can be easily removed as a proton.

The general reactions of alkynes are given below.

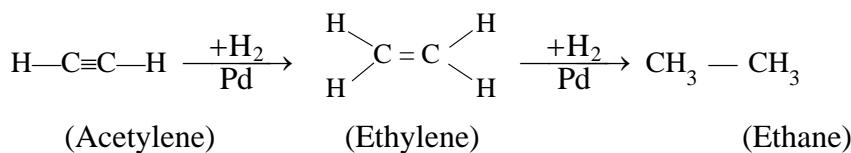
(I) ADDITION RECTIONS :

Alkynes can add two molecules of a reagent, while an alkene can add one molecule only.

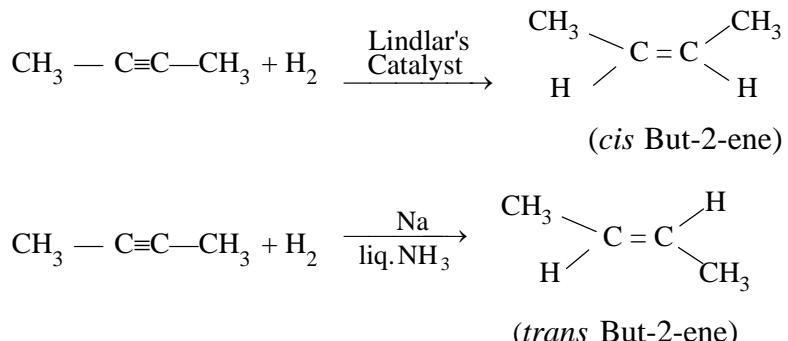


(a) Addition of Hydrogen (Catalytic hydrogenation) :

In the presence of catalyst like finely divided Pt, Pd or Raney nickel, alkynes add up two molecules of hydrogen forming the corresponding alkenes first and finally the alkanes.

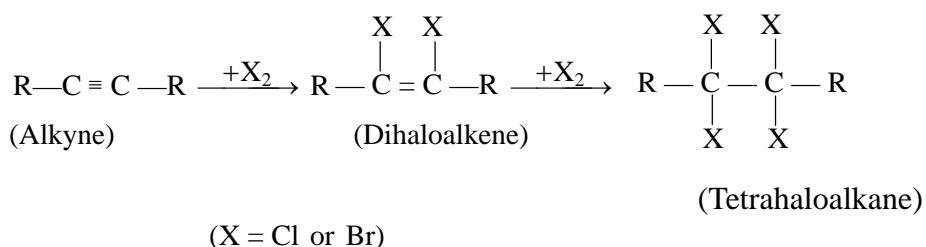


Catalytic hydrogenation of disubstituted alkyne with Lindlar's catalyst ($\text{Pd}-\text{CaCO}_3$) gives the *cis*-alkene, whereas reaction with Na or Li in liquid ammonia gives *trans*-alkene (Birch reduction)

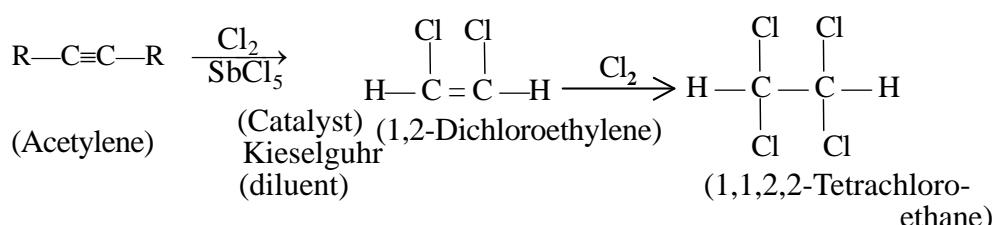


(b) Addition of halogens :

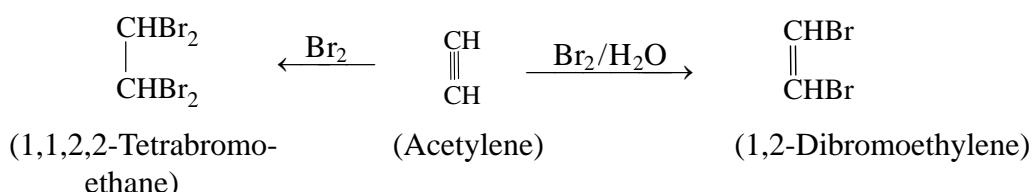
Alkynes add two molecules of halogens (chlorine or bromine) in the dark at room temperature forming first dihaloalkenes and then a tetrahaloalkanes.



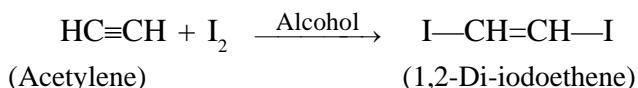
For example,



Acetylene reacts with bromine water to give the dibromide, whereas with bromine (liquid) in the absence of any solvent gives tetrabromide.



Acetylene di-iodide only is obtained with iodine, when the reaction is carried out in alcoholic solution.



The order of reactivity of halogen is

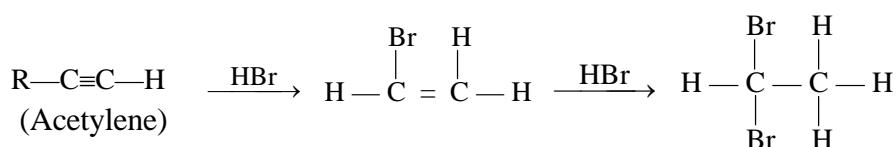
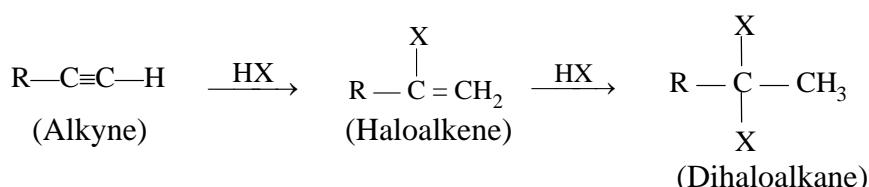
\text{F} > \text{Cl} > \text{Br} > \text{I}



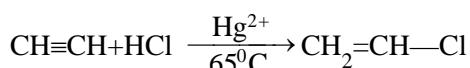
(c) **Addition of hydrogen halides :**

Alkynes add two molecules of halogen halides forming haloalkenes in the first step, then gemdihalides in the second step.

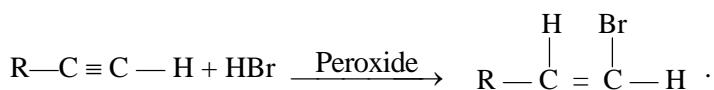
The addition of hydrogen halide to unsymmetrical alkynes follows Markownikoff's rule in both the steps. The order of reactivity is $\text{HI} > \text{HBr} > \text{HCl}$.



Dilute HCl reacts with acetylene at 65°C in the presence of mercuric ion when only one molecule of HCl is added giving vinyl chloride.



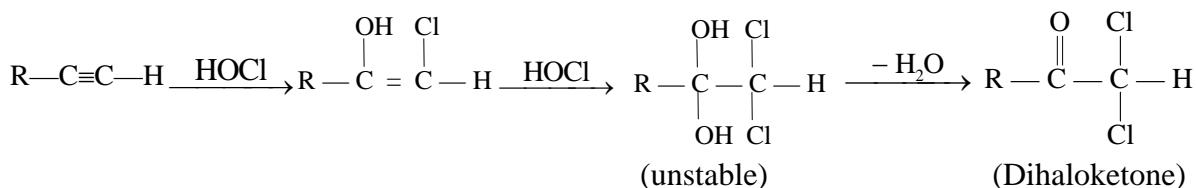
Peroxide have the same effect on the addition of HBr to alkyne as on alkene.



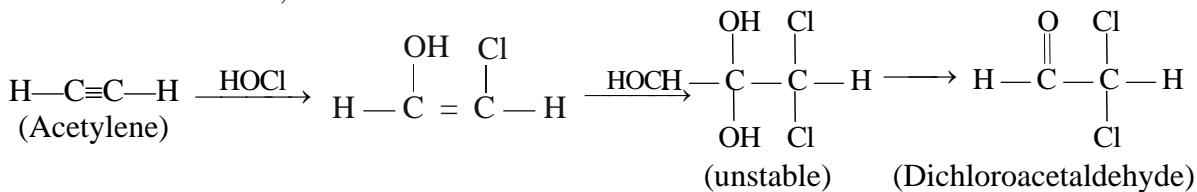
(d) Addition of Hypohalous acid :

Alkynes add two molecules of hypohalous acid (HOX) in two steps forming a dihaloaldehyde in case of acetylene or a dihaloketone in case of an alkyl acetylene.

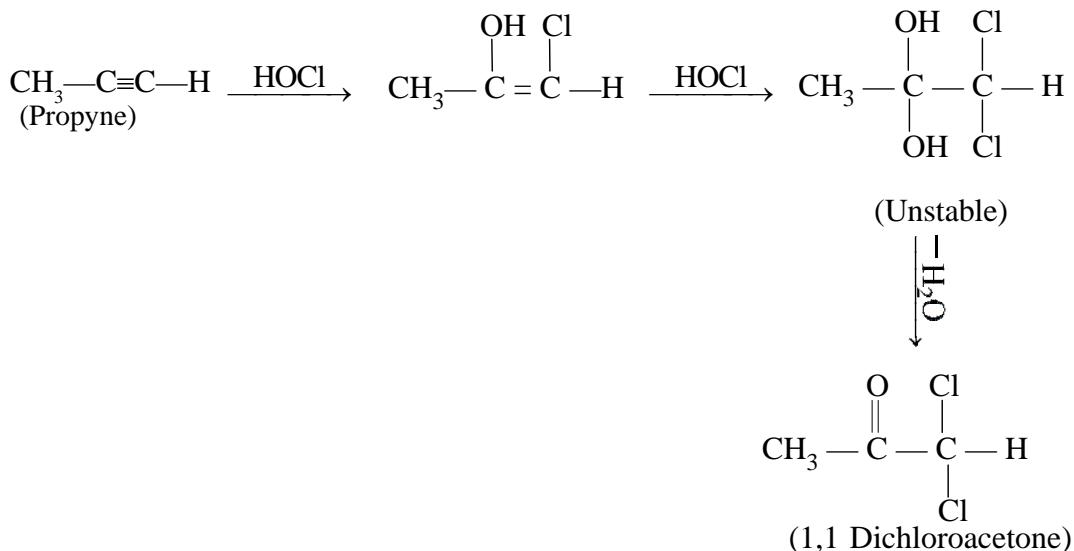
Addition takes place according to Markownikoff's rule.



When $R = H$,

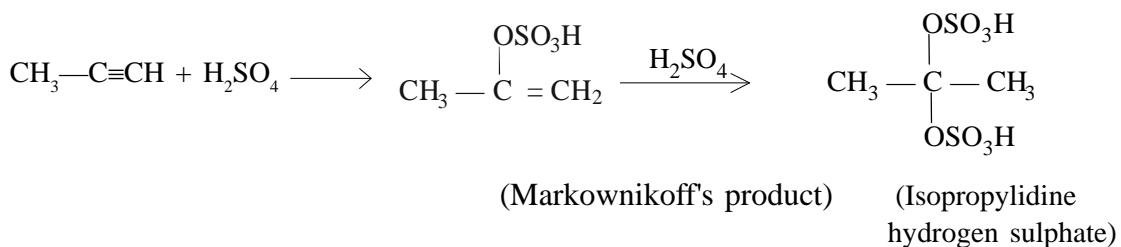


When R = CH₃,



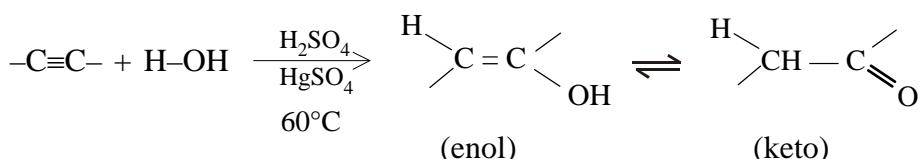
(e) Addition of Sulphuric acid :

Two molecules of sulphuric acid add to an alkyne molecule at room temperature to give dihydrogen sulphate derivative of alkyne in two steps, which is in accordance with Markownikoff's rule.

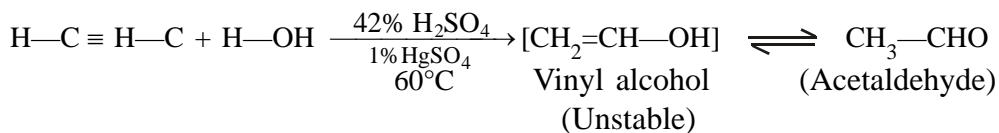


(f) Addition of Water :

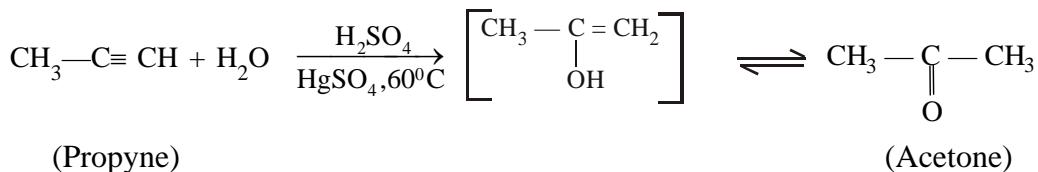
Water adds to alkynes in presence of dilute H_2SO_4 and mercuric sulphate catalyst. The addition takes place according to Markownikoff's rule to give initially an adduct called enol ($-\text{ene} + \text{ol}$). Enols are unstable and are immediately converted to stable keto compounds.



Thus when acetylene is passed through 42% H_2SO_4 in presence of 1% $HgSO_4$ at $60^\circ C$, acetaldehyde is formed.

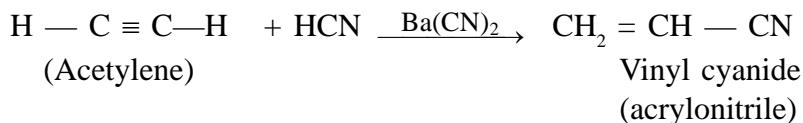


Propyne gives acetone under this condition.



(g) Addition of Hydrogen cyanide :

Alkynes add hydrogen cyanide in presence of barium cyanide to form alkenyl cyanides. Thus, acetylene with HCN gives vinyl cyanide (acrylonitrile), used for the preparation of synthetic fibre "orlon".



II. SUBSTITUTION REACTION :

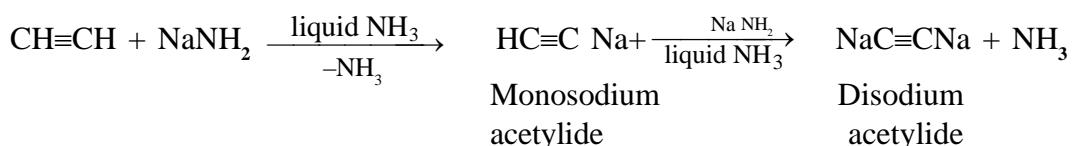
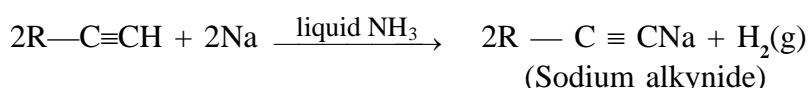
(a) Formation of metallic derivatives :

A hydrogen atom attached to triply bonded carbon atom is slightly acidic in nature and hence can be easily replaced by only strong base to form the corresponding salt called **acetylide** or **alkynide**.

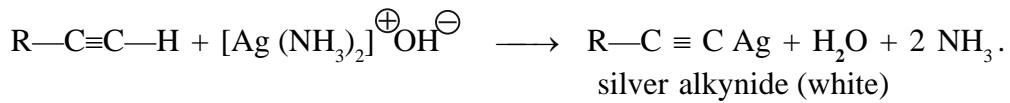
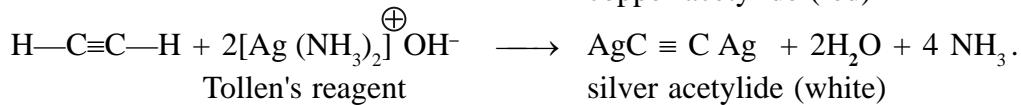
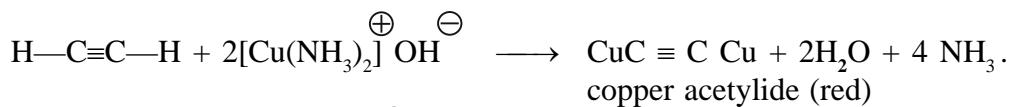
Alkynides are generally unstable and explosive. These are easily converted into alkynes when heated with dilute acids.

(i) Sodium alkynides :

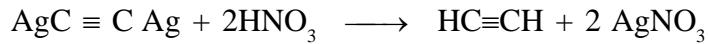
Acetylene and terminal alkynes react with sodium metal at 475K or sodamide in liquid ammonia as solvent to form sodium acetylide and sodium alkynide respectively with evolution of H_2 gas.



- (ii) Acetylene reacts with ammoniacal solution of cuprous chloride and silver nitrate to form the corresponding copper acetylidyne (red) and silver acetylidyne (white) precipitate.

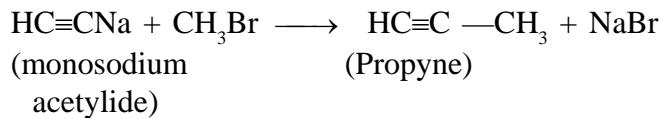


These alkynides are unstable and explode in dry state. Hence, they should be decomposed while still wet by warming with dilute mineral acid which liberate back the alkynes.

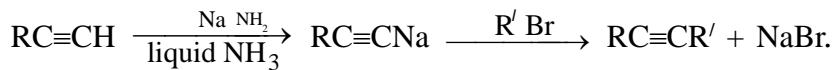


(b) Alkylation of Alkynes :

Monosodium acetylidyde on treatment with alkyl halides preferably a bromide, forms a higher homologue of acetylene.

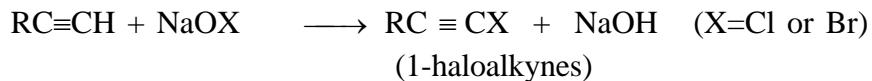
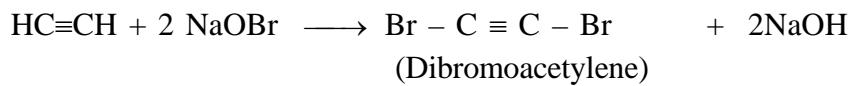
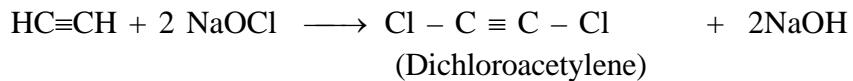


The above reaction may be carried out with 1-alkynes.



(c) Substitution by halogens :

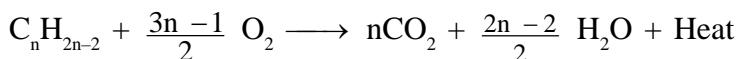
Acetylene and 1-alkynes react with NaCl or NaOBr to form the corresponding di- and monohalo derivatives.



(III) OXIDATION REACTIONS :

(i) Combustion :

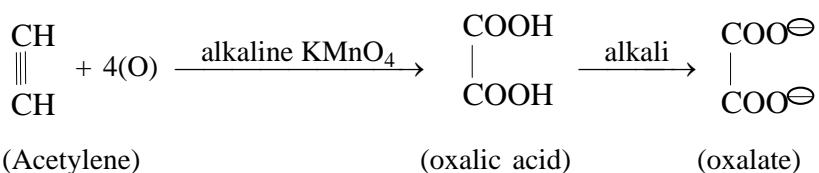
All alkynes burn in oxygen producing carbon dioxide and water as the end products. At the same time tremendous amount of heat is liberated.



Therefore, oxyacetylene flame is used for cutting and welding of metals.

(ii) Chemical oxidation :

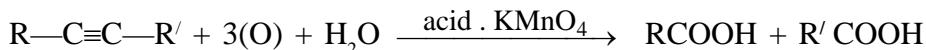
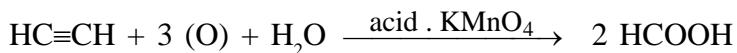
- (a) Alkaline potassium permanganate oxidises acetylene to salt of oxalic acid.



- (b) Acidified potassium dichromate oxidises acetylene to acetic acid,

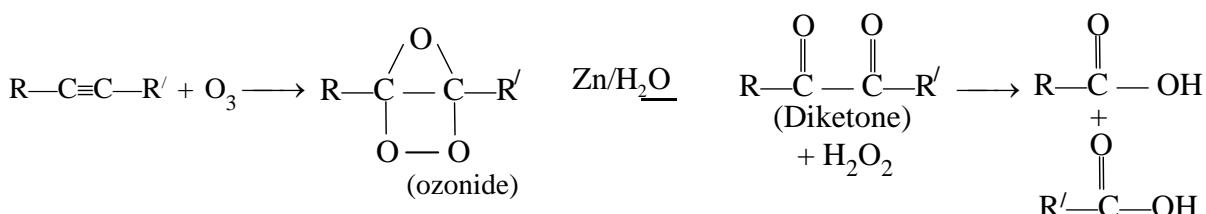


- (c) Acidified KMnO_4 oxidises acetylene to formic acid with cleavage of the triple bond.

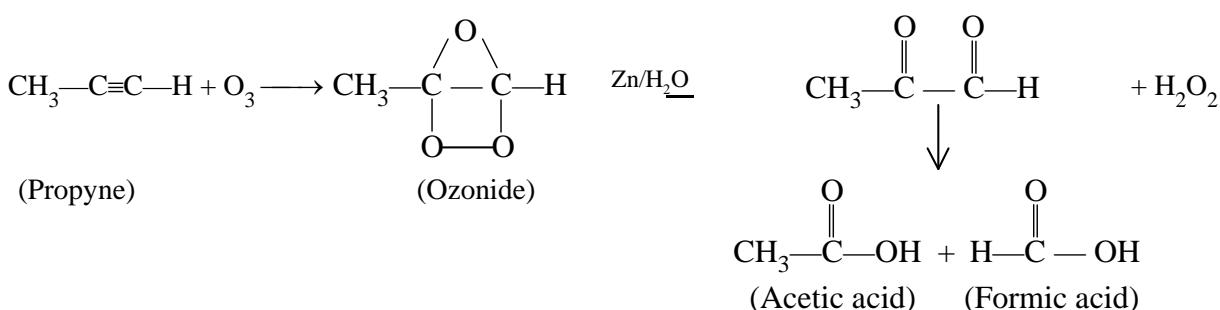
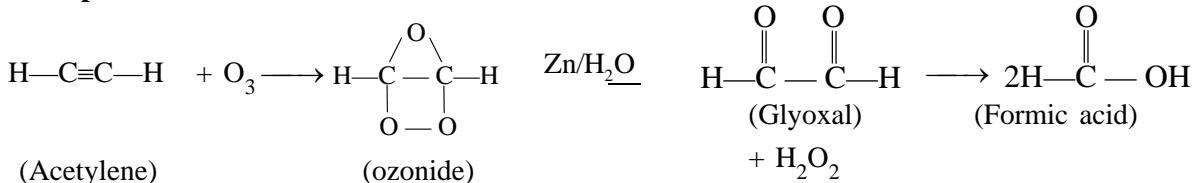


(iii) Ozonolysis :

Alkynes react with ozone. The rate of formation of ozonide is slower than that of alkenes. These ozonides on decomposition with $2n$ /water yield carboxylic acids.



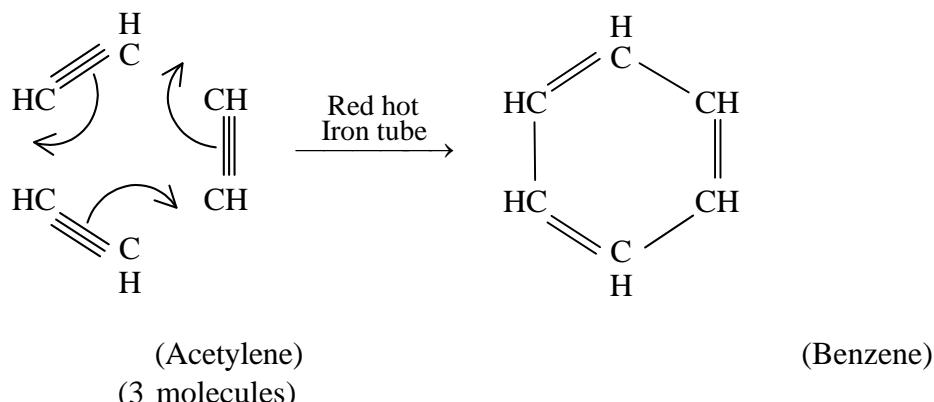
Examples :



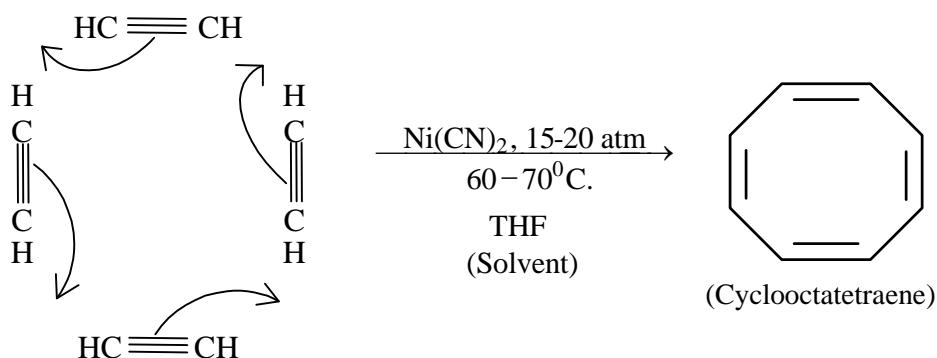
(IV) POLYMERISATION REACTION :

(i) Alkynes when passed through a red hot quartz or iron tube in the presence of chromic acid polymerise to yield aromatic hydrocarbons.

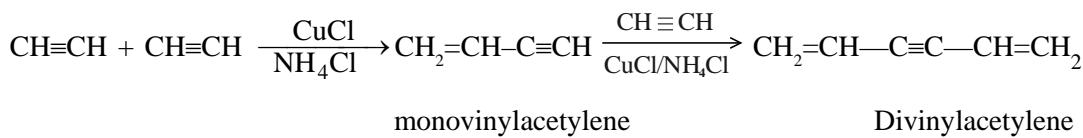
Thus, acetylene molecule trimerizes to produce benzene



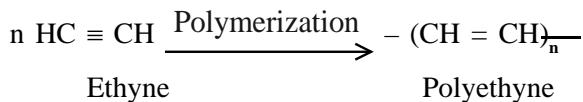
(ii) In the presence of nickel cyanide at high pressure, acetylene tetramerizes to produce cyclooctatetraene



(iii) When passed through CuCl solution containing NH_4Cl , acetylene forms a mixture of mono-and divinyl acetylene. Here linear polymerisation takes place.

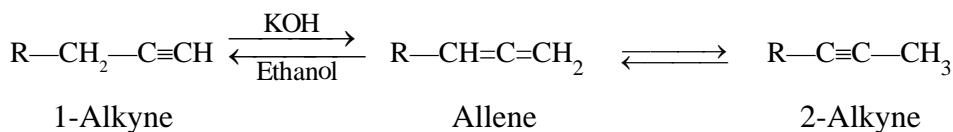


(iv) Linear polymerisation of ethyne takes place under suitable conditions to produce polyacetylene which conducts electricity. Thin films of polyacetylene can be used as electrodes in batteries.



(V) ISOMERISATION :

1-Alkynes when treated with KOH in ethanol readily isomerize to the more stable 2-alkynes.



The above rearrangement which take place through the formation of allene are called **acetylene- allene rearrangement**, which is reversible.

19.6 USES OF ACETYLENE :

1. Acetylene is used for the artificial ripening of fruits.
2. Acetylene is used for illumination purposes in hawker's lamp and light houses.
3. Oxyacetylene flame is used in welding, cutting and cleaning iron and steel.
4. It is used for the manufacture of acetaldehyde, acetic acid, alcohol etc.
5. Industrial solvents like westron and westrosol are prepared from acetylene.
6. It is used in the commercial production of polymers like synthetic rubber, plastics, fibres etc.

19.7 DISTINCTION OF ETHANE, ETHENE AND ETHYNE

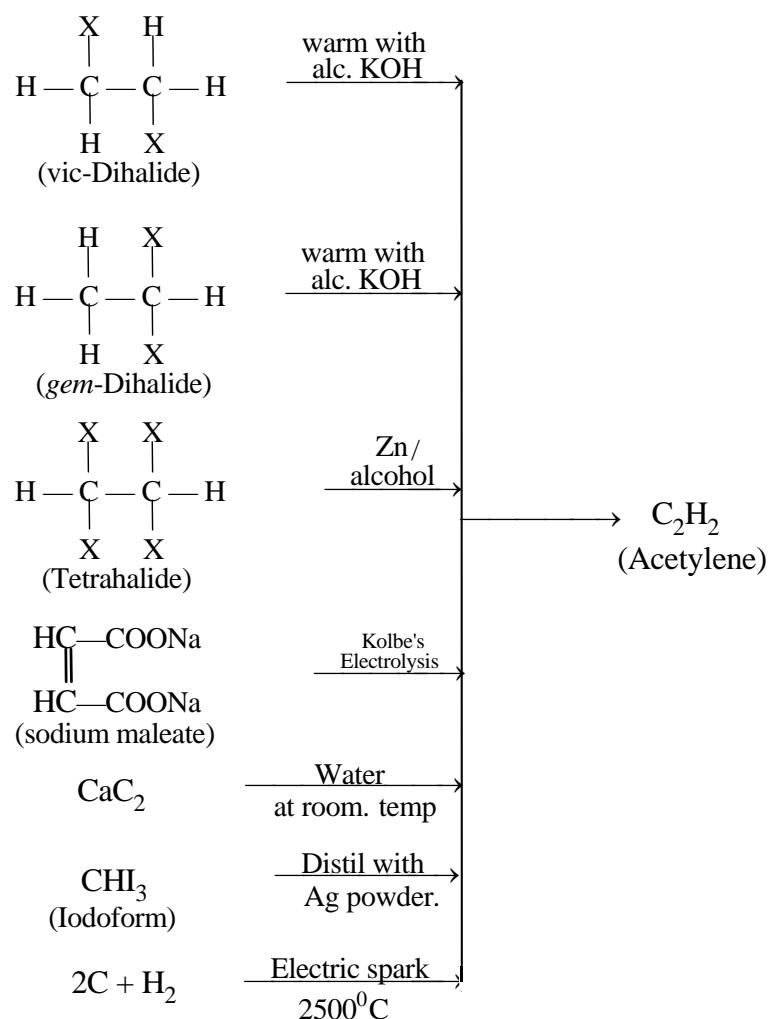
	Test	Ethane	Ethene	Ethyne
1.	Burning	Burns with a nonluminous flame	Burns with a luminous flame	Burns with a luminous flame
2.	Bromine water	No change in colour of the solution	Colour of bromine water discharged	Colour of bromine water discharged.
3.	Baeyer's reagent	No reaction	Decolourises	Decolourises
4.	Ammoniacal silver nitrate solution.	No reaction	No reaction	White ppt.
5.	Ammoniacal cuprous chloride solution	No reaction	No reaction	Red ppt.

CHAPTER (19) AT A GLANCE

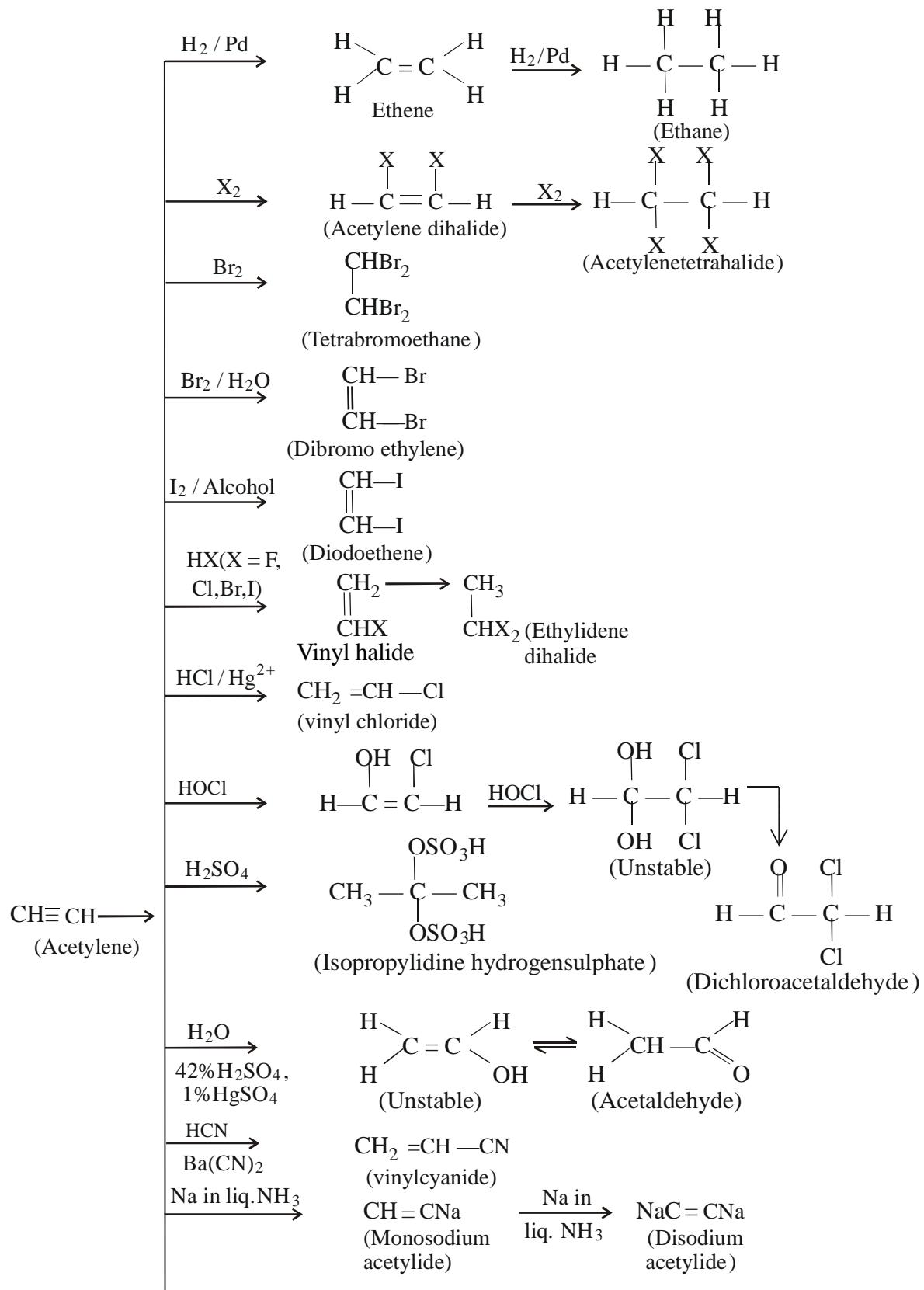
ALKYNES :

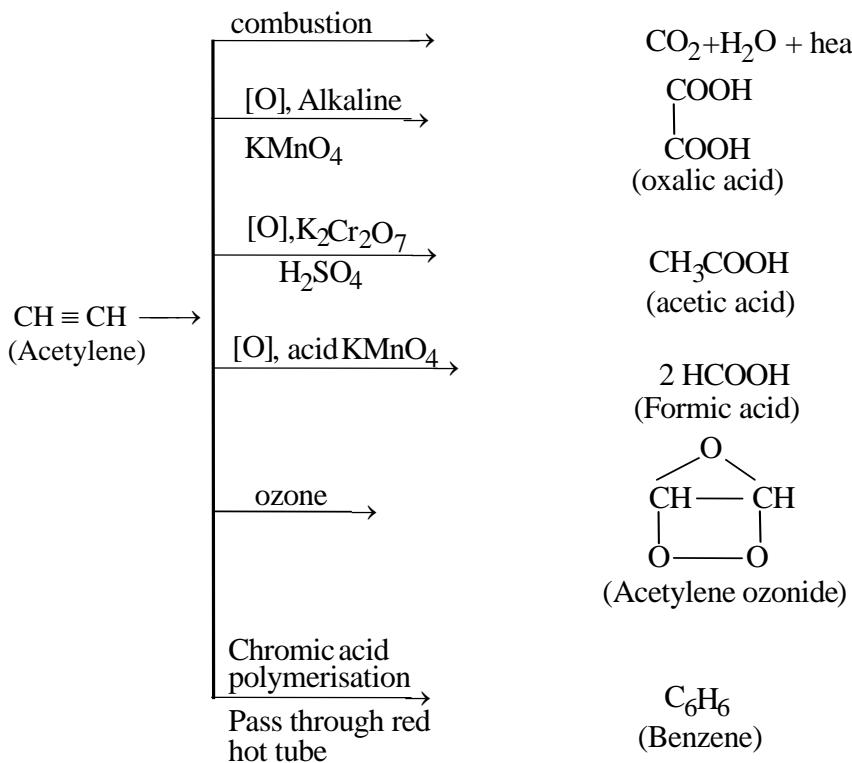
General Formula : C_nH_{2n-2}

1. Preparation of Acetylene :



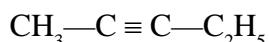
2. Properties of Acetylene :




QUESTIONS
(A) Short Questions (one mark each)

1. In acetylene, the triple bond between two carbon atoms consists of
 - One sigma and two pi bond,
 - One sigma and one pi bond
 - Two sigma and the pi bond.
2. How will you convert acetylene to acetic acid ?
3. Indicate the hybridisation state of carbon atom in acetylene.
- 4.(a) Which compound is formed when acetylene is passed into 42% H_2SO_4 at 60°C in the presence of HgSO_4 ?

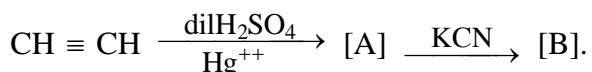
(b) How is acetylene converted to acetaldehyde ?
5. How many sigma & pi bonds are present in acetylene molecule ?
6. What is the IUPAC name of the compound.



7. How do you get acetylene from ethylenedibromide ?
8. What is Baeyer's reagent ?
9. Name a reagent which can differentiate 1- Butyne from 2- Butyne through a precipitation reaction

(B) Short Questions (two marks each)

1. Complete the following reaction :



2. What happens when acetylene is treated with hydrogen bromide ?
3. How is acetylene prepared from calcium carbide ?
4. How can you obtain benzene from acetylene ?
5. How to get ethane from acetylene ?
6. State a reaction with equation to establish the acidic character of ethyne molecule.
7. How would you distinguish ethylene and acetylene ? Give one specific test for each.
8. Identify A, B and C. Explain the reaction.

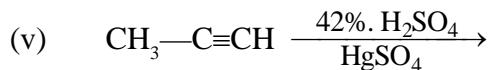
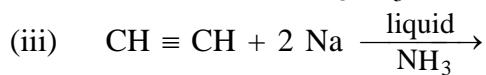


9. What is the type of hybridisation of orbitals of carbon involved in a acetylene molecule?
10. Explain why acetylene exhibits slightly acidic character whereas ethane does not have such a property.
11. What happens when acetylene is passed through ammonical silver nitrate solution. Give equation.
12. Suggest a test to distinguish but-1-yne and but-2-ene. Give equation.

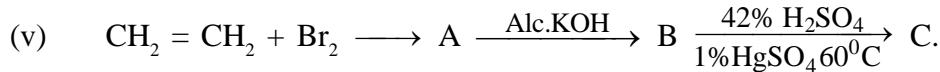
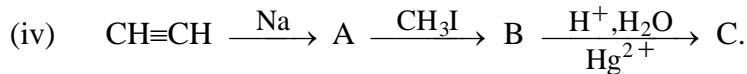
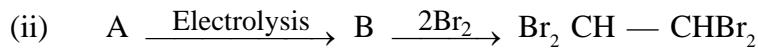
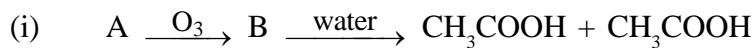
(C) Other short and objective questions : (Three marks each)

1. Write the structural formulae and IUPAC names of all isomeric butynes C_4H_6 .
2. Describe what is meant by sp-hybridisation at carbon.
3. Explain why acetylene is linear.
4. Write the reaction of ozonolysis of 2-butyne.
5. Write the structural formulae of alkyne which on ozonolysis gives a mixture of acetic acid and propionic acid.
6. Explain why the hydrogen atoms of acetylene are acidic.
7. What happens when acetylene is passed through ammoniacal CuCl solution ?

8. Complete the following equations :



9. Identify the compound A, B and C.



10. How the following conversions are made :

(i) Ethane to Ethyne and vice versa.

(ii) 1, 1, 2, 2-tetrabromoethane to acetylene and vice versa.

11. Fill in the blanks :

(i) Acetylene is prepared by the electrolysis of _____.

(ii) An alkyne has general formula _____.

(iii) 1-Alkyne forms white precipitate with _____ solution.

(iv) Acetylene is converted to ethane by _____.

(v) An alkyne decolourises _____ reagent.

(vi) Acetylene forms a red precipitate when passed through _____.

(vii) _____ is an excellent solvent and is known as westron.

Answer :

(i) Potassium fumarate or maleate

(ii) C_nH_{2n-2}

(iii) ammoniacal silver nitrate

(iv) hydrogenation

(v) Baeyer's

(vi) ammonical cuprous chloride solution

(vii) acetylene tetrachloride.

(D) Long Questions :

1. How is acetylene prepared from (a) calcium carbide (b) by electrolysis ?
How will you prove the acidity of hydrogen in acetylene ? What are its uses ?
2. How acetylene is prepared from calcium carbide ? What happens when acetylene reacts with HI ? How would you get benzene from acetylene ?
3. How acetylene is prepared in the laboratory ? How can you get ethane and benzene from acetylene ? Give equations : How will you prove that the acetylenic hydrogen atoms are acidic ?
4. How acetylene is prepared from calcium carbide ? What happens when acetylene reacts with HOBr ? Give equation.
5. Discuss the structure of acetylene molecule. Discuss two methods of preparation of alkynes.
6. How will you show that acetylene is an unsaturated compound ? How will you use it to prepare

(a) Benzene	(b) Acetaldehyde	(c) Ethane
(d) copper acetylidyde	(e) Ethene	(f) Propyne
7. Compare and contrast the properties of saturated hydrocarbon with unsaturated hydrocarbons.
Explain why the hydrogen atom in acetylene is acidic.
8. How acetylene is prepared from the following compounds ? (i) maleic acid (ii) calcium carbide Explain the acidic character of acetylenic hydrogen.
How does acetylene react with (i) Alkaline KMnO_4 solution (ii) HOCl
9. How acetylene is prepared in the laboratory ? Describe with diagram and chemical equation. How acetylene reacts with (i) Br_2 (ii) Na in liq NH_3 , Give two important uses of acetylene.
10. How acetylene is prepared from the following compounds.
(i) Calcium Carbide, (ii) Maleic acid
How does acetylene react with (a) HBr (b) Na/liq NH_3
Give two important uses of acetylene.

(E) Multiple Choice Question :

1. Propyne belongs to

(a) Paraffins	(b) Alkenes	(c) Olefins
(d) Alkynes.		
2. The general formula of alkyne is

(a) C_nH_{2n}	(b) $\text{C}_n\text{H}_{2n-2}$	(c) $\text{C}_n\text{H}_{2n+2}$
(d) C_nH_n .		
3. The C—C bond is shorter in

(a) Ethane	(b) Ethylene	(c) Acetylene
(d) Propane.		
4. When potassium maleate is electrolysed, the compound produced at the anode is

(a) Ethyne	(b) Ethane	(c) Ethene
(d) Propyne.		

5. The product of the reaction $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HCl}$ is
 (a) $\text{CH}_3\text{C}(\text{Cl})_2-\text{CH}_3$ (b) $\text{ClCH}_2-\text{CHCl}-\text{CH}_3$
 (c) $\text{ClCH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$ (d) $\text{CH}_3-\text{CH}_2-\text{CHCl}_2$
6. After ozonolysis of but-2-yne the product on hydrolysis is :
 (a) Formic acid (b) Acetic acid
 (c) Formic acid and acetic acid (d) Propionic acid.
7. The alkyne $\text{R}-\text{C}\equiv\text{C}-\text{R}$ does not react with
 (a) HOCl (b) Br_2 (c) O_3 (d) Ammoniacal cuprous chloride
8. Ethene and ethyne may be distinguished by using
 (a) Baeyer's reagent (b) Tollen's reagent
 (c) Bromine water (d) Schiff's reagent
9. A yellowish white precipitate was obtained on addition of ammoniacal silver nitrate solution to a hydrocarbon. The hydrocarbon could be
 (a) Ethane (b) Ethene (c) Ethyne (d) Toluene
10. Which of the following belongs to acetylene series :
 (a) C_7H_{14} (b) C_9H_{16} (c) $\text{C}_{12}\text{H}_{20}$ (d) $\text{C}_{15}\text{H}_{30}$
11. What is the number of possible alkynes with formula C_5H_8 ?
 (a) 12 (b) 3 (c) 4 (d) 5
12. Acetylene reacts with sodamide in liquid ammonia and then reacts with CH_3I producing
 (a) But-2-yne (b) 3-Methylbut-1-yne
 (c) Propyne (d) Acetylene tetraiodide
13. Acidic hydrogen is present in
 (a) Ethyne (b) Ethene
 (c) Benzene (d) Ethane
14. Lindlar's catalyst is
 (a) Na in liquid NH_3 (b) Pt in ethanol
 (c) Ni in ether (d) Pd with BaSO_4 and quinoline
15. When propyne is treated with aqueous H_2SO_4 in the presence of HgSO_4 , the major product is
 (a) Propanol (b) Propyl hydrogen sulphate
 (c) Acetone (d) Propanol
16. The compounds 1-butyne and 2-butyne can be distinguished by using
 (a) Bromine water (b) KMnO_4 solution
 (c) Tollens' reagent (d) Chlorine gas.

ANSWERS

- | | | | | | |
|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (c) | 4. (a) | 5. (a) | 6. (b) |
| 7. (d) | 8. (b) | 9. (c) | 10. (b) | 11. (b) | 12. (a) |
| 13. (a) | 14. (d) | 15. (c) | 16. (c) | | |

□□□

CHAPTER - 20

AROMATIC COMPOUNDS: AROMATIC HYDROCARBONS

20.1 INTRODUCTION

The term ‘aromatic’ was derived from the Greek word ‘*aroma*’ meaning pleasant smell. The aromatic compounds were so named because of their sweet odour. The sweet smelling compounds often contained groups like $—\text{OCH}_3$, $—\text{CHO}$, $—\text{CH} = \text{CH} — \text{COOH}$ attached to a phynyl ($\text{C}_6\text{H}_5—$) group. Coal tar was the main source of aromatic compounds. Compounds like phenol ($\text{C}_6\text{H}_5\text{OH}$) and benzene (C_6H_6) were the important aromatic compounds obtained as a result of distillation of coal tar. But subsequently the original meaning of term *aromatic* was abandoned when some odourless and vile-smelling substances containing C_6H_5 group were discovered. Thus aromatic compounds were better known as **benzenoid compounds** i.e it included benzene and its derivatives.

But now a days the scope of the term aromatic is not limited to benzenoid compounds only. It also includes some nonbenzenoid compounds e.g the heterocyclic compounds. Though they do not contain C_6H_5 group yet are found to be aromatic in nature.

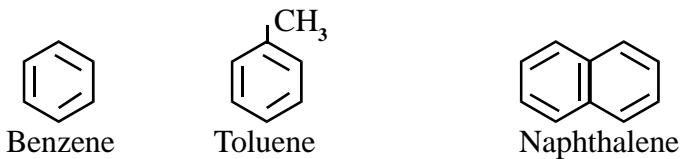
The aromatic compounds contain a higher percentage of carbon than the aliphatic ones and they produce sooty flames when heated over a copper foil.

20.2 AROMATIC HYDROCARBONS OR ARENES

Aromatic hydrocarbons are known as **arenes**. Benzene is the simplest member of the class. The general formula for benzene and its homologues is $\text{C}_n\text{H}_{2n-6}$. Benzene ($n=6$) has the molecular formula C_6H_6 . Other members include toluene ($\text{C}_6\text{H}_5—\text{CH}_3$) C_7H_8 ($n = 7$), xylene ($\text{C}_6\text{H}_4(\text{CH}_3)_2$) C_8H_{10} ($n=8$) etc.

Two benzene rings fused together constitute naphthalene. So naphthalne and its derivatives constitute another series of arenes. The general formula is $\text{C}_n\text{H}_{2n-12}$, the first member being naphthalene C_{10}H_8 ($n = 10$).

The general formula of arenes can be represented by C_nH_{2n-6y} , where y is the number of rings in the molecule. In benzene series y = 1 and in naphthalene series y = 2.

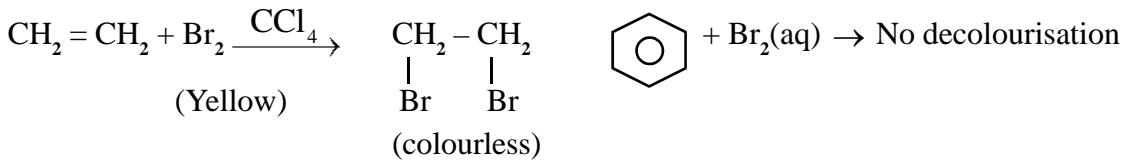


20.3 MEANING OF AROMATICITY

The unique properties exhibited by the aromatic compounds is termed as aromaticity. So the characteristics which attribute to the aromaticity of the compounds are :

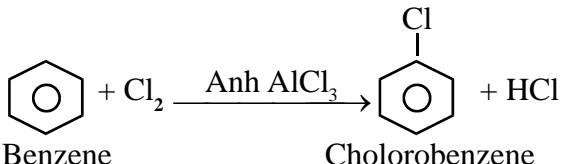
(i) High degree of unsaturation :

They are highly unsaturated compounds but very much resistant to addition reactions. It is to be noted that the aliphatic unsaturated compounds can readily undergo addition reactions.



(ii) Substitution reaction :

They undergo electrophilic substitution reactions though they are highly unsaturated. Examples of such reactions include nitration, sulphonation, halogenation of benzene.



(iii) Low heat of hydrogenation and combustion :

The aromatic compounds have low values of heat of hydrogenation and combustion. This is in favour of their stability.

(iv) Higher percentage of carbon (sooty flame) :

Unlike aliphatic compounds they contain a higher percentage of carbon and hence produce sooty flame having no residue when heated over a copper foil.

(v) Size of the ring & their structure :

These are cyclic compounds having five, six or seven membered rings. They are flat or planar molecules.

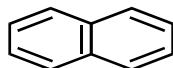
(vi) **Hückel's rule :-** All aromatic compounds must satisfy Hückel's $(4n + 2)\pi$ rule.

Hückel's Rule or $(4n + 2)\pi$ rule :

According to this rule, if in a planar cyclic system of overlapping p-orbitals the number of π electrons is $(4n + 2)$, then the system will have aromatic character. Here 'n' is either '0' or a positive integer ($n=0, 1, 2, 3 \dots$)



Benzene
 6π electrons
 $n = 1, (4n + 2)\pi$
 $= (4 \times 1 + 2)$
 $= 6\pi$ electrons
 $(4n+2)\pi$ rule satisfied
AROMATIC

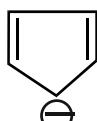


Naphthalene
 10π electrons
 $n = 2, (4n + 2)\pi$
 $= (4 \times 2 + 2)\pi$
 $= 10\pi$ electrons
 $(4n+2)\pi$ rule satisfied
AROMATIC

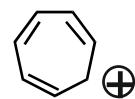
- e.g.(i) Benzene and naphthalene contain 6 and 10 π electrons respectively. They satisfy Hückel's $(4n+2)\pi$ rule and hence aromatic.
- (ii) Some cyclic ions obey Huckel's rule and exhibit aromatic character.



Cyclopropenylcation
 2π electrons



Cyclopentadienyl anion
 6π electron



Cycloheptatrienylcation
 6π electrons

- (iii) 1, 3 Cyclobutadiene and 1, 3, 5, 7 Cyclo-octatetrene contain 4π and 8π electrons respectively. They do not satisfy Huckel's $(4n+2)\pi$ rule and hence are not aromatic.



1, 3-Cyclobutadiene
 4π electrons
 $(4n + 2)\pi$ rule not satisfied
ANTI AROMATIC



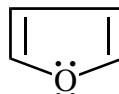
1, 3, 5, 7-Cyclooctatetraene
 8π electrons
 $(4n + 2)\pi$ rule not satisfied
NON - AROMATIC

- (iv) Hückel extended his rule to five and six membered nonbenzenoid heterocyclic systems.

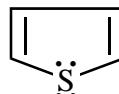


Pyridine
 6π electrons

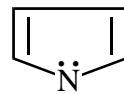
$(4n + 2)\pi$ rule is satisfied
AROMATIC



Furan



Thiophene



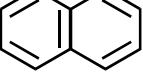
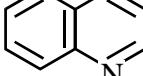
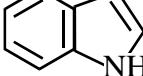
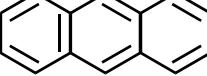
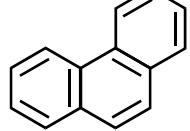
Pyrrole

There are four π electrons & 2 p-electrons on the heteroatom inside the ring. Thus,

$(4n+2)$ rule is satisfied.

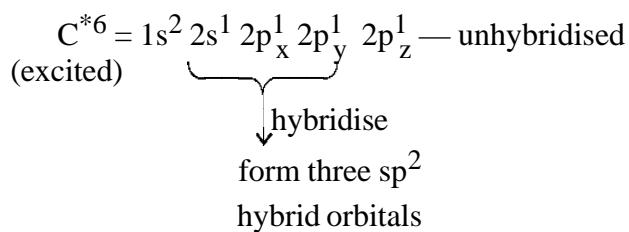
AROMATIC

Table 20.1**Examples of aromatic compounds obeying Hückel's Rule**

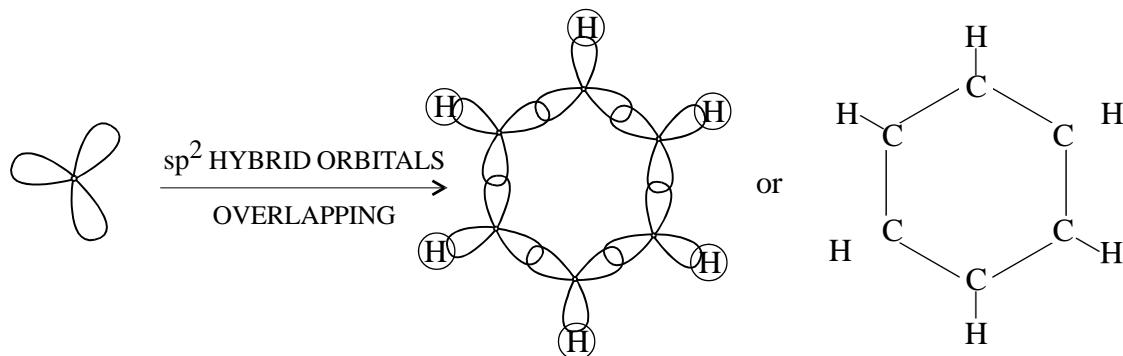
n	(4n+2) π electrons	Structures & Names of Aromatic Compounds					
0	2π		Cyclopropenylcation				
1	6	    	Benzene	Pyridine	Pyrrole	Furan	Thiophene
2	10		Naphthalene		Quinoline		Indole
3	14		Anthracene		Phenanthrene		

20.4 MOLECULAR ORBITAL STRUCTURE OF BENZENE

X-ray diffraction measurements reveal that benzene consists of a planar hexagon of six carbon atoms. C—C bond length is 1.39 \AA^0 and C—C—C bond angle is 120^0 . Therefore, it stands to reason that each carbon atom in benzene is sp^2 hybridised.

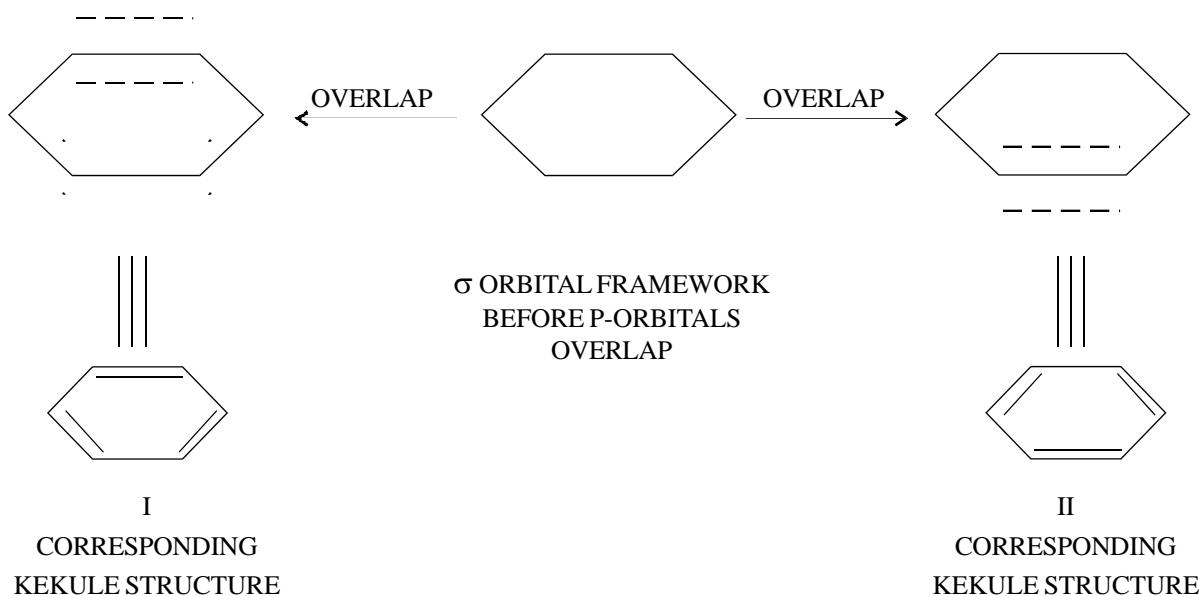


Each carbon utilises two of its hybrid orbitals in forming sigma bonds with two other carbon atoms and one hybrid orbital in forming a sigma bond with hydrogen. Thus each carbon atom is left with an unhybridised p-orbital. The following figure depicts the sigma bond framework of benzene resulting in planar hexagonal structure.

**Fig 20.1 : σ bond structure of benzene**

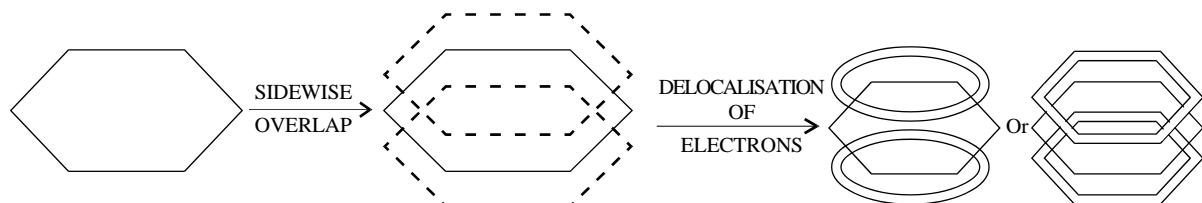
There are six unhybridised p-orbitals one for each carbon atom with two equal lobes. One of the lobes lies above and the other below at right angles to the plane containing the sigma frame work. These p-orbitals overlap laterally with each other in two different ways that lead to the formation of two Kekulé structures (I & II) as shown below is Fig.20.2.

These two Kekulé structures thus correspond to localised π bond formation.

**Fig.20.2 Overlapping of p-orbitals that leads to formation of two Kekulé structures (I & II)**

Again since the internuclear distances between the carbon atoms of the hexagon are equal, there appears no reason why a p-orbital will overlap in one direction only and not in both the directions. Therefore overlapping of p-orbital with adjacent p-orbitals in both the directions is considered.

The six unhybridised p-orbitals each containing an electron laterally overlap with each other forming a delocalised π molecular orbital, half of which is above the plane and half, below the plane just sandwiching the six carbon atoms in between, (fig. 20.3).



Separate p- orbitals on benzene ring may overlap on either side.

The six p- orbitals are delocalised, the lobes above and below the ring separately.

π molecular orbitals of benzene having a continuous annular cloud, one above and one below the carbon sextet.

Fig : 20.3 Formation of continuous π election annular clouds in benzene molecule.

Delocalisation of electrons stabilises the benzene ring. The actual energy of benzene is found to be less than that of the arrangement corresponding to any one of the two Kekule structures. The difference in energy between the energy of actual structure of benzene and that of the Kekule structure is known as resonance stabilisation energy or **resonance energy**.

Thus, the actual structure of benzene is not represented by any one of the two Kekule structures. It is a hybrid of the two structures. Benzene is represented by a regular hexagon with an inscribed circle that symbolises the six delocalised p-electrons. This structure is known as the **graphic formula** of benzene.

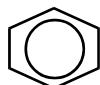
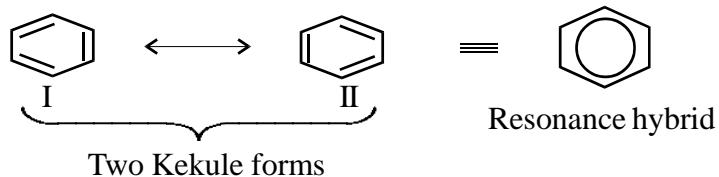


Fig : 20.4 Graphic formula of Benzene

Resonance description of the structure of Benzene :

The concept of resonance plays a vital role in describing the actual structure of benzene when the proposed Kekule structures were found to have certain drawbacks. According to this concept benzene was considered to be a resonance hybrid of the two Kekule canonical structures as shown below.



The resonance hybrid of the two Kekulé structures is in direct conformity with the X-ray diffraction studies, according to which

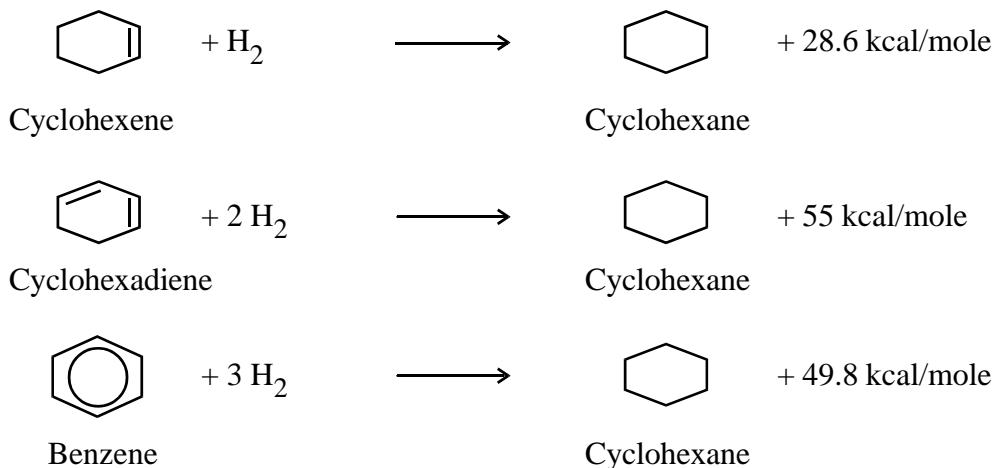
- (a) All the carbon - carbon bond lengths are equal i.e. 1.39 \AA^0 and are intermediate between C — C single bond distance (1.54 \AA^0) and C = C double bond distance (1.34 \AA^0).
- (b) The six carbon atoms are linked forming a hexagonal flat structure with bond angle 120° .

Stability of Benzene as explained by Resonance Theory:

The unusual stability of benzene was explained by the resonance hybrid structure of benzene. The resonance stabilisation energy or simply the resonance energy was really responsible in explaining the unusual stability of benzene. It was found that the hybrid structure of benzene was more stable than any of the Kekulé structures by about 36 kcal/mole of energy. This energy, commonly known as the **resonance energy** could be calculated indirectly from the measurements of heat of hydrogenation as follows.

The addition of hydrogen to a carbon- carbon double bond is an exothermic process. Hence some amount of heat energy is given out during the process of hydrogenation.

For example:



The heat of hydrogenation of one double bond in cyclohexene is 28.6 kcal/mole whereas that of cyclohexadiene is 55 kcal/mole (which is nearly twice the value for cyclohexene) as in this case there are two double bonds. If Kekulé structure of benzene is considered the value of heat of hydrogenation would be expected to be $3 \times 28.6 = 85.8$ kcal/mole. But when benzene is hydrogenated 49.8 kcal/mole of energy is liberated. The difference $(85.8 - 49.8) = 36$ kcal/mole between the calculated and observed value is known as the *resonance energy* of benzene. This is described by the following figure. (Fig.20.5).

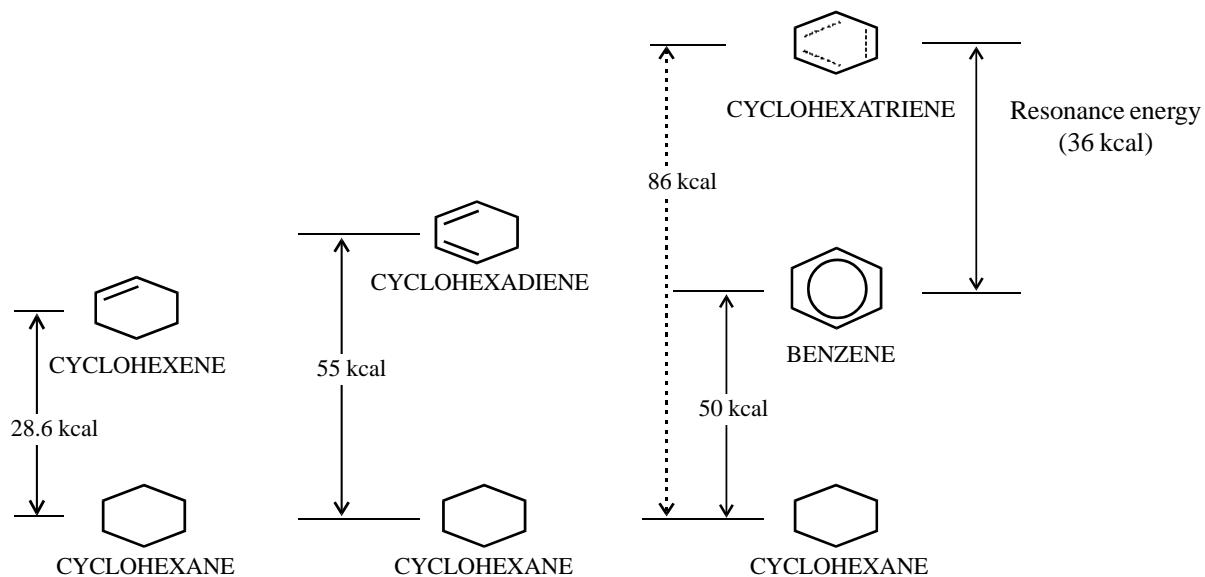
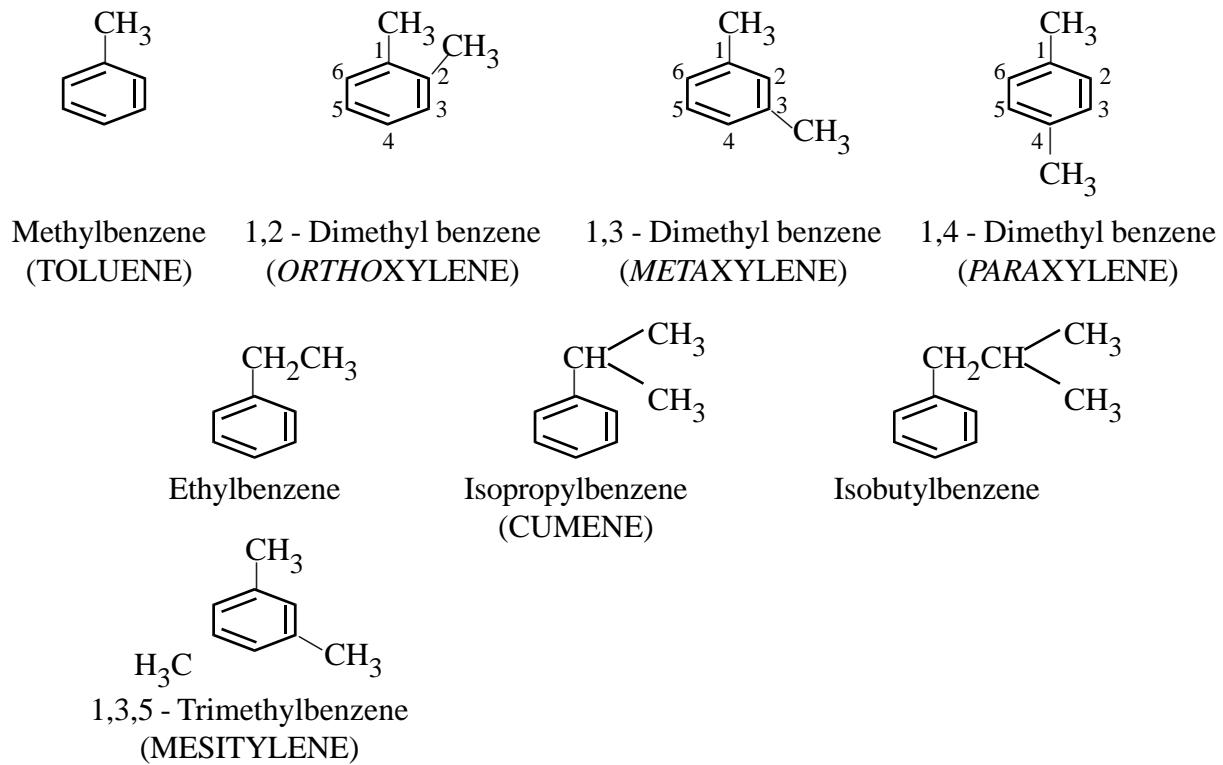


Fig : 20.5 Calculation of Resonance energy by the value of heat of hydrogenation.

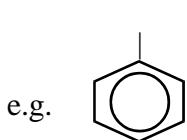
From the above discussion we can conclude that the hybrid structure of benzene is thermodynamically more stable than any of the imaginary Kekulé structures.

20.5 NOMENCLATURE OF AROMATIC COMPOUNDS :

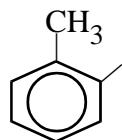
1. Hydrocarbons :- The trivial name of parent monocyclic arene is Benzene. Other members particularly lower arenes are also named by their trivial names approved by IUPAC. For example:



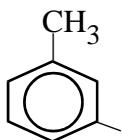
2. **Aryl group (Ar):-** Just as 'R' is used to represent alkyl group, the symbol 'Ar' is used to represent an aryl group. The hydrocarbon group left after removal of a hydrogen atom of benzene, the parent hydrocarbon is called a phenyl group which is represented by the symbol \emptyset , Ph or C_6H_5 .



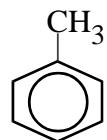
(Phenyl or \emptyset or
Ph)



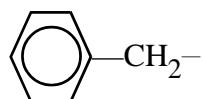
o-tolyl



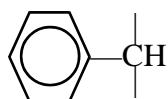
m-tolyl



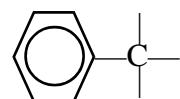
p-tolyl



benzyl



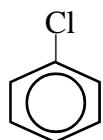
benzal



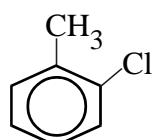
benzo

3. Halogen derivatives

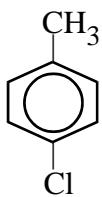
- (a) Nuclear substitution product (obtained by replacement of H atom of benzene ring by halogen atom)



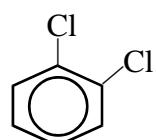
Chlorobenzene



o-chlorotoluene

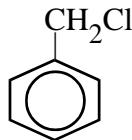


p-chlorotoluene

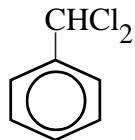


o-dichlorotoluene

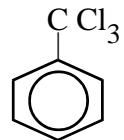
- (b) Side chain substitution product (obtained by replacement of H atom of side chain by halogen atom)



Benzylchloride



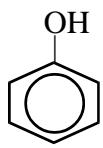
Benzalchloride



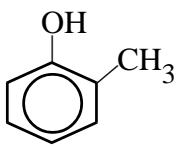
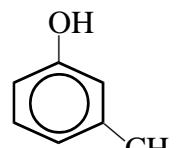
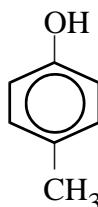
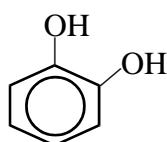
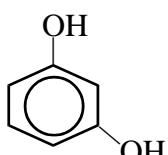
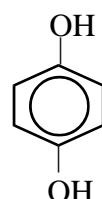
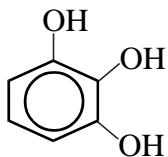
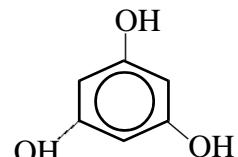
Benzotrichloride

4. Hydroxy derivatives

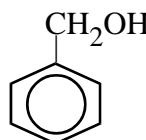
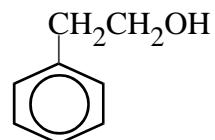
(a) *Nuclear substitution products (Phenols)*



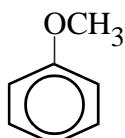
(Phenol)

2-Methylphenol
(*o*-cresol)3-Methylphenol
(*m*-cresol)4-Methylphenol
(*p*-cresol)1,2 - Dihydroxybenzene
(Catechol)1,3 - Dihydroxybenzene
(Resorcinol)1,4 - Dihydroxybenzene
(Quinol)1,2,3 - Trihydroxybenzene
(Pyrogallol)1,3,5 - Trihydroxybenzene
(Phloroglucinol)

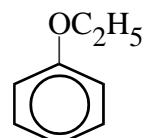
(b) *Side chain substitution products (Aromatic alcohols):*

Phenyl methanol
(Benzyl alcohol)β-Phenyl ethyl alcohol
(Phenyl ethanol)

5. Ethers

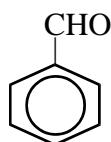


Methyl phenyl ether
(Anisole)

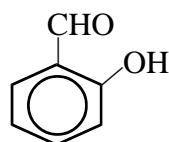


Ethyl phenyl ether
(Phenetole)

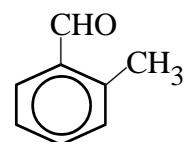
6. Aldehydes & Ketones



Benzaldehyde

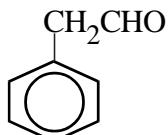


Orthohydroxy
benzaldehyde
(Salicylaldehyde)

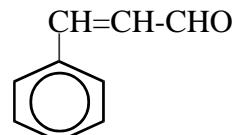


o- Tolualdehyde

e.g.



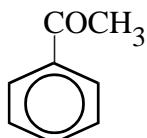
Phenylacetaldehyde



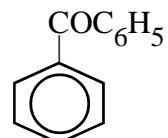
Cinnamaldehyde

A $\begin{array}{c} \diagup \\ > \end{array}$ C = O group when attached to a benzene ring, the compound is known as **phenones**.

e.g.

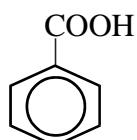


Methyl phenyl ketone
(Acetophenone)

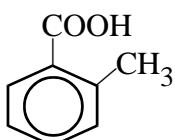
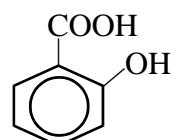
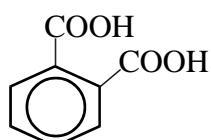
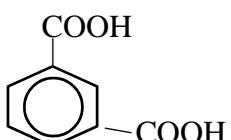


Diphenyl ketone
(Benzophenone)

7. Carboxylic Acids.

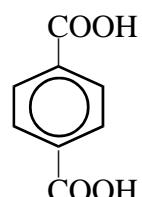


Benzoic acid

o- Methyl benzoic acid
(o-Toluic acid)o- Hydroxy benzoic acid
(Salicylic acid)Phthalic acid
(Benzene -1,2 dicarboxylic acid)

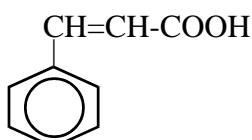
Isophthalic acid

(Benzene -1,3 dicarboxylic acid)



Terephthalic acid

(Benzene -1,4 dicarboxylic acid)



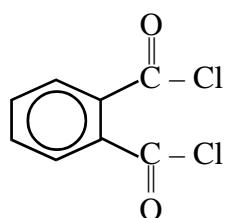
Cinnamic acid

8. Acid derivatives

(i) Acid chlorides

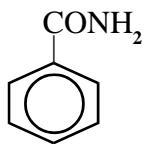


Benzoyl chloride

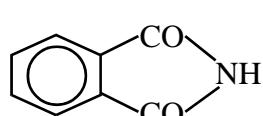


Phthaloyl chloride

(ii) Acid amides

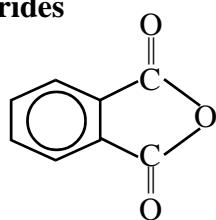


Benzamide



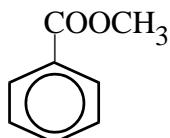
Phthalimide

(iii) Acid anhydrides

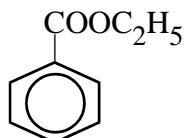


Phthalic anhydride

(iv) Esters

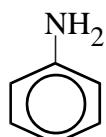
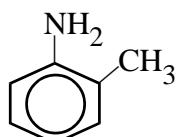
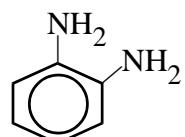
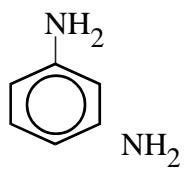


Methyl benzoate

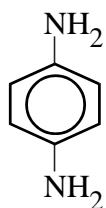


Ethyl benzoate

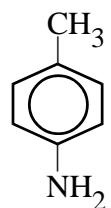
9. Amines

Aminobenzene
(Aniline)o- Aminotoluene
2- Amino toluene
(o-toluidine)o- Phenylene diamine,
(1,2 - Diaminobenzene)

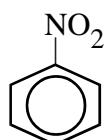
m- Phenylene diamine



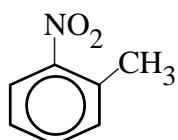
p- Phenylene diamine

p- Aminotoluene
or 4 - Amino toluene
or p - toluidine

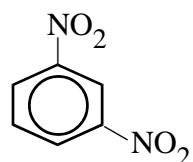
10. Nitro compounds

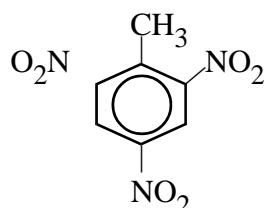


Nitrobenzene

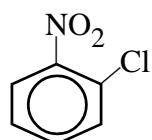


o-Nitrotoluene

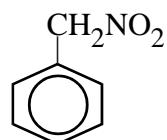
1,3 - Dinitrobenzene
(m- Dinitrobenzene)



2,4,6-Trinitrotoluene
(TNT)

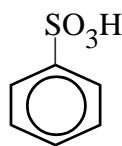


o-Chloronitrobenzene

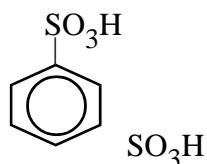


Phenyl nitromethane
(side chain substitution product)

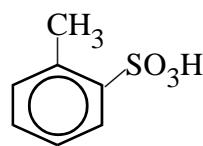
11. Sulphonic acids



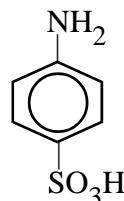
Benzene
sulphonic acid



Benzene-1, 3-disulphonic
acid

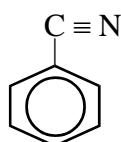


o- Toluene sulphonic acid

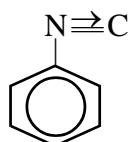


p- Amino benzene sulphonic acid

12. Cyanides & isocyanides

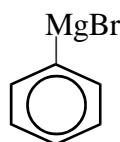


Phenylcyanide
(Benzonitrile)

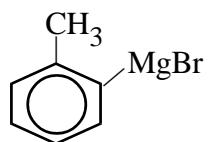


Phenyl isocyanide

13. Grignard reagent

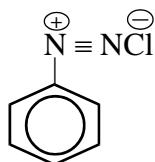


Phenyl magnesium bromide

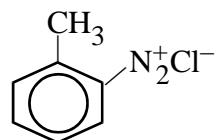


o- Tolyl magnesium bromide

14. Diazonium salts



Benzene diazonium chloride



o-Toluene diazonium chloride

20.6 METHODS OF PREPARATION OF BENZENE

Carbonisation of bituminous coal is done to get coal chemicals and coke.

Carbonisation of coal

Carbonisation of coal is undertaken to manufacture coke which is used in iron and steel industry as a reducing agent. When coal is heated above 673K in closed retorts (in absence of air) coal becomes soft and plastic. The volatile materials are obtained as distillate.

Low temperature carbonisation (723-973K) :

In this method, coal is heated in absence of air up to 973K. A large amount of coal tar is produced along with ammonia, light oil, coke oven gas and coke.

- (1) **From coal tar :** It is a thick, black viscous liquid obtained as a result of low temperature carbonisation of coal. It is considered to be a rich source of aromatic compounds. Coal tar is subjected to fractional distillation.

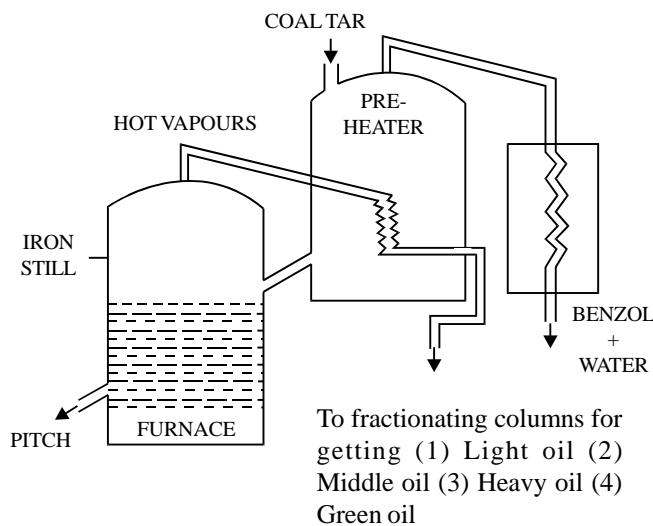


Fig.20.6 Fractional distillation of coal tar

Four main fractions are usually collected leaving behind a residue of 'pitch' which is used mostly for surfacing roads.

Table 20.2 Fractions obtained in coaltar distillation.

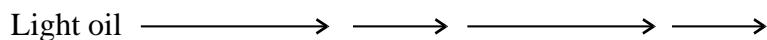
Fraction	Temp. range	Chief components
I Light oil	<170 ⁰ C	Benzene, toluene, xylene.
II Middle oil	170 — 230 ⁰ C	Phenol, cresols, naphthalene
III Heavy oil	230—270 ⁰ C	Cresols, naphthalene
IV Anthracene oil	270—400 ⁰ C	Anthracene
V Pitch	Residue left	—

The light oil fraction is worked up properly for the recovery of benzene.

FRACTION I. Light oil fraction :

This fraction is so called as it is lighter than water. Besides benzene, toluene and xylenes (BTX), light oil also contains traces of basic substance like pyridine, methyl pyridines and acidic substances like phenol and cresols.

Light oil is first washed with conc. H₂SO₄ to remove the basic substances like pyridine, thiophene etc. This is followed by treatment with dil. NaOH which removes acidic compounds like phenols. Conc.H₂SO₄ H₂O dil.NaOH H₂O

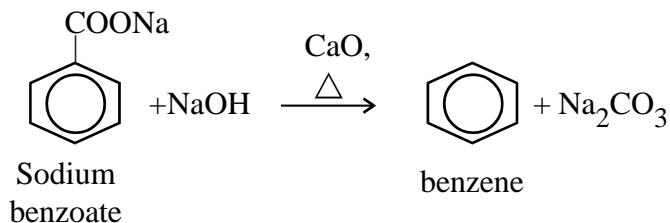


The oil thus purified is subjected to further fractionation. The following products are obtained at various ranges of temperatures.

- (i) Benzene (40⁰C)
- (ii) Toluene (110⁰)
- (iii) o-, m-, p-xylanes (145⁰)
- (iv) Residue solvent naphtha

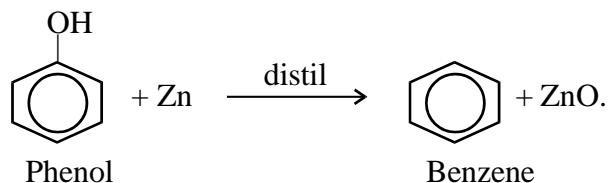
2. Decarboxylation of benzoic acid.

Sodium salt of benzoic acid when heated with sodalime produces benzene.



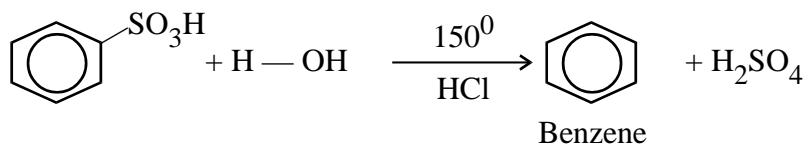
3. From phenol (by deoxygenation)

When distilled with Zn dust, phenol is deoxygenated giving benzene.



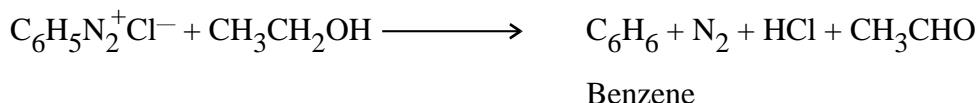
4. From benzene sulphonic acid

Benzene sulphonic acid when treated with superheated steam in presence of HCl at 150^0C produces benzene.



5. From benzene diazonium chloride.

Benzene diazonium chloride when heated with ethanol yields benzene.



20.7 PROPERTIES OF BENZENE

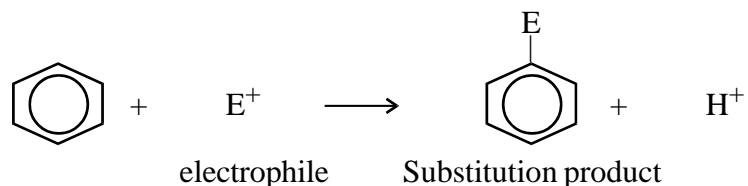
1. Physical

- (i) Colourless mobile liquid
- (ii) Petrol -like odour
- (iii) Lighter than water. Insoluble in water but soluble in organic solvents.
- (iv) Boils at 353K & its freezing point is 280K.

2. Chemical :

A. Electrophilic substitution reactions:

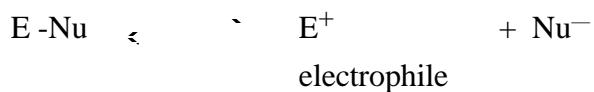
Benzene is stable due to resonance. Although it contains three C = C bonds, yet it is not prone to addition reactions. It shows substitution reactions more readily. Since it has a delocalised π M.O containing 6 π electrons it serves as a source of electrons and therefore can be attacked by electrophiles, (electron seeking). Thus,



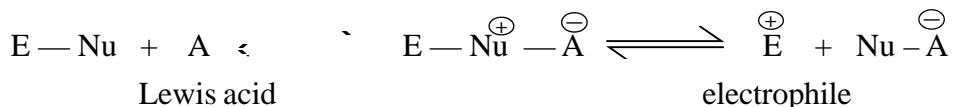
GENERAL MECHANISM FOR ELECTROPHILIC SUBSTITUTION

STEP I : Generation of Electrophile

- (a) by spontaneous dissociation

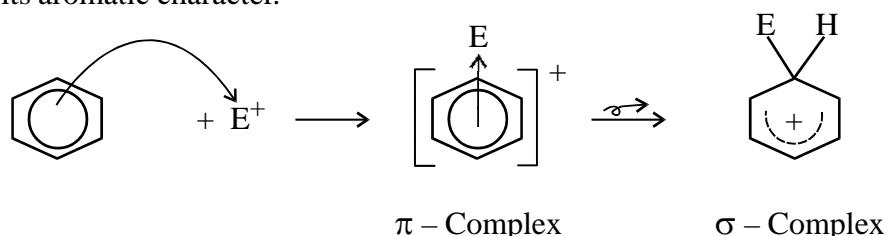


- (b) by acid catalysed dissociation

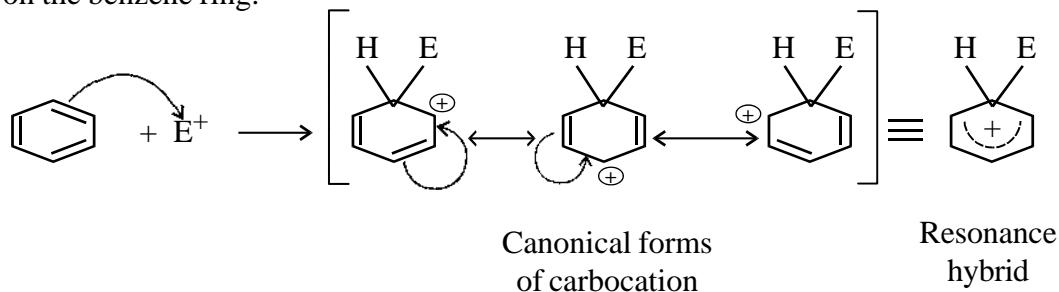


STEP II : Formation of π complex which rearranges to give σ - complex

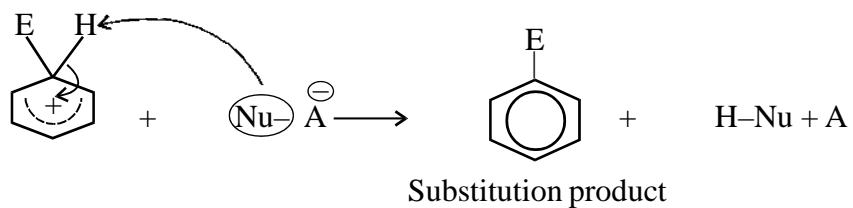
In this step π – complex is formed due to loose association of the electrophile with the benzene ring. The electrophile is not attached to any specific position of ring. π – Complex is unstable, it readily rearranges (\rightleftharpoons) giving the resonance stabilised σ – complex, or arenium ion which loses its aromatic character.



Thus, σ -complex is a resonance stabilised carbocation produced by the attack of electrophile on the benzene ring.

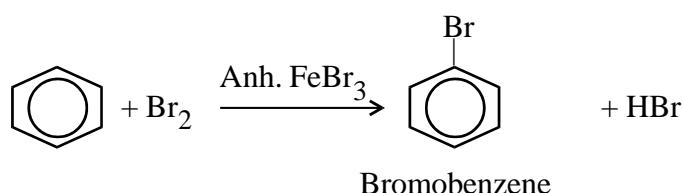
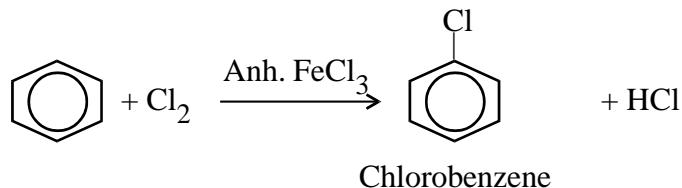


STEP III. Elimination of H^+ from the σ – complex by the base : $\text{Nu}-\text{A}^\ominus$ to yield the final substitution product, thus restoring the aromatic character

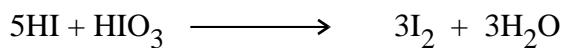
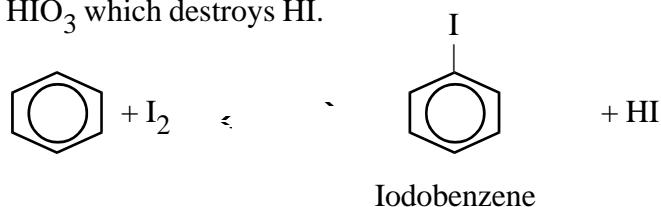


Examples of electrophilic substitution reactions:

- (i) **Halogenation :** Benzene reacts with Cl_2 or Br_2 in presence of lewis acid catalyst like anhydrous FeCl_3 , FeBr_3 , AlCl_3 etc to form chlorobenzene or bromobenzene respectively.



However, iodination is a reversible process. It is to be carried out in presence of an oxidising agent like HIO_3 which destroys HI .

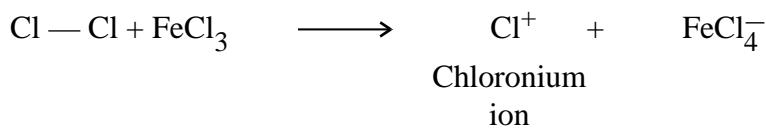


Fluorination of benzene is very fast reaction and is difficult to control.

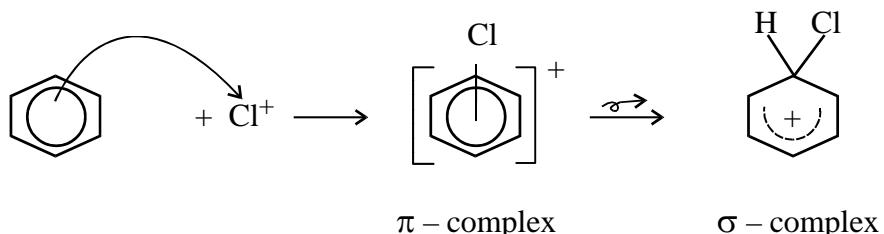
Mechanism :

- (a) **Generation of electrophile(Cl^+)**

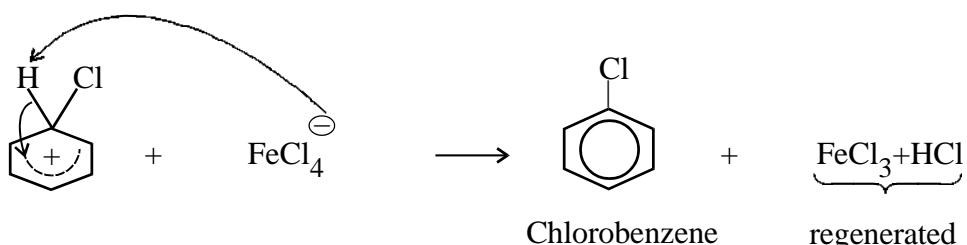
Polarisation of chlorine molecule takes place in presence of lewis acid FeCl_3 forming the chloronium ion(Cl^+).



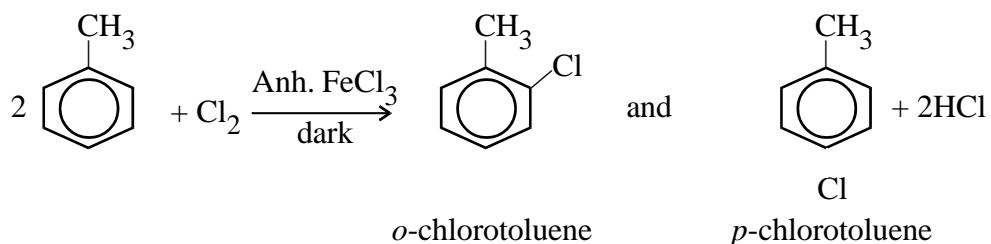
(b) Attack by electrophile leading to the formation of σ – complex



(c) Elimination of a proton by the base FeCl_4^- and formation of substitution product

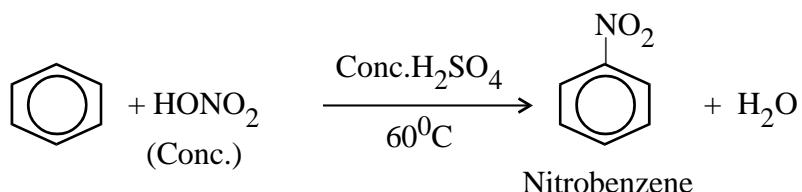


In case of toluene a mixture of two products, ortho and para chlorotoluene is obtained. This is because —CH₃ group is ortho and para directing.



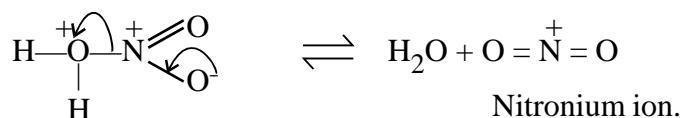
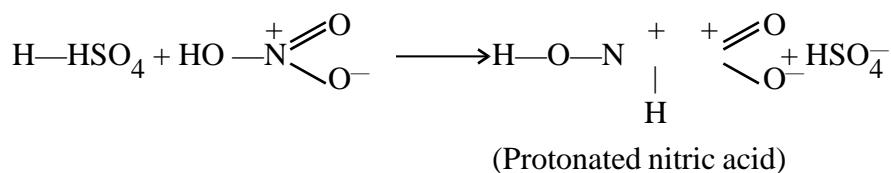
(ii) Nitration

Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 at 60°C to form nitrobenzene.

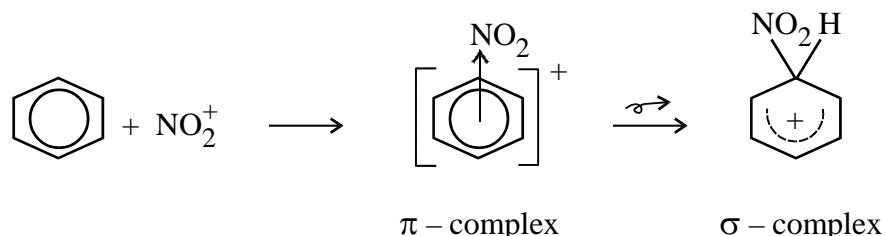


Mechanism:

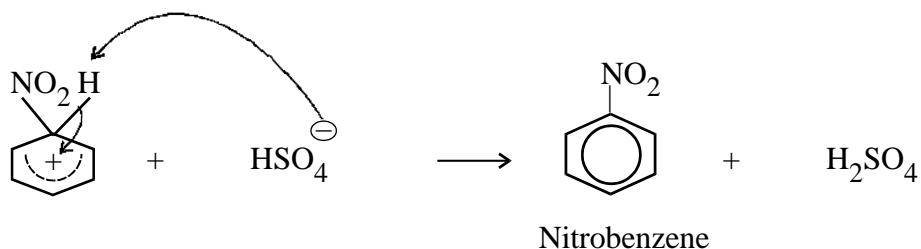
(a) Generation of electrophile, NO_2^+ (Nitronium ion)



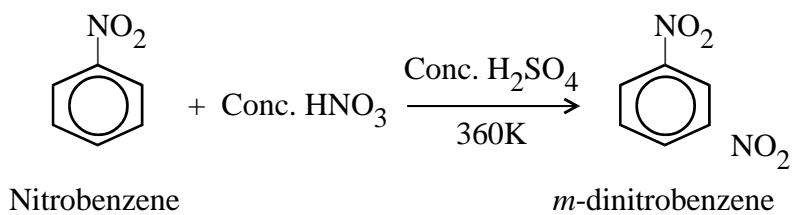
(b) Formation of σ – complex



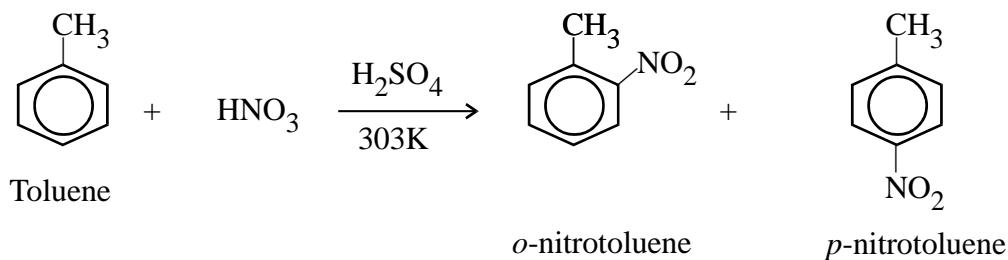
(c) Elimination of H^+ and formation of substitution product



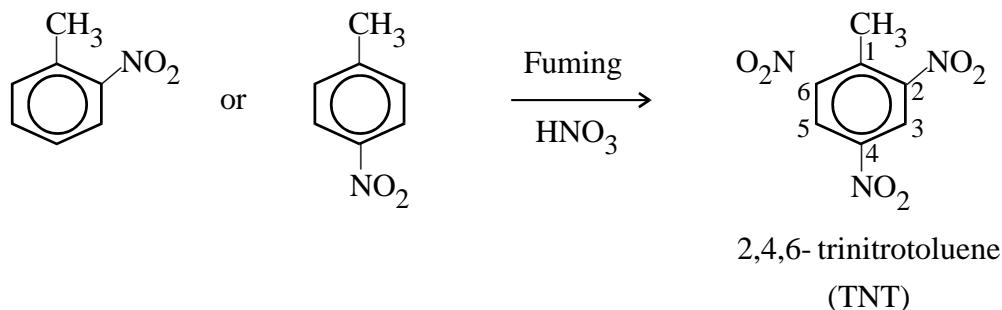
On further nitration at higher temperature di- and tri- nitrobenzene can be obtained. The incoming nitro group occupies the meta position relative to the position of nitro group already present. This is because —NO_2 group is meta directing.



Nitration of toluene is easier than benzene. This is because $-\text{CH}_3$ group is electron releasing and it makes the ring system electron rich. Since methyl group is ortho and para directing, the product is a mixture of *o*-nitrotoluene and *p*-nitrotoluene.

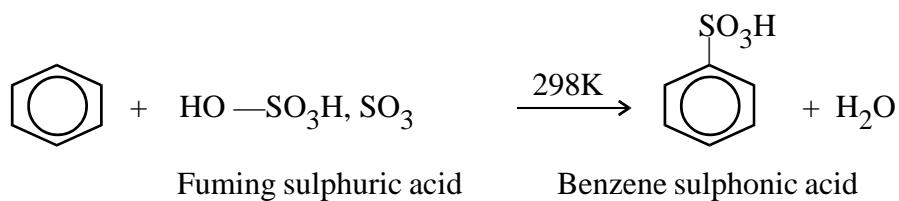


Further nitration of toluene is carried out with fuming nitric acid which results in the formation of 2,4,6- trinitrotoluene (TNT), a well-known explosive.

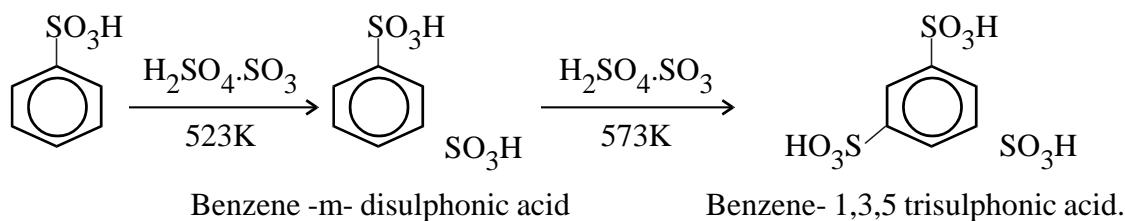


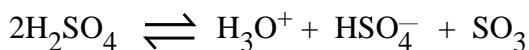
(iii) Sulphonation

Benzene when treated with conc. H_2SO_4 at $80^\circ C$ or fuming H_2SO_4 at $298K$ undergoes sulphonation producing benzene sulphonic acid.

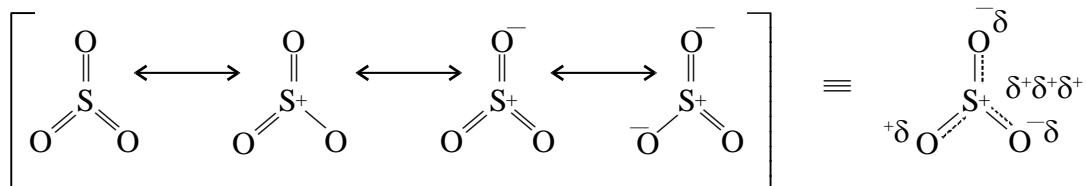
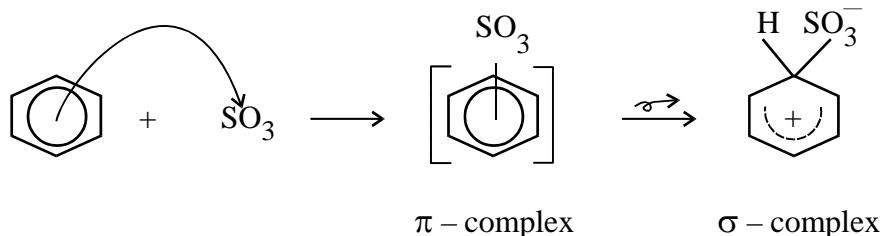
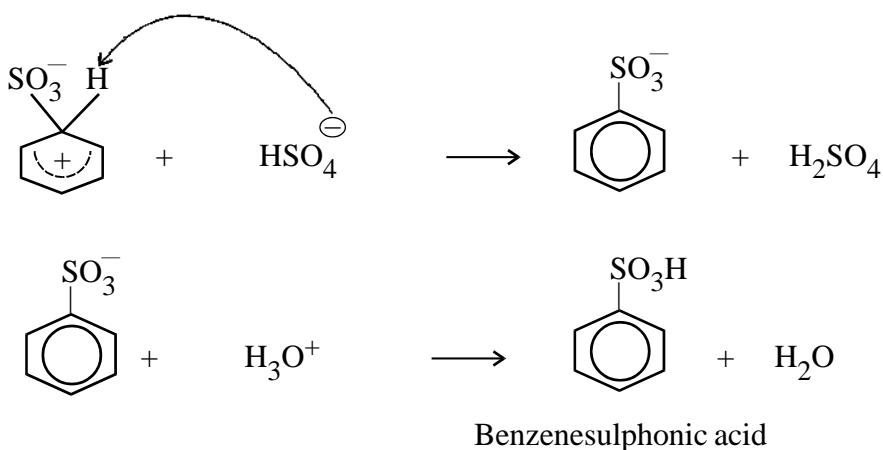


Benzene sulphonic acid may be further sulphonated producing benzene -m- disulphonic acid and benzene- 1,3,5 trisulphonic acid.



Mechanism:**(a) Generation of electrophile (SO_3)**

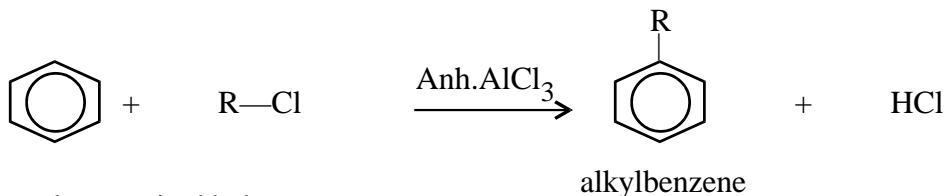
Here SO_3 molecule is the electrophile. Although SO_3 is a neutral molecule, yet due to resonance it has dipolar structure where 'S' carries +ve charge.

**(b) Formation of σ -complex****(c) Elimination of proton.****(iv) Friedel Crafts reaction**

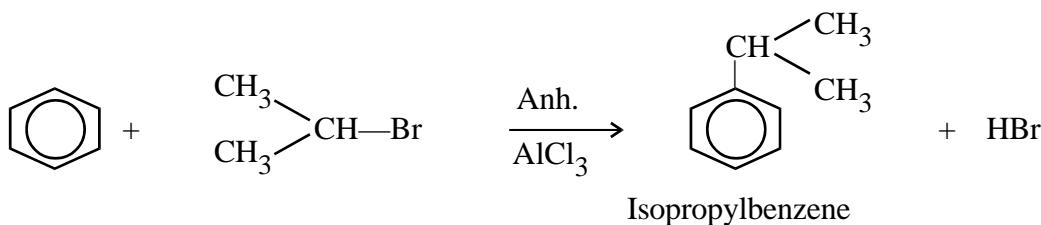
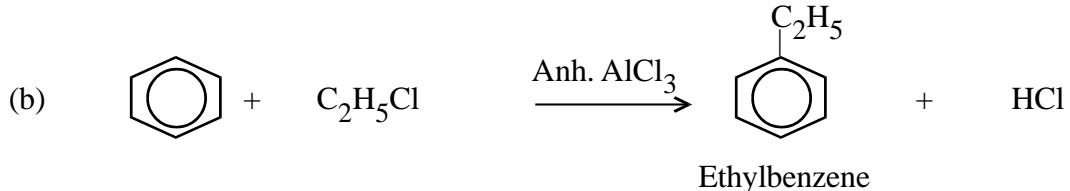
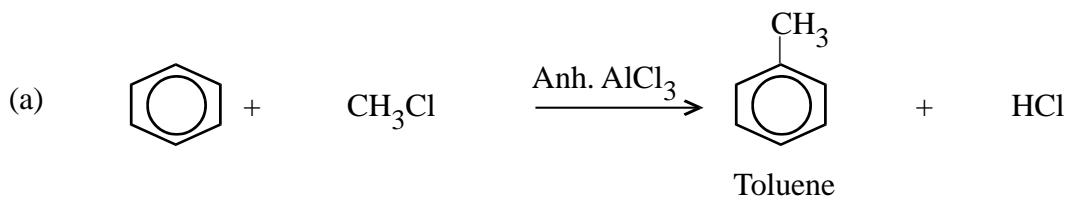
This reaction, discovered by **Charles Friedel** and **M. Crafts**, finds its use in synthetic organic chemistry. The reaction is studied under two heads, namely (a) Friedel Craft's alkylation and (b) Friedel Crafts acylation.

Friedel Crafts alkylation :

When benzene reacts with an alkyl halide (RX) in the presence of anh. AlCl_3 as catalyst, it undergoes F—C alkylation forming the corresponding alkylbenzene.

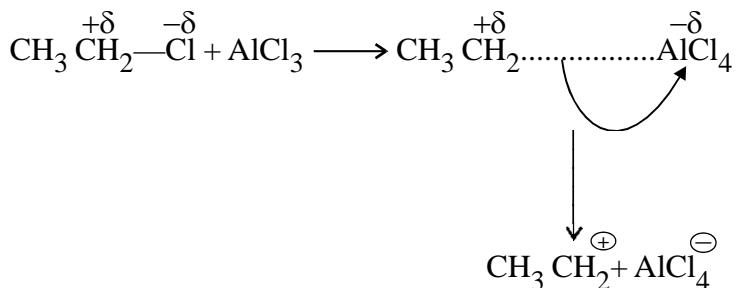


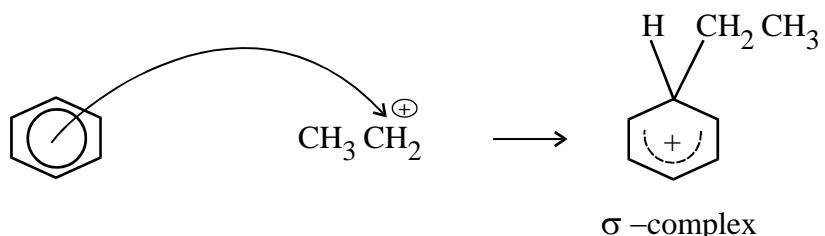
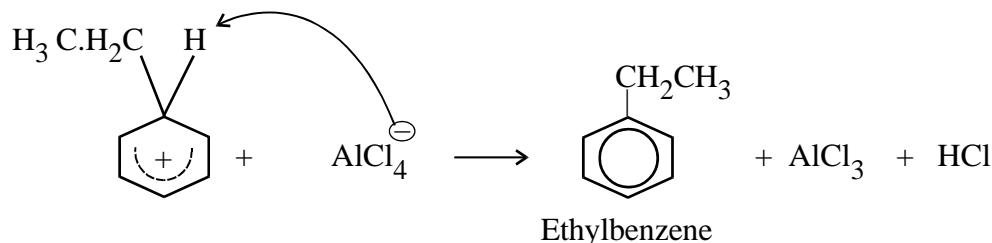
Some examples are cited below.



Mechanism

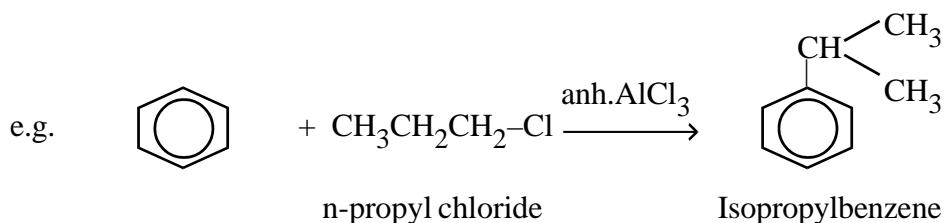
(a) Generation of electrophile



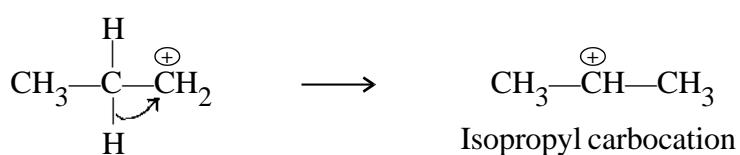
(b) Formation of σ - complex(c) Elimination of Proton (H^+)

Limitations of F—C alkylation

1. *Alkyl group higher than CH_3CH_2* can not be introduced to the benzene ring as it tends to undergo skeletal rearrangement.



This is due to the fact that n-propyl carbocation undergoes rearrangement forming stable isopropyl carbocation.



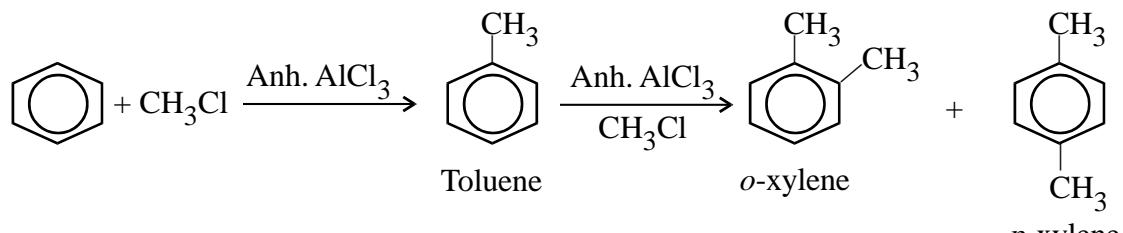
2. *Presence of meta-directing group:*

F—C alkylation is hindered due to the presence of meta-directing group. This is because, a meta directing group is electron withdrawing. It deactivates the benzene ring thereby lowering the electron density in the ring.

For example, nitrobenzene does not respond to F—C reaction.

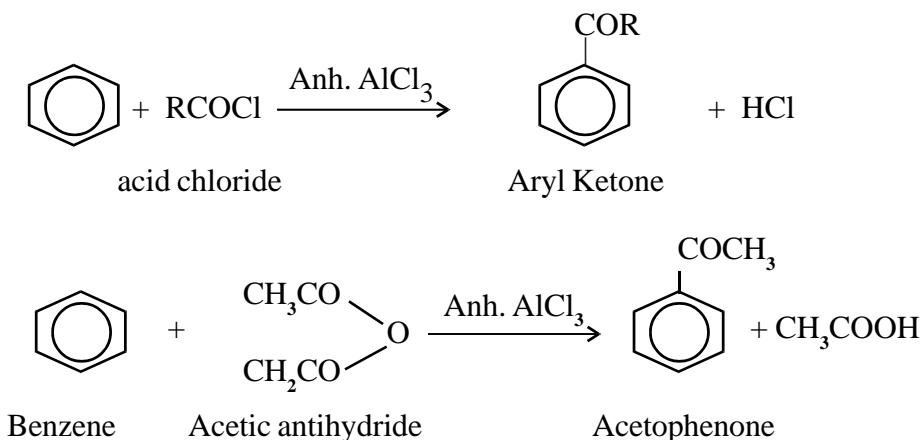
3. *Polyalkylation :*

Alkyl group is electron releasing. Presence of an alkyl group activates the benzene ring making it prone to further alkylation. Thus, a polyalkyl derivative is formed.

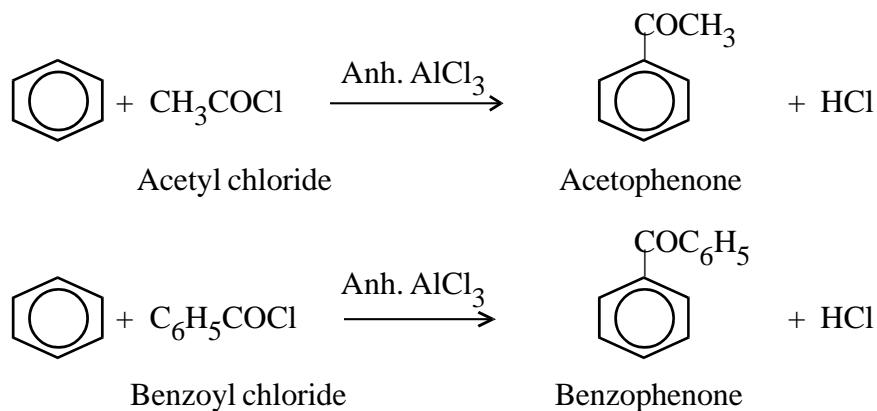


Friedel Craft Acylation

Benzene when reacts with acid chlorides or acid anhydrides, in presence of anh. AlCl_3 undergoes acylation forming the corresponding acyl derivative.



Some examples are cited below.

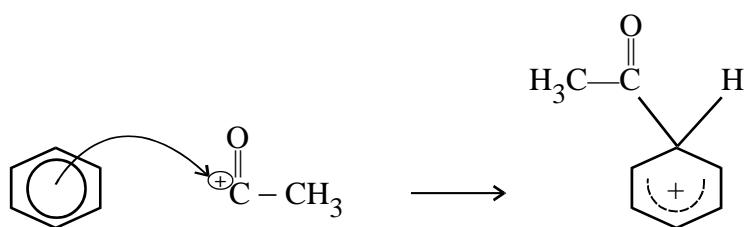


Mechanism

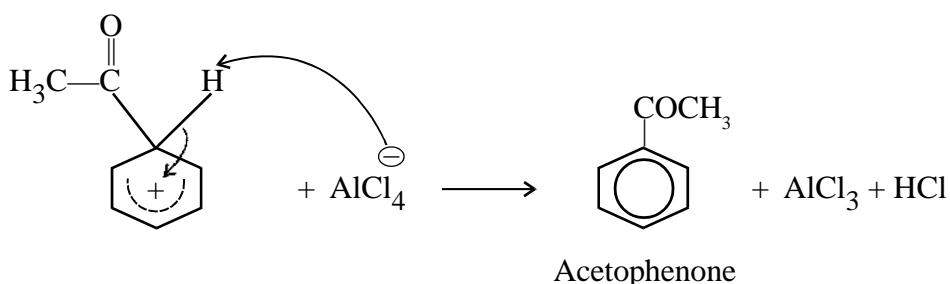
(a) **Generation of electrophile**



(b) Formation of σ – complex

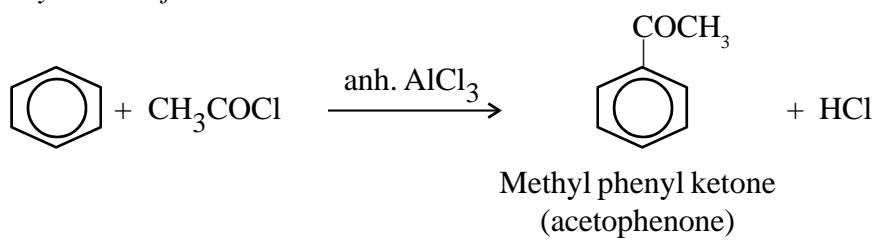


(c) Elimination of Proton (H^+)

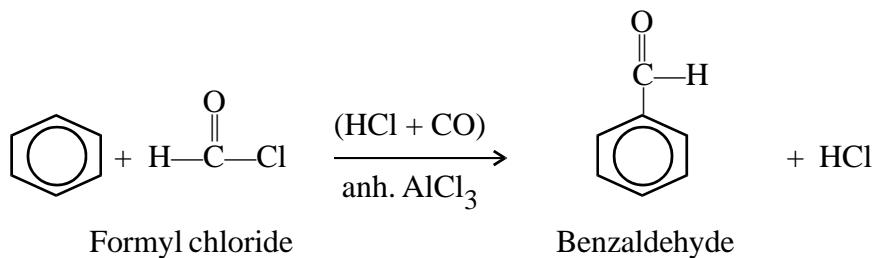


Synthetic application of F—C acylation

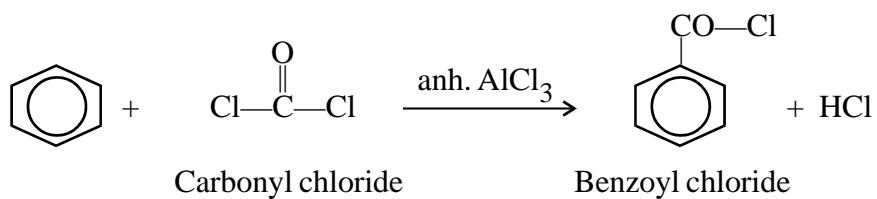
(a) *Synthesis of ketones*



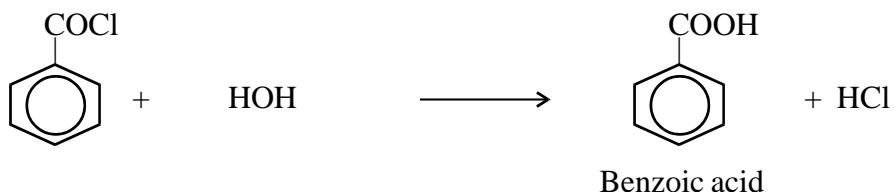
(b) *Synthesis of aldehydes (Formylation)*



(c) Synthesis of acid chloride & carboxylic acid



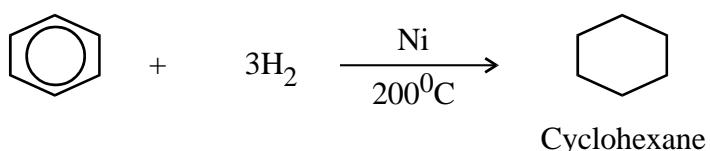
Benzoyl chloride upon hydrolysis yields benzoic acid.



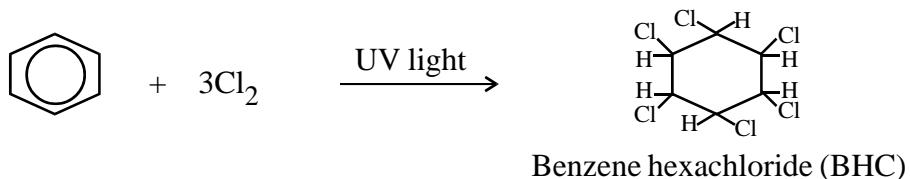
(B) Addition reactions

(i) Catalytic hydrogenation :

Benzene adds on three moles of hydrogen in presence of Ni at 200^0C forming cyclohexane.



(ii) Addition of halogen : Benzene adds on three moles of Cl_2 in presence of UV light to form benzene hexachloride (BHC)



BHC exists in nine stereoisomeric forms out of which the γ (Gamma) isomer known as Lindane is a powerful insecticide. The chairform of γ -isomer is shown below.

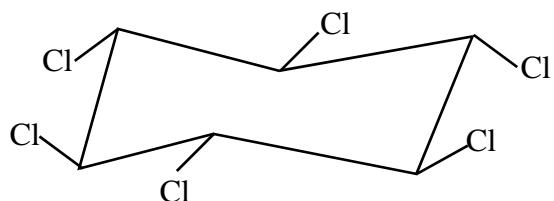
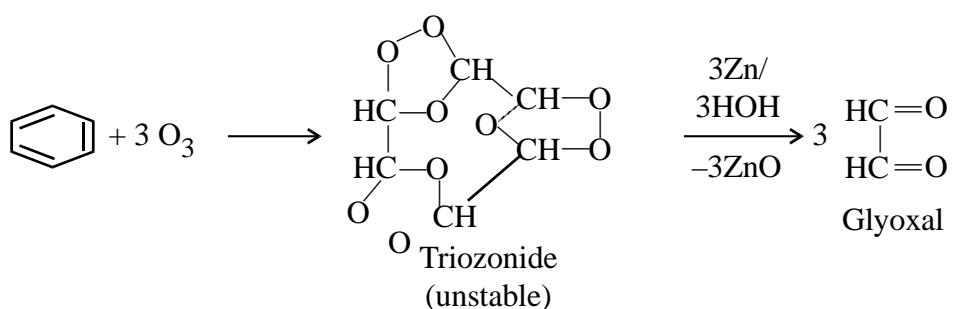


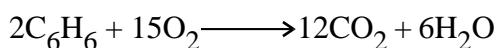
Fig. 13.16 Structural formula of γ - isomer of BHC.

(iii) **Addition of Ozone**

Benzene adds on three moles of ozone to form unstable triozonide. The triozonide on hydrolysis yields three molecules of glyoxal.

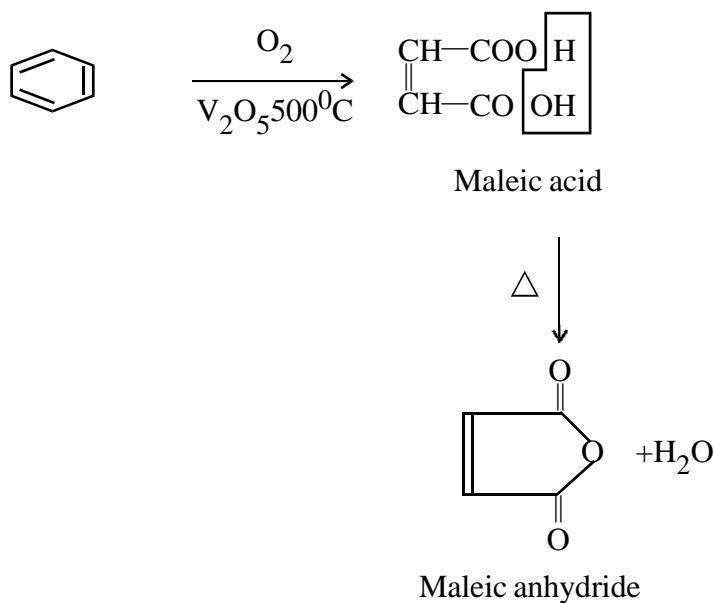
(C) **Oxidation reactions**

- (i) *Combustion* : Benzene burns with a sooty flame producing CO_2 and water vapour.

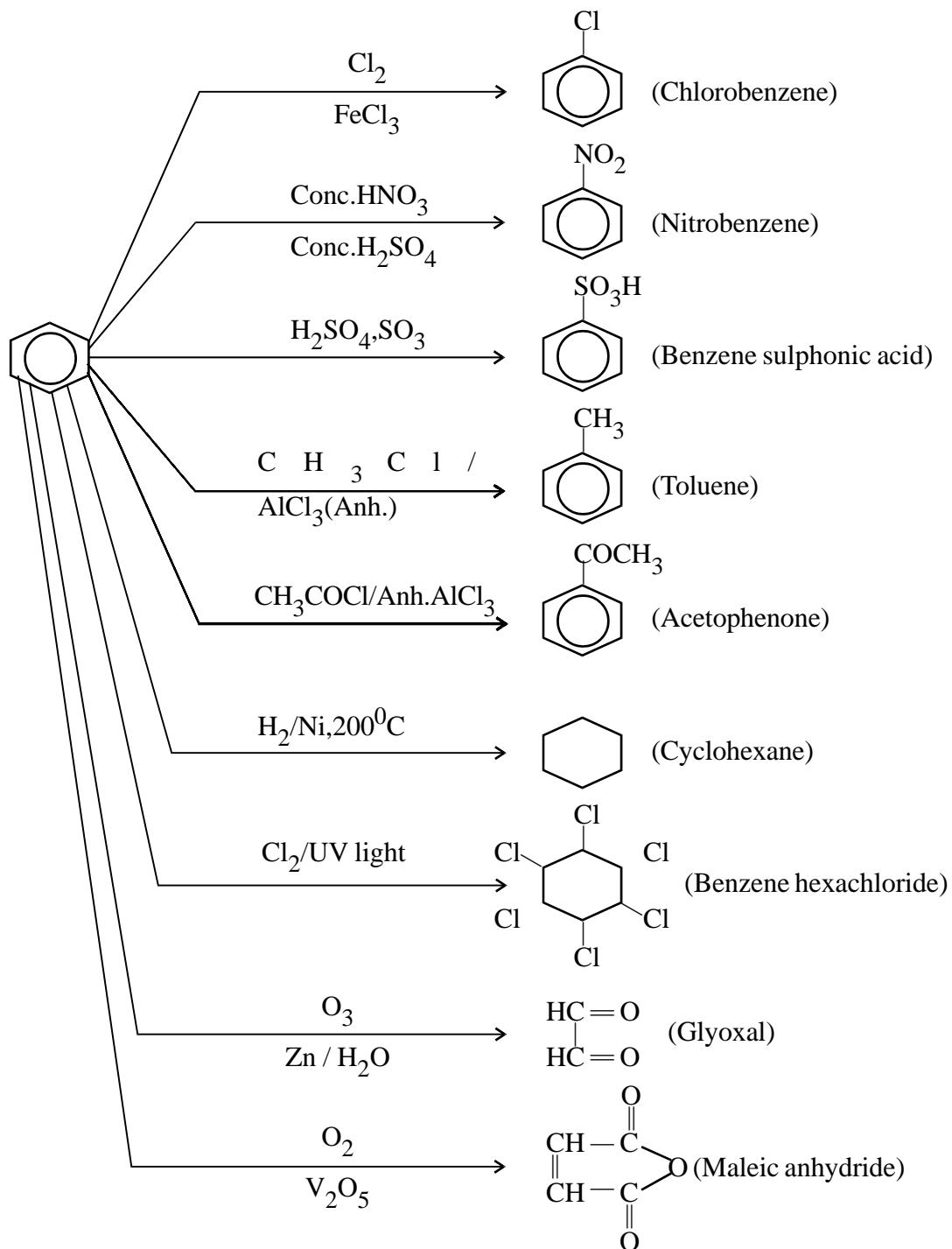


- (ii) *Catalytic oxidation*

When vapour of benzene mixed with oxygen is passed over vanadium pentoxide at 500^0C , maleic anhydride is formed.



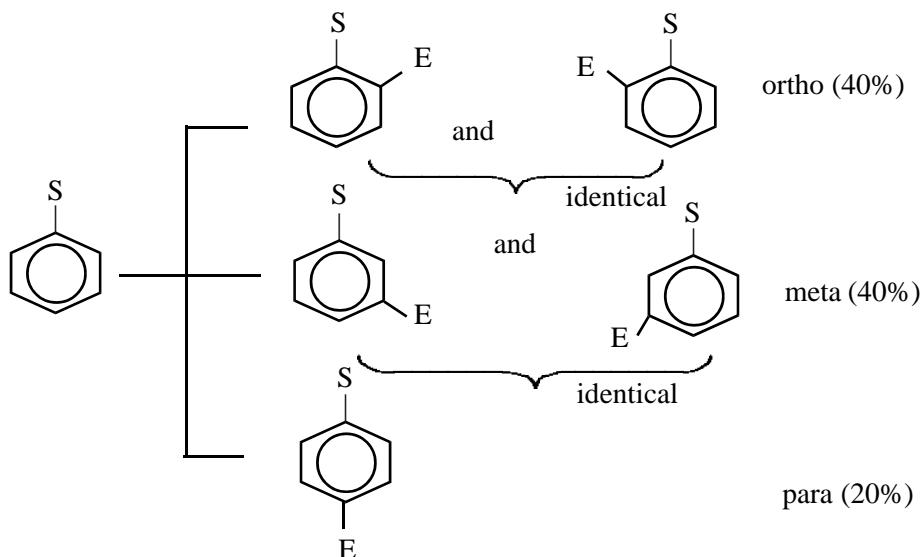
Reactions of benzene :



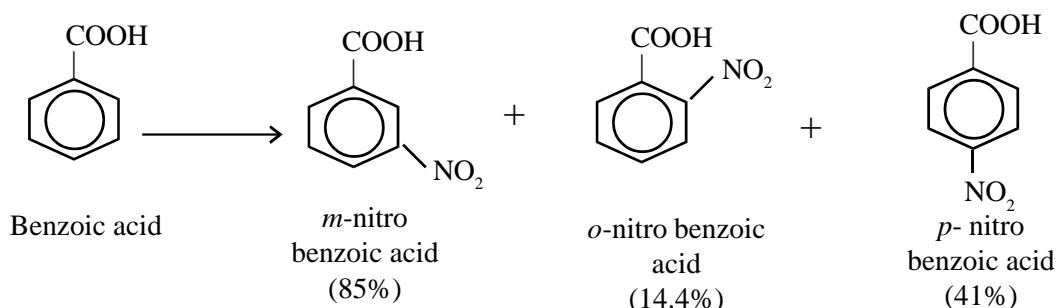
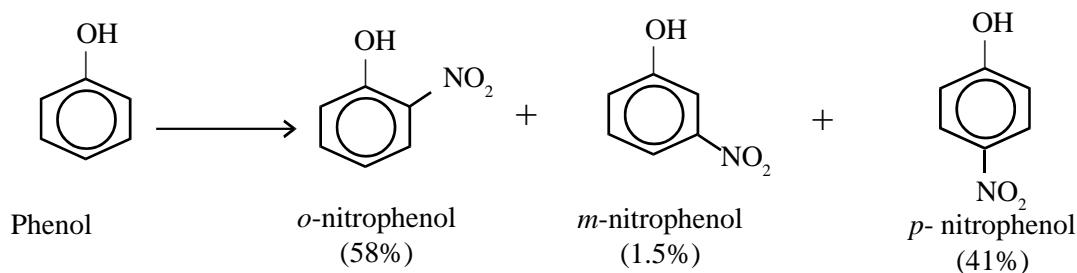
20.8

DIRECTIVE INFLUENCE OF SUBSTITUENTS

The electrophilic substitution reactions of benzene have been discussed elaborately. When electrophilic substitution is considered in case of benzene with already one substituent (s), the electrophile ‘E⁺’ may enter any of the remaining positions. The possible disubstitution products are :-



The arrangement of substituents on the benzene ring is called **orientation**. In actual practice the above proposition is never observed. When phenol is nitrated the main products are ortho and para but nitration of benzoic acid produces mainly meta isomer.



Thus we say that

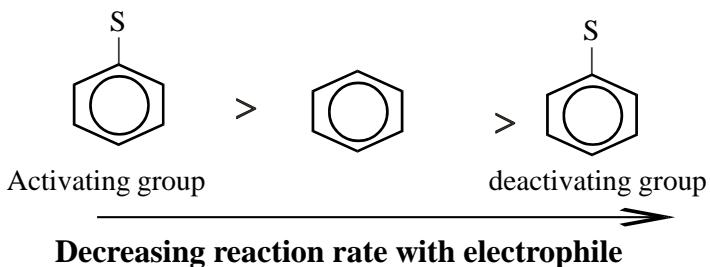
-OH group is ortho and para directing.

-COOH group is meta directing.

ACTIVATING AND DEACTIVATING INFLUENCE OF SUBSTITUENTS.

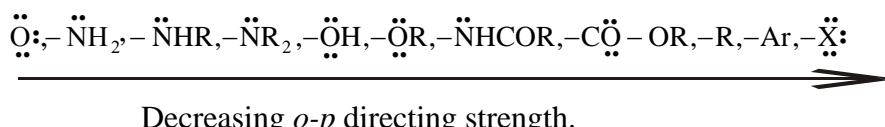
The position of the incoming electrophile is determined by the substituent already present in the benzene nucleus. The substituent may increase or decrease the rate of second substitution reaction compared to the rate of substitution in benzene itself. Thus the substituent which enhances the rate activates the benzene ring and that which lowers the rate deactivates the benzene ring. The substituents are thus known as activating and deactivating substituents respectively.

Experimentally it has been found that ortho-para directing substituents are ring activators excepting halogens whereas meta directing substituents are ring deactivators.



Ortho and para directors.

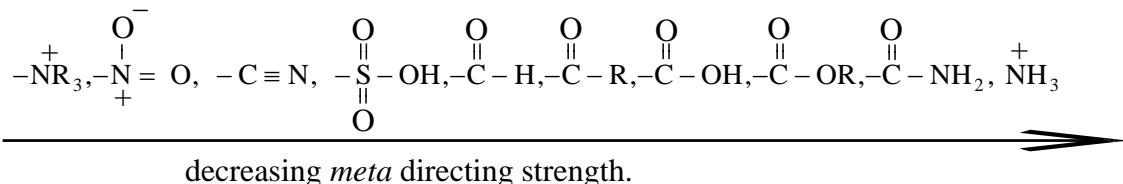
- They direct the incoming electrophile to enter the ortho and para positions only.
- They activate benzene nucleus, excepting halogens.
- They are electron donating groups.
- The groups are arranged in decreasing order as shown below.



Meta directors.

- They direct the incoming electrophile to enter to the meta position.
- They deactivate benzene nucleus.

- iii. They are electron withdrawing groups
- iv. The groups are arranged in the decreasing order as shown below.



Interpretation of deactivating and activating effects :

The activating and deactivating effects of substituents in the benzene ring can be explained by 1) charge distribution theory (CDT)

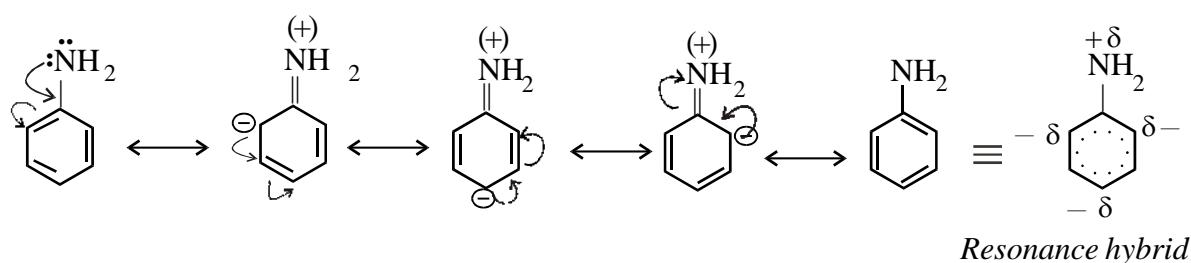
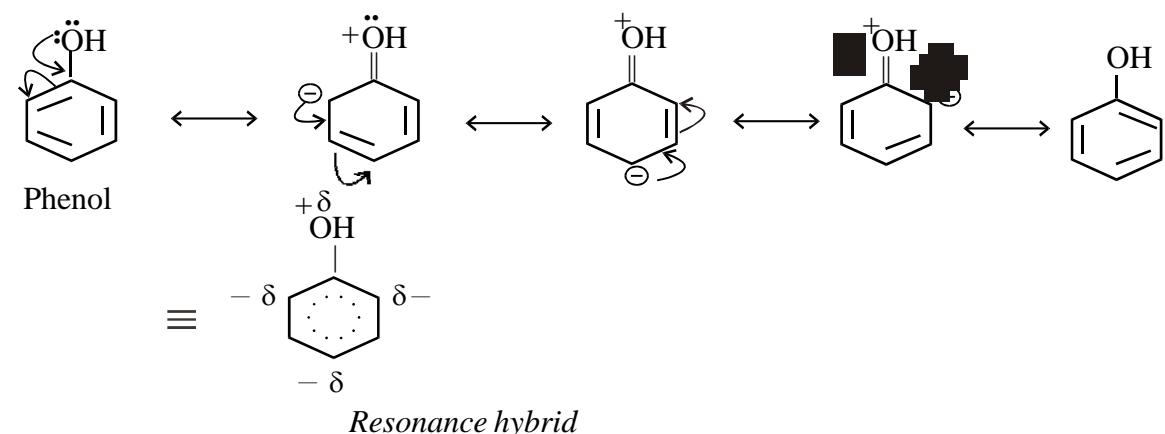
2. Stability of σ - complexes.

1. C.D.T. :

The charge distribution in mono substituted benzene depends on i) Inductive effect, ii) Mesomeric or Resonance effect (M). These two effects reinforce each other in some cases and oppose each other in some other cases. The two electronic effects determine whether the electron density of the ring is enhanced or lowered and thus consequently predict the activating and deactivating influence of the substituent 's' already present in the benzene ring.

a) When the substituent is electron donating :

Let us take the case of phenol and aniline



In the above two cases the electron density in the ring is enhanced and the benzene ring system is activated to electrophilic attack. Since the electron density is relatively greater at ortho and para positions the electrophile preferentially enters the rings at these positions.

Due to more electro negativity of 'O' and 'N' than 'C' atom in phenol and aniline, both these compounds exercise – I effect and tend to withdraw electron from the ring.

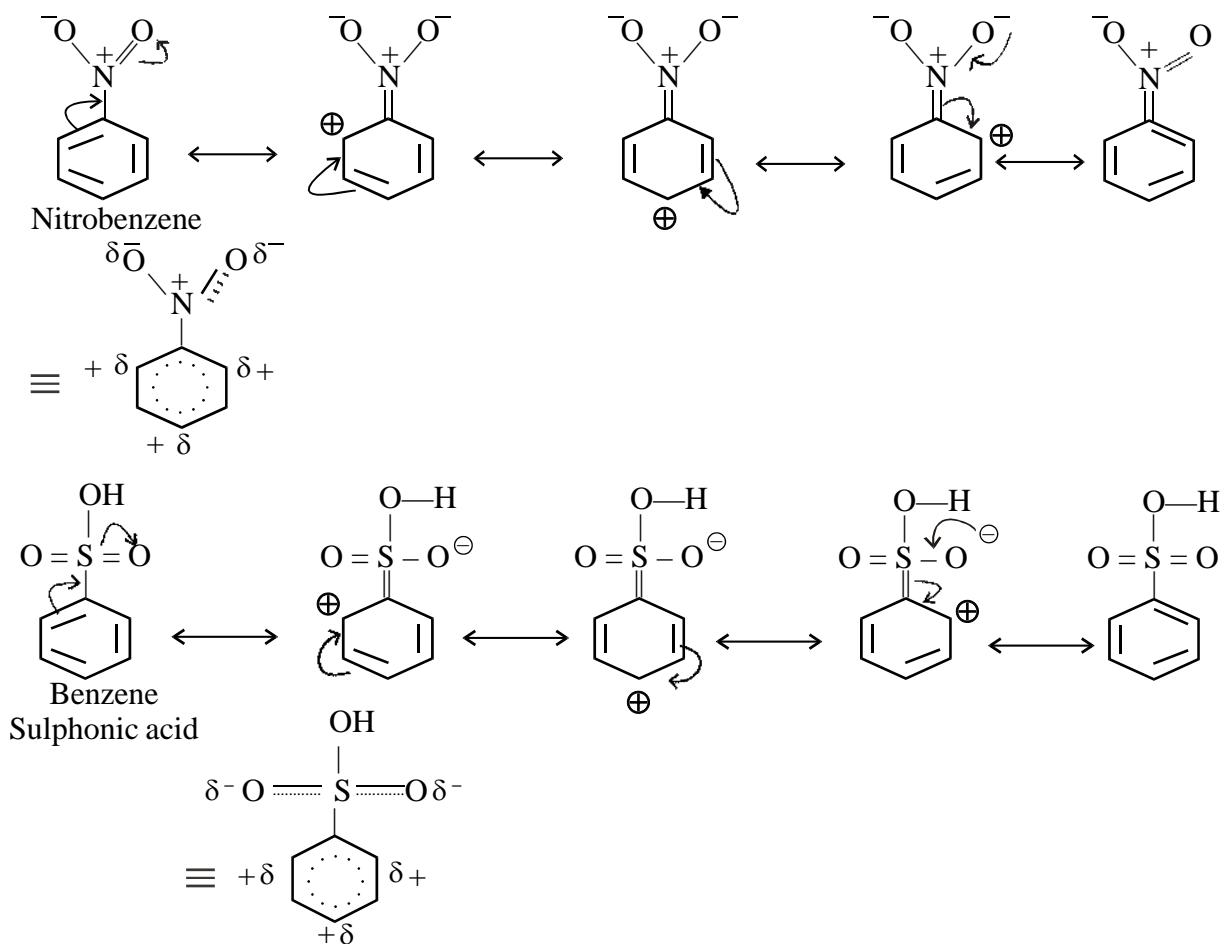
Again there is resonance effect due to presence of $\ddot{\text{O}}$, $\ddot{\text{N}}$ atom attached to benzene ring. Both these effects oppose each other but the net result is increase of electron density of the ring and more so in o- and p- position.

Compound	Electron displacement		Net result
	(I)	(M)	
i) Phenol	-I	+M	$O-P$ directing and ring activating groups
ii) Aniline	-I	+M	

Thus the incoming electrophile would attack the ring at ortho and para position and the electron donating groups are ortho and para directing.

b. When the substituent is electron withdrawing

Let us take the case of nitrobenzene and benzene sulphonic acid.

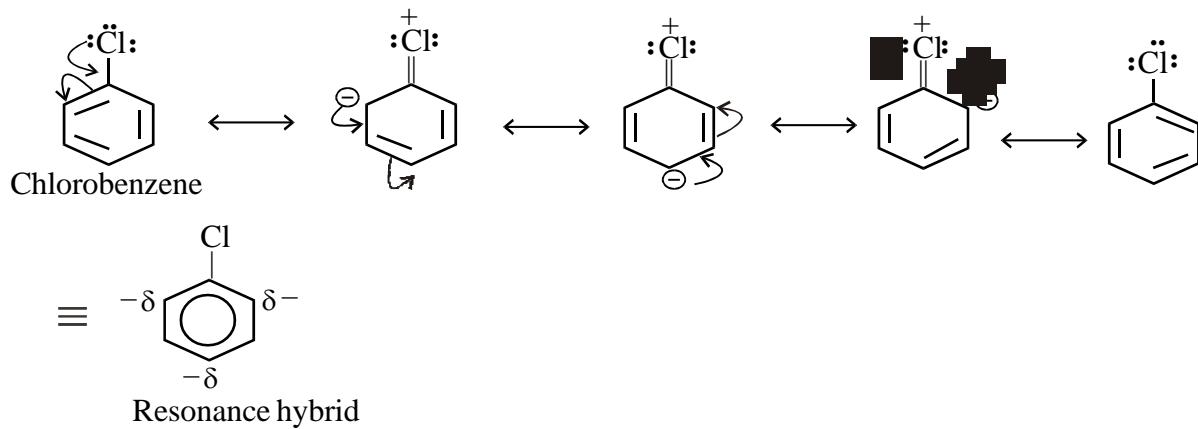


In the above two cases the resonance effect ($-M$) and the inductive effect ($-I$) reinforce each other i.e., they act in the same direction. These is a drain of electron from the benzene ring and therefore the ring gets deactivated. Since the positive (+) charge appears in $\sigma - p$ position, the electrophile preferentially attacks at the meta position. So the electron withdrawing groups are meta directing.

Compound	Electron displacement		Net result
	(I)	(M)	
Nitrobenzene	$-I$	$-M$	<i>m</i> -orienting and ring deactivating group.
Benzene sulphonic acid	$-I$	$-M$	

Anomalous behaviour of halogen substituent

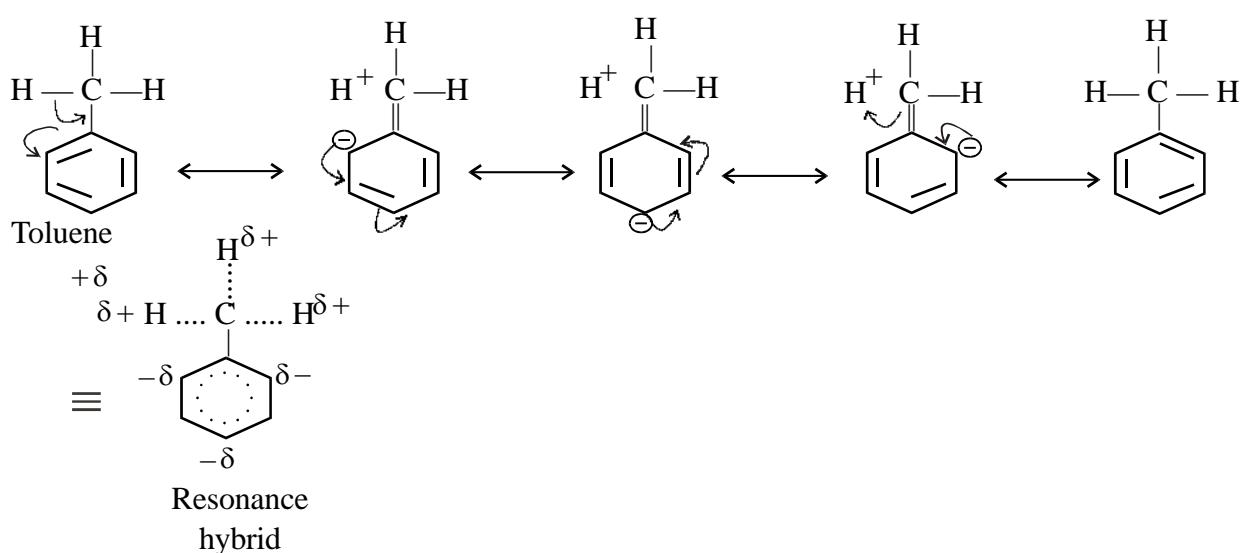
The halogen atom because of its unshared pair of electron exhibits resonance.



From the structure or resonance hybrid it can be said that halogen atom is $\sigma - p$ directing and like other $\sigma - p$ directing groups it is expected that the halogen atom activates the benzene ring to electrophilic attack. But the halogen atom, on the contrary, is a ring deactivator. This is due to the fact that the $-I$ effect predominates over the $+M$ effect (resonance) and the net result is drift of electron from the ring.

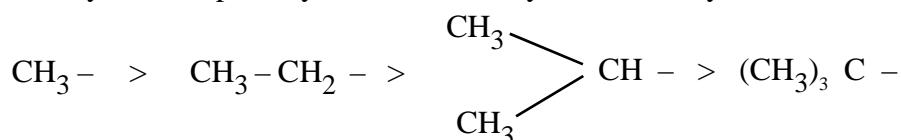
Directive influence of the alkyl groups

Alkyl groups do not possess unshared pair of electrons but they are $\sigma - p$ directing and act as ring activators. This can be explained on the basis of hyperconjugation or 'no-bond resonance'. Here interaction of σ electrons of C-H bond with π electrons of the double bond is taken into account.

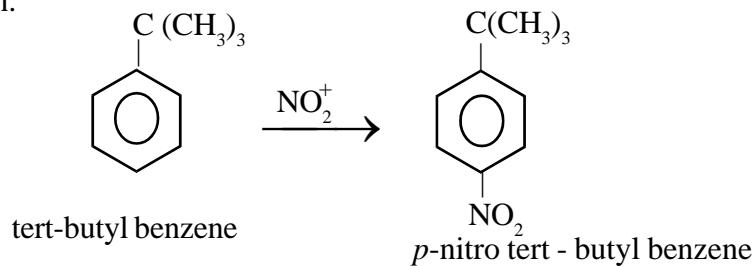


From the structure of resonance hybrid it is evident that the electron density is enhanced in the o-p positions by the appearance of $-\delta$ charge. Hence alkyl groups activate the ring and are o-p directing. The relative ability of the alkyl groups to participate in hyperconjugation is in the order.

Methyl > primary > secondary > tertiary.



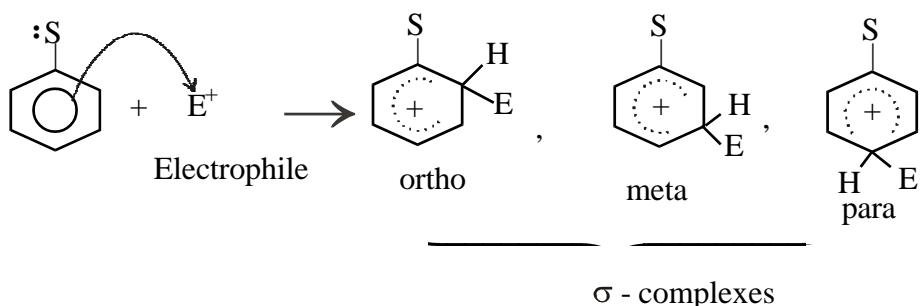
This is because the alkyl group must possess at least one H atom on the C atom joined to the ring carbon. tert-butyl benzene on nitration gives only para isomer. This is due to steric hindrance caused by bulky methyl groups not allowing the electrophile to enter at the ortho position.



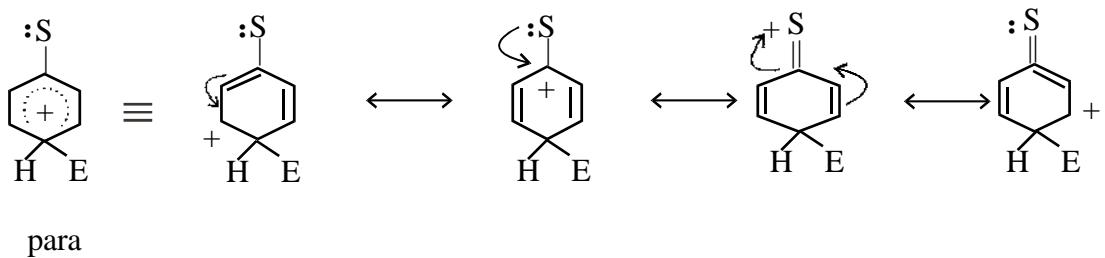
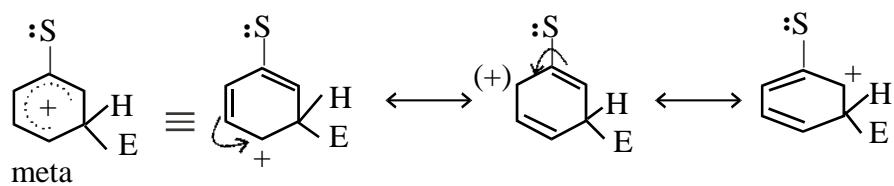
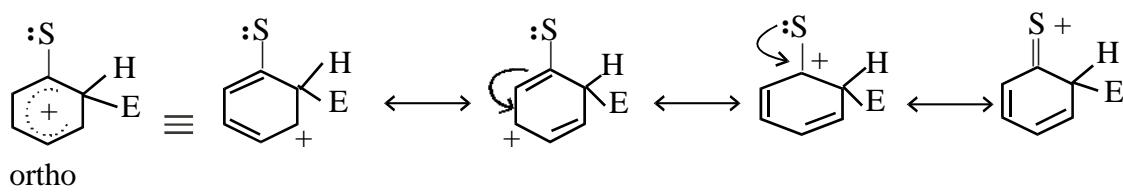
2) Stability of σ - complex (Carbocation)

In electrophilic substitution reaction of mono substituted benzene there is formation of π complex which immediately rearranges to form σ complex. The stability of the σ - complex formed in case of ortho, meta and para attack of the electrophile enables us to predict the directive influence of the group already present in the benzene nucleus.

i. When the group already present is electron donating.

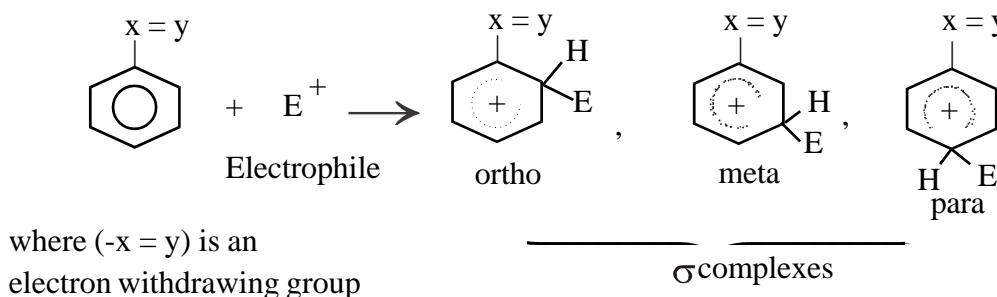


Wheland structures for the carbocation (σ - complexes)

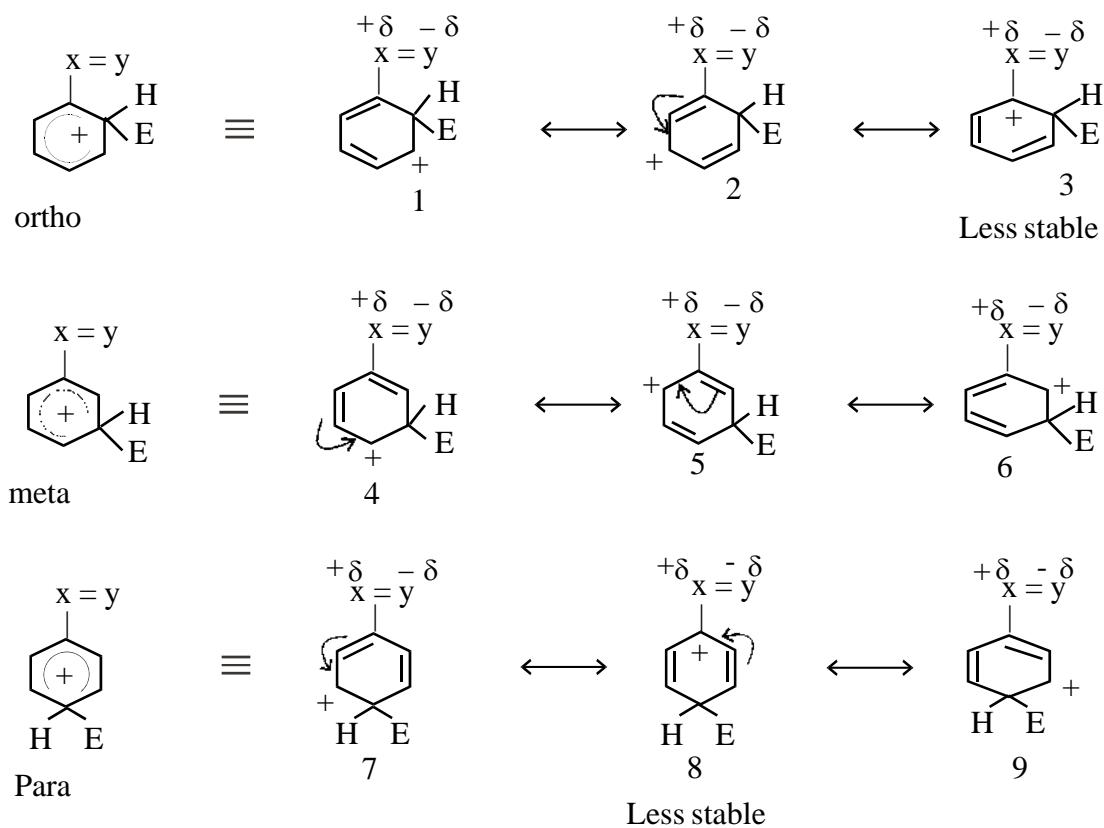


Thus there are more number of resonating forms for Wheland carbocation in case of ortho and para substituents. The ortho and para attack of the electrophile results in more stabilized carbocation. It can therefore be concluded that the electron donating groups allow the electrophile to enter at the ortho and para positions only or in other words it can be said that the electron donating groups are o-p directing.

ii) when the group already present is electron withdrawing



Wheland structures for the carbocation



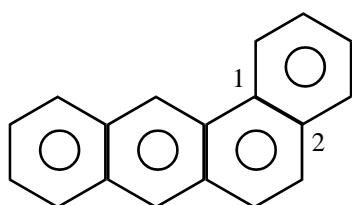
In structures 3 and 8 the two +ve charges are adjacent to each other. The repulsive interaction leads to high energy and therefore the contributing structures are less stable. They do not contribute to the resonance hybrid. Consequently there are 3 resonating structures for meta attack and two for each ortho and para attack. Hence the carbocation ion intermediate formed in case of meta attack is comparatively more stable than that for ortho and para attack.

Thus the electron withdrawing groups allow the electrophile to enter at the meta position or in otherwords it can be concluded that the electron withdrawing groups are meta directing.

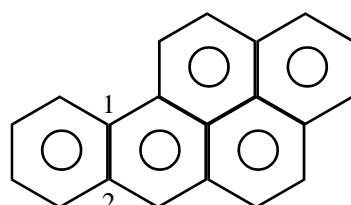
20.9 CARCINOGENICITY AND TOXICITY

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and carcinogenic by nature. Their carcinogenic activity is further influenced by the presence of certain groups like $-\text{CH}_3$, $-\text{OH}$, $-\text{CN}$, $-\text{OCH}_3$, etc.

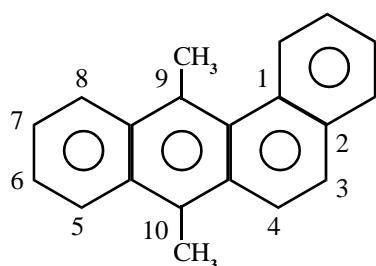
Examples are :



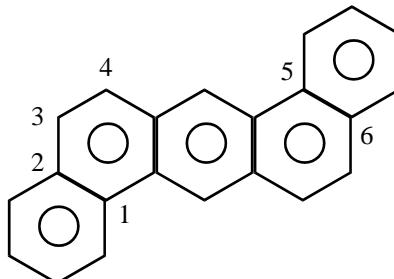
1, 2 - Benzanthracene



1, 2 - Benzpyrene



9, 10 - Dimethyl-
1, 2 - benzanthracene

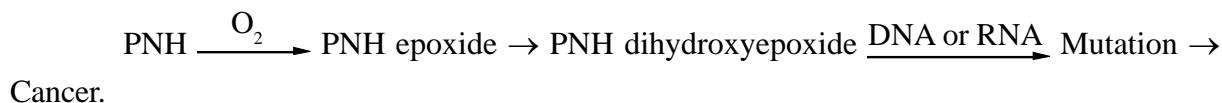


1, 2, 5, 6 -
Dibenzanthracene

Polynuclear hydrocarbons are formed by the incomplete combustion of organic matter such as coal, petroleum, tobacco etc and hence widely present in the environment causing human cancer. Naturally the root of the fatal disease cancer can be substantially evaded by the elimination of carcinogens from the environment.

When these polynuclear hydrocarbons enter into human body, undergo biochemical reactions and are converted into their oxides called epoxides and then into dihydroxyepoxides. On reaction with the purine bases such as guanine, present in DNA and RNA of the human cells, these hydroxides affect both structure and characteristics. Even at this stage purine because of bigger size can not fit into the double helix of DNA. This damage causes mutation and consequently leads to cancer.

Schematic representation of carcinogenic effect of polynuclear hydrocarbons (PNH) can be given as:



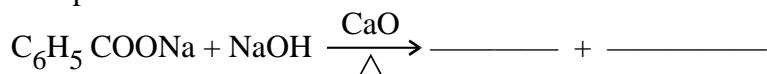
CHAPTER (20) AT A GLANCE

1. Aromatic compounds contain a higher percentage of carbon atom and produce a sooty flame when heated over a copper foil.
2. The general formula of arenes is C_nH_{2n-6y} where y refers to no. of rings.
3. *Hückel's Rule* :- All aromatic compounds must satisfy Hückel's $(4n + 2)\pi$ rule. The rule states that in a cyclic system of overlapping p-orbitals the no. of π electrons should be $(4n+2)$.
4. The six carbon atoms in benzene are sp^2 hybridised, C—C bond length is 1.39 \AA^0 and C—C—C bond angle is 120^0 .
5. Resonance stabilisation energy for benzene is 36 kcal/mole.
6. Coal tar is a thick, black, viscous liquid obtained as a result of low temperature carbonisation of coal. It is a rich source of aromatic compounds.
7. Benzene can be isolated from the light oil fraction of coal tar.
8. Benzene undergoes electrophilic substitution reactions like nitration, sulphonation, halogenation and Friedel Craft's reaction.
9. 2,4,6 Trinitrotoluene (TNT) is a well known explosive.
10. **Friedel Craft's reaction :** Benzene reacts with alkyl halide or acyl halide in presence of anh. $AlCl_3$ forming the corresponding alkyl benzene and acyl derivative of benzene respectively. The reactions are known as F—C alkylation and F—C acylation.
11. Nitrobenzene can not exhibit Friedel Craft reaction.
12. γ — isomer of benzene hexachloride (BHC) is known as Gammexane.
13. Benzene upon oxidation in presence of V_2O_5 forms maleic anhydride.
14. The arrangement of substituents on the benzene ring is called orientation.
15. The electron donating groups activate the benzene nucleus and they are ortho and para directors.
16. The electron withdrawing groups deactivate the benzene nucleus and they are meta directors.
17. The halogen atom is o-p directing but is a ring deactivator.
18. The alkyl groups do not possess unshared pair of electrons but they are o-p directing and act as ring activators.
19. Hyperconjugation is no-bond resonance.
20. Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and carcinogenic activity is influenced by substituents like methyl, hydroxy, cyano, methoxy etc. which disrupt cellular metabolic processes.

QUESTIONS

A. Very Short answer type (1 mark)

- (i) Give the structure of Gammexane.
- (ii) Give the structural formula of p-xylene
- (iii) Give the graphic formula of benzene
- (iv) State Huckel's rule
- (v) Complete



- (vi) What is the electrophile used in case of nitration of benzene ?
- (vii) Name the fraction from which benzene can be isolated in coal tar distillation.
- (viii) What is the main source of aromatic compounds ?
- (ix) A cyclic hydrocarbon molecule has all the carbon and hydrogen atoms in a single plane. All C – C bonds have same length which is less than 1.54\AA^0 , but more than 1.34\AA^0 . What is the C – C – C bond angle in the molecule ?
- (x) Name the reaction where Lewis acid is used as catalyst for aromatic substitution.

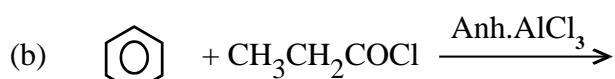
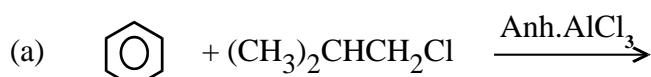
(B) Short answer type (2 marks)

- (i) Write a note on 'Aromaticity'
- (ii) Starting from benzene how can you prepare cyclohexane ?
- (iii) What happens when toluene is oxidised by acidified KMnO_4 solution ?
- (iv) Aromatic compounds undergo substitution reactions, explain with one reaction.
- (v) Although benzene is highly unsaturated normally it does not undergo addition reactions Give reasons.
- (vi) What happens when acetylene is passed through heated iron tube ?
- (vii) What happens when benzene reacts with methyl chloride in presence of anh. AlCl_3 ?
- (viii) What happens when [each 2 marks]
 - (a) Benzene is oxidised in presence of V_2O_5 .
 - (b) Benzene is subjected to ozonolysis.
 - (c) Benzene is treated with Cl_2 in presence of sunlight.
- (ix) Write the position isomers of xylene.
- (x) What happens when excess of Cl_2 is passed through boiling toluene in presence of sunlight.

- (xi) Nitration of toluene is easier than benzene— why ?
- (xii) What is TNT ? How is it formed from toluene ?
- (xiii) Nitrobenzene does not respond to Friedel Craft reaction — why ?
- (xiv) What happens when benzene reacts with Cl_2 in presence of UV light ?
- (xv) Metanitrophenol is less acidic than orthonitro phenol — why ?
- (xvi) What is Friedel Craft's acylation ?
- (xvii) State and explain Huckel's rule
- (xviii) What are the numbers of π -electrons in benzene and naphthalene ?
- (xix) Name four *o*- and *p*- directing groups.

(C) Long answer type : (10 marks)

1. What are different reactions exhibited by aromatic compounds ? Give an example of each reaction and explain.
2. (a) How is benzene obtained from light oil coal tar distillation.
 (b) How the following groups are introduced in the benzene ring ?
 $-\text{CH}_3, -\text{NO}_2, -\text{SO}_3\text{H}$
3. Write notes on
 Friedel Craft's reaction
4. Discuss the molecular orbital structure of benzene.
5. Predict the product & suggest the mechanism.



6. Discuss any one electrophilic substitution reaction in benzene.

(D) Multiple Choice type question with answers.

1. When phenol is distilled with zinc dust the product is

(a) Toluene	(b) Benzene
(c) Xylene	(d) None of the above
2. In Benzene the 'C' atoms are

(a) sp^3 hybridised	(b) sp^2 hybridised
(c) sp hybridised	(d) Unhybridised

3. Coal tar is a main source of
(a) Aromatic compounds (b) Aliphatic compounds
(c) Cycloalkanes (d) Heterocyclic compounds

4. The following products are formed by fractional distillation of Coal tar. Which one is basic ?
(a) Phenol (b) Toluene
(c) Anthracene (d) Pyridine

5. All bonds in benzene are equal due to
(a) tautomerism (b) I-effect
(c) Resonance (d) Isomerism

6. Phenol is less acidic than
(a) *o*-Cresol (b) p-methoxy phenol
(c) p-nitrophenol (d) Ethanol

7. Nitro group in nitrobenzene is
(a) ortho director (b) meta director
(c) para director (d) ortho & para director

8. Nitration of benzene is
(a) Nucleophilic substitution (b) Electrophilic substitution
(c) Homolytic substitution (d) Electrophilic addition

9. The compound that is most reactive towards electrophilic nitration is
(a) Toluene (b) Benzene
(c) Benzoic acid (d) Nitrobenzene

10. Anhydrous AlCl_3 is used in Friedel Craft reaction because it is
(a) electron rich (b) soluble in ether
(c) insoluble (d) electron deficient

11. In which can the C—C bond length in same
(a) But -2-ene (b) But-1-ene
(c) Benzene (d) Prop-1-yne

12. Which of the following pairs will give the same bond angle ?
(a) Ethane & ethyne (b) ethane & ethene
(c) Ethene & benzene (d) Ethyne & benzene

13. The reaction of Toluene with Cl_2 in presence of FeCl_3 gives predominantly
(a) m-chlorotoluene (b) benzoyl chloride
(c) o - & p chlorotoluene (d) benzal chloride

14. Nitration is easy in case of
(a) Toluene (b) Nitrobenzene
(c) Chlorobenzene (d) Sulphobenzene

15. Benzene reacts with chlorine in presence of sunlight to form
(a) 666 (b) BHC
(c) Gammexane (d) All

(E) Fill in the blanks :

1. Aromatic hydrocarbons burn with _____ flame.
 2. _____ is an important source of aromatic compounds.
 3. _____ fraction of coaltar mainly contains benzene..
 4. Polymerisation of acetylene gives _____.
 5. γ -Isomer of benzene hexachloride is called _____
 6. Aromatic compounds are stabilised by _____.

7. An electron withdrawing substituent in benzene orients the incoming electrophile in the _____ position.
8. Toluene on oxidation with CrO_2Cl_2 gives _____.
9. The number of π electrons in the aromatic ring is equal to $(4n+2)$. This is in accordance with _____ rule.
10. Benzene on oxidation with V_2O_5 gives _____.
11. Benzene on ozonolysis gives _____.
12. Anthracene is a _____ compound.
13. Benzene when treated with Conc. H_2SO_4 at 80^0C produces _____.
14. No. of π electrons in naphthalene is _____.

ANSWERS

D. MULTIPLE CHOICE QUESTION

- | | | | | |
|------|-------|-------|-------|-------|
| 1. b | 6. c | 11. c | 16. c | 21. b |
| 2. b | 7. b | 12. c | 17. a | 22. c |
| 3. a | 8. b | 13. c | 18. b | 23. b |
| 4. d | 9. a | 14. a | 19. c | 24. d |
| 5. c | 10. d | 15. b | 20. c | |

- E.**
- | | | | |
|---------------|----------------------------|--------------|----------------------------------|
| 1. Luminous | 2. Coaltar | 3. Light oil | 4. poly ethyne or poly acetylene |
| 5. Gammaxene | 6. Resonance | 7. Meta | 8. Benzoic acid |
| 9. Hückel's | 10. Maleic anhydride | 11. Glyoxal | |
| 12. Benzenoid | 13. Benzene sulphuric acid | 14. 10 | |



UNIT – XIV

CHAPTER - 21

ENVIRONMENTAL CHEMISTRY

21.1 INTRODUCTION

The word ‘Environment’ literally means surroundings. So the ‘Environment’ is considered as a composite term for the conditions in which an organism lives and consists of air, water, soil, sunlight, food etc. which are the basic needs of all organisms to survive.

The basic components of the environment are :

- (a) Abiotic or non-living components which are further sub-divided into
 - (i) Atmosphere or air
 - (ii) Hydrosphere or water
 - (iii) Lithosphere or the rocks and soil.
- (b) Biotic or living components comprising of flora and fauna.
- (c) Energy components consisting of solar energy geochemical energy, geothermal energy, nuclear energy etc.

Thus the environmental studies deal with the sum of all social, economical, biological, physical and chemical interrelations with our surroundings. Focus on environmental studies was concentrated in the year 1972 when United Nations Conference on the Human Environment was held at Stockholm showing alarming concern over environmental pollution. Its main object is to enlighten the people about the importance of protection and conservation of our environment and the need to restrain human activities leading to indiscriminate release of pollutants into the environment.

ENVIRONMENTAL CHEMISTRY is a part of environmental education. It may be defined as the study of the sources, reactions, transport, effect and fate of chemical species in the air, water and soil and the effect of human activity upon these. Precisely environmental chemistry is the science of chemical phenomena in the environment.

21.2 ENVIRONMENTAL POLLUTION

The undesirable change in the physical, chemical or biological characteristics of air, water and soil is known as pollution. It may harmfully affect life and therefore becomes a potential health hazard to a living organism. In otherwords, the direct or indirect change in any component of the biosphere that is harmful to living organisms is known as pollution.

The substance that causes pollution is known as a pollutant. It may include chemical or geochemical substances like dust, sediment, grit etc, biotic component and its products or physical factor like heat which badly affect the environment.

Environmental Pollutants :

The pollutants that affect air, water and soil are environmental pollutants. They are :

- 1) Gases - Carbon monoxide (CO), Sulphur dioxide (SO_2), Oxides of nitrogen (NO and NO_2), Halogens (Cl_2 , Br_2 , I_2)
- 2) Metals - Mercury, Lead, Zinc, Iron, Nickel, Tin, Cadmium, Chromium etc.
- 3) Deposited matter - Smoke, Soot, Dust, Dirt, Tar etc.
- 4) Fluorides
- 5) Acid droplets - Sulphuric acid, Nitric acid.
- 6) Organic substanses - Ether, Benzene, Acetic acid etc.
- 7) Agrochemicals - Fertilisers and Biocides (Pesticides, Fungicides, Nematicides, Bactericides etc)
- 8) Radioactive waste
- 9) Solid waste
- 10) Photochemical oxidants - Ozone, Photochemical smog, PAN (Peroxy Acetyl Nitrate), Aldehyde Ethylene etc.
- 11) Noise

The order of priority of pollutants and the medium as stated in UNEP (United Nation Environment Programme) document is as follows.

Order of priority	Medium
1. SO_2 + suspended particles	Air
Strontium, Caesium	Food
2. Ozone	Air
DDT and organochlorine compounds	Biotic, Man
3. NO_3 , NO_2	Air, Drinking water
Nitrogen oxides.	
4. Mercury compounds	Food, water
Lead and cobalt.	
5. Petroleum hydrocarbons	Sea
Carbon monoxide	Air
6. Fluorides	Water (Fresh water)
7. Asbestos	Air
Arsenic	Drinking water
8. Mycotoxins and microbial contaminants	Food.

21.3 AIR POLLUTION

The word pollution has been derived from the Latin word “pollutioem” meaning the art of making dirt. The earth is surrounded by an insulating blanket known as atmosphere. We live in an ocean of air. The air envelope, called the atmosphere protects the earth from extremes of heat and cold and from the harmful rays of sun. Without air life is impossible, since air contains substances that all living things require. Pollution of air is imbalance in the quality of air caused as a result of introduction of some foreign elements from natural and man made sources to the air so that it becomes harmful to living organisms.

Composition of air

The air envelope that surrounds the earth is composed of mixture of gases. Normal composition of clean air is as follows:

Gases	Percent(by volume)
Nitrogen	78.084
Oxygen	20.997
Argon	0.934
Carbon dioxide	0.0314
Methane	0.0002
Hydrogen	0.00005
Other gases	minute

21.3.1 Sources of air pollution :

Pollution of air results from emission of gaseous substances from industry, automobiles, thermal power stations, domestic combustion etc. The important sources of air pollution are discussed below.

1: Industrial chimney wastes :

Chemical industries like paper and pulp mills, fertiliser plants, petroleum refineries, steel plants etc. produce certain solid, liquid or gaseous substances by which the land, water and air get polluted.

The most common gases responsible for causing pollution are carbon dioxide, carbon monoxide, sulphur dioxide, oxides of nitrogen, hydrogen sulphide etc.

2. Automobiles:

The toxic vehicular discharges now-a-days have become a serious threat to ambient air quality. The vehicles discharge a lot of poisonous gases like carbon monoxide (about 77%), oxides of nitrogen (about 8%) and unburnt hydrocarbons (about 15%). Besides these gases there are particulates of lead and traces of aldehydes, esters, ethers, peroxides and ketones which are chemically active and these combine in presence of sun light forming highly toxic photochemical smog in the atmosphere. Noise is a serious type of pollution arising from road traffic, air craft and machineries. Loud speaker and record players also add noise to air. Noise can cause psychological disorders due to constant strain on nervous system.

3. Burning of fossil fuels and fires

Poisonous gases like carbon dioxide, carbon monoxide, sulphur dioxide, oxides of nitrogen, methane etc. are released into the atmosphere by increasing use of fossil fuels, coal etc. The concentration and quality of these pollutants depend upon the type of fuel being used. For example SO_2 , coming out through the chimneys of most of the

factories gets oxidised to sulphur trioxide which when react with rain water gets converted to sulphuric acid. This is known as **acid rain**. Acid rains cause global ecological problem affecting land flora and fauna.

4. **Thermal Power stations**

For augmentation of energy generation a number of thermal power stations are set up in our country by NTPC (National Thermal Power Corporation). The consumption of coal by thermal plants is several million tonnes. The main pollutants are sulphur dioxide, oxides of nitrogen, fly ash and hydrocarbon.

5. **Radioactive pollution :**

Radioactive pollution has become a potential health hazard now-a-days . The pollution is due to production of nuclear fuel, testing of nuclear weapons, use of nuclear energy in power plants and more over the use of radio isotopes in medicine, industries and scientific research.

The air pollutants from various sources are as follows:

1. **Carbon compounds :**

These include both CO and CO₂. CO is produced as vehicular exhaust whereas CO₂ is released by complete combustion of fossil fuels.

2. **Sulphur compounds :**

These are mainly SO₂, H₂S and H₂SO₄. The pollutants are released by combustion of fossil fuels.

3. **Oxides of nitrogen :**

These mainly include NO, NO₂ and HNO₃.The pollutants are released by power plants, automobiles and industries.

4. **Hydrocarbons :**

These include benzene, benzpyrenes etc. which are released into the atmosphere by industries and automobiles.

5. **Ozone :**

The level of O₃ rise in the atmosphere due to different human activities.

6. **Metals :**

These include lead, nickel, beryllium, tin, vanadium, titanium, cadmium etc which are realeased during metallurgical process and also as automobile exhaust in the form of solid particles, liquid droplets or gases.

7. **Fluorocarbons:**

These are released by the industries and insecticide spray.

8. Particulate matter:

These include dust, grit, fly ash and other suspended particulate matter (SPM)

9. Photochemical products :

These mainly include photochemical smog, PAN etc which are released mostly by automobiles.

10. Other Toxicants :

These include complex chemical substances released during manufacturing processes.

21.3.2 Harmful effects of air pollutants :

1. **Carbon dioxide :** As a result of burning of fossil fuel for domestic cooking, heating and the fuel used in power plants, industries, carbon dioxide is released into the atmosphere. An increase in concentration of CO₂ in the atmosphere contributes significantly to global warming, green house effect.

Green-house effect

CO₂ is present exclusively in the troposphere. The temperature on the surface of the earth is maintained by the energy balance between the sun rays striking the earth and the heat radiated back into the outer space. This is, ofcourse under normal condition i.e. with normal concentration of CO₂. But when there is an increase in CO₂ concentration, the thick layer of CO₂ functions like the glass panels of a green house or the glass windows of a motor car. This layer only allows the sunlight to filter through it reaching the earth but prevents the heat being reradiated by earth back to the outerspace. Thus, most of the heat is absorbed by CO₂ layer and water vapours in the atmosphere which ultimately results in heating up of the earth's atmosphere. The effect is known as **Green house effect**.

2. Carbon monoxide :

The chief source of CO is automobile exhaust. Besides this, natural processes like forest fires, natural gas emission, volcanic eruption, marsh gas production etc. serve as other sources of carbon monoxide.

CO causes difficulty in breathing, causes headaches and also irritation of mucous membrane. On inhalation, carbon monoxide passes into the blood stream through lungs. Inhaled CO combines with blood haemoglobin forming carboxy haemoglobin. This does not permit the transport of oxygen from lungs to the cells. Thus, oxygen carrying capacity of the blood gets diminished. This leads to oxygen deficiency known as *hypoxia*. The gas is fatal over 1000 ppm causing unconsciousness in an hour and ultimately death in a few hours.

3. Sulphur dioxide

The major sources of SO_2 are burning of fossil fuels in thermal power plants and smelting industries. Petroleum refineries and automobiles also release SO_2 into the atmosphere.

SO_2 causes intense irritation in eyes and respiratory tract. In upper respiratory tract it is absorbed and cause swelling and stimulate mucous secretion. Exposure to 1 ppm level of SO_2 leads to constriction of air passage causing significant breathing problem. It reacts with moist air, fogs, H_2O_2 , O_3 etc. forming H_2SO_4 which acts as a stronger irritant than SO_2 . It corrodes lime stone and metals.

4. Oxides of nitrogen

Vehicular exhaust is the major source of oxides of nitrogen which include both nitric oxide and nitrogen dioxide. NO is produced by the combustion of N_2 and O_2 during lightening discharge and by bacterial oxidation of NH_3 in the soil. Besides, these oxides of nitrogen are also released into the air by electric power plants and other chemical industries. NO, on combination with atmospheric oxygen produces NO_2 gas. NO_2 gas is the chief constituent of photochemical smog. At high concentration NO_2 causes variety of diseases like lungs cancer, pneumonia and emphysema (inflammation).

5. Hydrogen sulphide

The oceans release about 30 million tons of H_2S gas every year whereas land releases about 60 to 80 million tons. About 3 million tons of H_2S are released by the industries per year. But the chief industrial sources of H_2S are users of sulphur containing fuels. Other sources include decaying vegetation and organic matter, sulphur springs, coal pits, volcanic eruption etc.

At low concentration H_2S causes headache, nausea, coma and even death. At 5 ppm its unpleasant odour may affect digestive system destroying appetite. Higher concentration may cause conjunctivitis and irritation of mucous membrane.

6. Hydrocarbons

The chief source of hydrocarbons are the motor vehicles. About 40% of the vehicular exhaust hydrocarbons are unburnt fuel components, the rest are the products of combustion. Plants and bacteria are the natural sources of hydrocarbons. Human activities may contribute nearly 20% of hydrocarbons emitted to the atmosphere.

Hydrocarbons have carcinogenic effect on lungs. Aromatic hydrocarbon benzene, emitted from gasoline causes lungs cancer. The most potent cancer inducing hydrocarbon pollutant is benzpyrene. It is present in small amount in smoke, charcoal boiled stakes, tobacco and gasoline exhaust. Decay of garbage and aquatic vegetation may produce

marsh gas (methane) which is a gaseous pollutant. Higher concentration of it may cause explosion.

Hydrocarbons combine with oxides of nitrogen under UV-component of light forming pollutants like PAN (Peroxy acetyl nitrate) and O₃. These pollutants are known as *photochemical smog* which cause irritation of eye, nose and throat and allied respiratory distress.

Acid rains

The important gaseous pollutants are oxides of nitrogen and sulphur. These oxides are produced by combustion of fossil fuels, automobile exhaust, power plants and domestic fires. These oxides are swept up into the atmosphere and react with water in the atmosphere to form sulphuric and nitric acids. These acids formed in the air soon come down to the earth with the rain and so the name *acid rain*. The acid rain is infact a cocktail of H₂SO₄ and HNO₃. The ratio of the two acids depends on the relative quantities of the oxides of S and N emitted. 60-70% of acidity is attributed to H₂SO₄ whereas 30-40% to HNO₃.

Acid rains have assumed global ecological problems and their impacts are far reaching. They increase acidity of soil, cause acidification of lakes and streams, thereby affecting aquatic life, affect production of crops and moreover pose an invisible threat to human health. They also corrode buildings, statues, monuments, bridges, railings etc. Levels of heavy metals like Al, Mn, Zn, Cd, Pb, Cu etc. in water increases beyond safe limit. Many useful bacteria and blue green algae are destroyed due to acidification, thus causing ecological imbalance.

7. Ozone

Ozone is formed in the atmosphere through chemical reactions involving certain pollutants like SO₂, NO₂, aldehydes etc. upon absorption of UV radiation. The ozone layer of the atmosphere has two interesting and interrelated effects. It absorbs UV light, thereby protecting all the life on earth from harmful effects of radiation. Again, by absorbing UV radiation it heats up the stratosphere causing temperature inversion. As a result of inversion of temperature, the vertical mixing of the pollutants becomes limited and dispersal of pollutants is caused over larger areas near the earth's surface. Thus, a dense cloud of pollutants hangs over the atmosphere in highly industrialised areas causing several unpleasant effects. So, the layer of ozone acts as a destroyer as well as a protector.

Increase in ozone concentration near earth's surface reduces yielding of crops to a marked extent. It has also adverse effect on human health. Thus, while a higher concentration of ozone in the atmosphere protects us, at the same time it becomes harmful when it comes in direct contact with us.

Ozone is intimately connected with life sustaining processes. Any depletion of ozone layer has catastrophic effect on life systems on the earth. Some pollutants may enter stratosphere, react with ozone and are converted to other products thereby depleting ozone layer. Major pollutants responsible for depletion of ozone include chlorofluoro carbons (CFC), nitrogen oxides (coming from fertilisers) and hydrocarbons. Depletion of ozone leads to change in temperature and rainfall failure on earth. Harmful U.V radiations due to thinner ozone layer or hole in it directly affect us causing skin cancer known as *melanoma*. The other disorders are cataracts, destruction of aquatic life, vegetation and loss of immunity.

8. Fluorocarbons

Industrial processes of phosphate fertilisers, ceramics, aluminium, fluorinated plastic, uranium and other metal involve release of fluorides into the atmosphere. The pollutant is in gaseous and particulate state. Fluoride level of air is $0.05\text{mg}/\text{m}^3$. Fluoride in air mainly comes from smoke of industries, volcanic eruptions and insecticidal sprays.

Though fluorocarbons are helpful in protecting tooth decay in man, yet higher percentage of these are highly toxic. Fluoride pollution in man and animals is mainly through water. In plants, the tip burn disease is due to higher concentration of fluorides.

9. Metals

The most common metals present in the air are Zn, Cd, Pb and Hg. The main sources of the metals are industries and human activities.

- i) **Mercury:** It is a liquid volatile metal. The compounds of Hg are used during the manufacture of fungicide, preparation of paints, cosmetics etc. Inhalation of $1\text{mg}/\text{m}^3$ Hg containing air for 3 months may cause death. Nervous system is badly affected. Liver, the vital organ of the body may be damaged. Other symptoms include headache, anxiety, loss of appetite, eye sight problem etc.
- ii) **Lead :** Lead compounds are used as antiknock substances, therefore are released in to the air with the vehicle exhaust as lead halides. Inhalation of lead causes reduced haemoglobin formation. Kidney and liver get affected by lead poisoning.
- iii) **Cadmium:** It is released to air by the industries and other human activities. It is poisonous even at very low level. It is emitted as vapour and quickly forms the oxide, sulphate and chloride. It affects liver and kidney and causes hypertension, emphysema. It is also carcinogenic in mammals.
- iv) **Zinc :** It is released into air by industries in the form of white zinc oxide fumes. It is highly toxic to man.

10. Particulate matter

Small solid particles like dust, smoke particles and liquid droplets suspended in air are known as suspended particulate matter. The natural sources are soil and rock debris, volcanic eruption and forest fire. Besides they may be released into air by fuel combustion, industrial operation, vehicular exhaust etc. The particulate matter is injurious to health. Inhalation leads to respiratory diseases like tuberculosis and also cancer. Cotton dust inhalation leads to occupational disease '**Byssinosis**'.

11. Radioactive emission

Disintegration of radioactive substance takes place with emission of radiation like alpha, beta and gamma rays. These radiations upon reaction with living tissues damage them. The harmful effects of radiation are cancer, damage of central nervous system. Besides these, the skin, eye and the living tissues are badly affected.

12. Toxicants

There are some toxic substances which are responsible for causing serious health hazards. They are:

- i) **Asbestos** : It is a mineral fibre used in cement pipes, roofing product, cement sheets etc. The fibre is nondegradable and it causes cancer.
- ii) **Arsenic** : It is a byproduct in metal refining process. It is carcinogenic.
- iii) **CCl₄ and CHCl₃** : CHCl₃ degrades slowly forming highly toxic phosgene. Both CCl₄ and CHCl₃ are carcinogenic.
- iv) **Chromium** : It is used in stainless and alloy steel. It has carcinogenic properties.
- v) **Nickel** : It is used in petroleum and metal products, electrical goods. It is strongly carcinogenic.
- vi) **Vinyl chloride** : It is used for preparation of polyvinyl chlorides (PVC). It causes brain and lungs cancer.

21.3.3 Units of measurement of air pollutants

The concentration of air pollutants is expressed in forms of

- 1) **Parts per million (ppm)** : It is the volume of the pollutant present in one million volume of air. The measurement of volume of pollutant and that of air are measured at standard temperature (25°C) and pressure (76cm of Hg).
- 2) **Microgram per cubic meter ($\mu\text{gm}/\text{m}^3$)**

It is the amount of pollutant in μgm ($1\mu\text{gm}=10^{-6}\text{gm}$) present in one cubic metre of air. In highly polluted air, the concentration may be expressed as mg/m^3 .

21.3.4 Control of Air pollution

Although air pollution can not be totally eliminated, yet its harmful effects may be minimised. The people should be aware of environmental health problems arising out of rapid, unplanned industrial growth and road traffic. The two main sources of pollution are industries and motor vehicles. The control of air quality in both the cases can be made to minimise air pollution.

1. Control of Industrial Pollution

The air quality control implies limiting the emission of pollutants. To check the air pollution by industrial plant chimney wastes several measures are adopted for removal of particulate matter and gaseous pollutants from the wastes. The most common equipment used for removal are cyclone collectors, electrostatic precipitators, bag filter and scrubber.

i) **Cyclone collectors**

The waste gas is subjected to centrifugation. The suspended particles move towards the wall of cyclone body and then to its bottom. The dust particles get thrown on the periphery and the clean gas escapes out from the centre of cyclone.

ii) **Electrostatic precipitators**

These are working on the principle of charging the dust by the application of high voltage electricity. The particles settle down finally. These are safe and simple to operate.

iii) **Bag filters**

It consists of filter bags made up of bag materials like cotton, glasswool, teflon, ceramic fibre or polyester etc. The dust laden gas is passed through it. The dust gets filtered and clean air escapes out. The dust collected are removed by shaking the bag periodically.

iv) **Scrubbers**

The harmful gases released by different factories can be removed by spraying cool water in a device called **scrubber**. The gaseous pollutants are absorbed in appropriate liquid to bring the pollutant from gaseous to liquid or solid state. The different types of scrubbers used are spray type, ventury scrubbers, impingement scrubbers etc.

Pollution due to industries may be eliminated by the use of electricity in place of coal fuel. Solar energy may also be taken up for the purpose.

The extent of air pollution can be minimised by self cleaning process of air. This can be achieved by increasing vegetation in the nearby locality and providing green belt between residential and industrial areas.

The control of air pollution may also be made by implementation of law. All Industries should follow the absolute emission standard fixed by Pollution Control Board.

2. Control of vehicular pollution

- i) *Checking the emission of pollutants from vehicular exhaust:*
 - a) use of good quality fuel.
 - b) use of additives to improve combustion
 - c) injecting air into the exhaust for converting exhaust compounds to less toxic materials. Recently thermoreactor, a simple attachment, has been devised which when fitted to exhaust tail pipe can convert CO into pure oxygen.
 - d) updating the design of engine.
 - e) more exact timing of fuel feeding.
 - f) using new proportion of gasoline and air.
 - g) perfect tuning of carburettor and maintenance of the engine.
 - h) installation of catalytic converters to convert NO_x to nitrogen.
- ii) *Use of filters :* The emission of hydrocarbons can be controlled by the use of filters. The filters capture and recycle the escaped hydrocarbons in this engine.
- iii) *Control through law :* Through motor vehicle act some laws are to be enforced for proper design of engines.

21.4

WATER POLLUTION

Water is very essential for the existence of every living being. We use water for drinking, cooking our food, growing our crops, irrigating our lands, generating electricity, running several industries and moreover for keeping ourselves clean. Water is very familiar to every one of us. More than three fourths of earth's surface is covered with water. It is present in the earth crust and in the form of rain, cloud, snow and hail in the atmosphere.

Pollution of water is defined as “the addition of any substance to water that is harmful to living beings”. In chemical sense water is never pure. Dissolved as well as suspended impurities are present in it. These include suspended matter like clay, silt and sand, dissolved minerals like Ca, Mg and Na salts and dissolved gases like N_2 , NH_3 , CO_2 and H_2S . These natural impurities are present in very low amounts and therefore do not pollute much. Polluted water is bad smelling, turbid, unpleasant and is unfit for drinking, bathing and washing purposes.

21.4.1 Sources of Pollution

The chief sources of water pollution are discussed below:

a) **Sewage and other waste:**

The water borne waste derived from domestic waste, animal and food processing plants is known as *sewage*. It includes human excreta, cloth, paper, soap, detergent etc. This is due to uncontrolled dumping of wastes into ponds, lakes, streams and rivers. Decomposition of sewage and other wastes is largely aerobic process, therefore leads to oxygen depletion which adversely affect fish and aquatic life. Public sewage contains microorganisms like bacteria, moulds, yeasts, viruses, eggs of helminthes algae etc. So, discharge of sewage into rivers and other water bodies create health hazards to mankind.

These pollutants chiefly consist of carbonaceous organic materials which are converted to CO_2 and water by oxidation. The extent of pollution is measured in terms of biological oxygen demand (BOD) or chemical oxygen demand (COD). BOD is the amount of oxygen required for biological oxidation by microbes in any unit volume of water.

2) **Industrial wastes**

The sources of industrial effluents (pollutants) include wastes from breweries, tanneries, paper, pulp, textile, sugar and steel industries. The pollutants are metallic wastes, suspended solids, phenols, toxins, acids, salts, dyes, cyanides etc. However, these pollutants can be categorised as follows:

- i) **Inorganic substances** like chlorides, carbonates, nitrogen etc. pollute water making it unfit for drinking and also encourage the growth of microorganism.
- ii) **Organic substances** like phenol, alcohol etc. increase the BOD depleting the oxygen content.
- iii) **Heavy metals like lead**, mercury, arsenic and poisonous substances like cyanides, acetylene etc. cause harmful and irreversible damages to plant and animal life.
- iv) **Colour producing** dyes change the colour of water, decrease the oxygen level thereby affecting aquatic life.
- v) **Acids and alkalies** rapidly change pH of water affecting fish and other aquatic life.

3. **Agricultural discharges**

Modern agriculture has become a major source of pollution, since it relies heavily on a wide range of synthetic chemicals which include various types of fertilisers and biocides (pesticides, herbicides and weedicides). Excess use of fertilisers and pesticides cause maximum damage to natural ecosystem.

- i) **Fertilisers** : Artificial fertilisers applied to modern agriculture ultimately reach the rivers, lakes and streams etc. through irrigation, rainfall, drainage etc. affecting the ecosystem. Due to excessive use of nitrogenous fertilisers many crops lack potassium. Again, excessive potash treatment is bad. It decreases the amount of valuable nutrients in foods such as ascorbic acid (vitamin C) and carotene. Excess use of fertilisers leads to accumulation of nitrates and phosphates in water. It normally makes water unfit for drinking, but also creates harmful diseases. The water if taken by us are converted to nitrites by microbial flora of intestine. The nitrites then combine with haemoglobin of the blood forming methaemoglobin, so that oxygen carrying capacity of the blood is inhibited. Severe damage to vascular and respiratory system is caused. Similarly, accumulation of phosphates in water leads to depletion of dissolved oxygen due to excessive algal growth. It results in death of fish and other aquatic life.
- ii) **Pesticides**: These are the chemicals used for killing plant and animal pests. The chemicals do not degrade or degrade very slowly in nature and therefore, are toxic to the ecosystem. The most toxic biocides include DDT (dichlorodiphenyl trichloroethane), BHC (Benzene Hexachloride), Chlordane, Methoxychlor, Aldrin, Endrin and PCB (Polychlorinated biphenyl). These pesticides are quite persistent and accumulate in the tissues of aquatic and other animals. DDT, gamma xane have been banned by some countries due to their long acting toxicity.

4. **Radioactive wastes**

Most of the nuclear arm tests are carried out in oceans. As a result radioactive materials like strontium - 90 and caesium -137 are released. The amount of C-14 and tritium also increase on the water surface of oceans. These radioactive pollutants kill the marine life and enter bodies of all living organisms directly or indirectly in the food chain causing pathological and genetic damage to us. A lot of heat is generated by nuclear tests destroying the marine life in the vicinity.

5. **Thermal pollution**

Heat is generated as a result of burning of fuel in industrial plants. Nuclear plants use water as coolant. The water, after absorbing heat is let out into seas and rivers. Due to rise in temperature of water some marine species may die and some others may not reproduce at all. Due to rise in temperature water lacks the ability to dissolve gases in it. It has been found that for 10°C rise in temperature the oxygen content in water is reduced by 17 percent. This oxygen depletion is more pronounced in sea water than in fresh water since salt water has low specific heat. The oxygen depletion is detrimental to marine life.

6. Shipping water pollution or oil pollution

The major shipping water pollution is due to oil. Oil is spilled into the seas during the process of transport, loading and unloading from ships. Besides production and refining of oil has become another source for oil pollution. Off shore oil drilling also adds quite a huge quantity of oil into the sea. Oil can remain in sea for at least more than a year. Hydrocarbons are chief components of oil. The microorganisms from the sea decompose hydrocarbons and during the process the oxygen content of water is greatly reduced. Spreading of oil over water isolate water from the contact with atmospheric oxygen. A continuous film of oil is formed which inhibits photosynthesis and formation of oxygen. Thus, aquatic life (both plant and animals) is adversely affected. Oxygen content reduction results in death of sea fish and sea birds. More than one million sea birds are reported to have been killed by oil pollution.

21.4.2 Effects of water pollution

Major effects of water pollution are studied under two heads namely (1) Human and animal health (2) Loss of recreational area.

1) Human and animal health

Pollution of water poses a great danger to both human and animal health. Oil and thermal pollution ultimately result in destroying aquatic plants and animals. Pollution due to use of artificial fertilisers and radioactive waste have become potential health hazards to both human and animals. Besides, contamination of water with some heavy metals like mercury, lead, arsenic, cadmium, copper, barium, zinc etc. has toxic effect on the body which are discussed below:

- i) **Mercury** : The concentration of mercury in aquatic environment is increased day by day due to industrial activities such as manufacture of electrical equipments, paper making, mining etc. Mercury can not be easily excreted. Once it enters the food chain its concentration gradually goes on increasing. The disease, resulting from mercury poisoning is usually known as “**Minimata disease**” since there was outbreak of mercury poisoning in Japan among the residents who ate food from Minimata bay contaminated with methyl mercury. Mercury poisoning causes diseases like abdominal pain, headache, diarrhoea, blurring of vision, apathy and mental derangement.
- ii) **Arsenic** : It is a long acting slow poison in small quantity, but at the same time causes infant death if taken in large doses. Arsenic poisoning causes liver cirrhosis, lung cancer, hyperkeratosis, ulcer in GI tract and mental disorder.

- iii) **Lead** : The aquatic environment around industrial belt is rich in lead concentration. Poisoning of lead causes loss of appetite, damage of liver, kidney and brain, convulsion, vomiting and anaemia.
- iv) **Copper** : High concentration of copper in water causes hypertension, uremia, sporadic fever.
- v) **Cadmium** : High concentration of cadmium in drinking water can cause bone deformation, growth retardation, diarrhoea, kidney damage, hypertension and anaemia.
- vi) **Barium**: Poisoning due to barium results in paralysis, colic pain, vomiting, excessive salivation, paralysis.
- vii) **Selenium** : It is not very common. Its high concentration can cause fever, nervousness, vomiting, blindness, low blood pressure.
- viii) **Cobalt** : High concentration of cobalt in water causes bone deformation, low blood pressure, paralysis etc.

2. Loss of recreational areas

Recreational activities in sea beaches suffer serious economic damages due to pollution of water. When water contains some toxic substances or there is high bacterial count in water it gets polluted. Water becomes depleted in oxygen as microorganisms die and decay. The fishes present in sea requiring a high level of oxygen either die or move out. In heavily polluted areas the death of algae, rotting mats of floating debris, solid wastes and some oil spills have caused considerable damage to valuable beach resources. Pollution due to mercury and other chemicals also hamper the recreational activities.

21.4.3 Prevention and Control of Water pollution :

Pollution of water due to biodegradable pollutants may be controlled at source by their treatment for reuse and recycling. The non-degradable pollutants such as heavy metals, mineral oils, biocides, plastic materials etc. are removed by suitable methods. The various ways and techniques used for control of water pollution are discussed below:

i) Stabilisation of ecosystem

The most scientific and reliable way to control water pollution is made by stabilisation of ecosystem. The principles underlying the method include reduction of waste input, harvesting and removal of biomass, trapping of nutrients, aeration and fish management. Species diversity and ecological balance in water bodies may be restored by various biological and physical methods to prevent water pollution.

ii) **Reutilisation and recycling of waste**

There are various kinds of wastes such as industrial effluents, sewage of municipal and other systems, thermal pollutants and radioactive wastes which may be recycled to beneficial use. Recycling is the process by which the municipal and industrial waste water can be treated for reuse. For example, the municipal wastes like sewage and sullage may be recycled to generate cheaper fuel gas and electricity. A new technology has been developed by the NEERI, Nagpur for management of radioactive wastes and chemical wastes of atomic power plants, reclamation of waste water and to supply cheap piped gas and generate electricity by recycle of urban wastes.

iii) **Removal of pollutants**

Appropriate methods such as adsorption, electrodialysis, ion exchange, reverse osmosis etc. are used for removal of various pollutants like radioactive, chemical and biological pollutants present in water body. The most widely and commonly used technique is reverse osmosis. This is based on the removal of salts and other substances by forcing the polluted water through a semi-permeable membrane under a pressure exceeding osmotic pressure. As a result, water flows in the reverse direction to the normal osmotic flow. To desalinate the brackish water and for purifying the water from the sewage, reverse osmosis is commonly used.

Council for Scientific and Industrial Research (CSIR) has developed techniques for removal of different pollutants from polluted water. These are as follows:

1. **Ammonia :** This can be removed by ion exchange technique. A weak acidic Cation exchange takes place which removes NH_3 in the form of ammonium sulphate. Ammonium sulphate is used as fertiliser.
2. **Mercury :** Mercury-selective ion exchange resin is used for the removal of mercury from chlor-alkali effluent plants.
3. **Phenolics :** Waste water of pulp and paper mills, petroleum refineries, tanneries and resin plants contain phenol and its derivatives. These can be removed by using polymeric adsorbents.
4. **Colouring matter :** The waste water from printing and saree dyeing industries could be decolourised by an electrolytic decomposition technique.
5. **Sodium salts:** Reverse osmosis method can be used for the removal of sodium salts. Sodium sulphate from a rayon mill effluents could be easily removed by this technique.

21.4.4 International standards for drinking water :

Drinking water must be pure otherwise it may cause serious diseases. International standards have been laid down for the water to be used for drinking as given below with the chemicals allowed to be present and maximum limits upto which they are permitted.

TABLE - 21.1

Chemical/ Condition	Source	Tolerable Limit	Use/Harms of higher conc.
(i) Fluoride	Added externally	1 ppm or 1 mg dm^{-3}	Protects tooth decay High conc. ($> 10 \text{ ppm}$) are harmful to bones and teeth.
(ii) Lead	Lead pipes used for transport of water	50 ppb or $\mu\text{g dm}^{-3}$	Lead poisoning (damages kidneys, liver and brain)
(iii) Other metals	-	Zn = 5 ppm Cu = 3 ppm Fe = 0.2 ppm Al = 0.2 ppm Mn = 0.05 ppm Cd = 0.005 ppm	-
(iv) Sulphates	-	< 500 ppm	Higher conc. has laxative effect
(v) Nitrates	-	50 ppm	Excess causes methemoglobinemia (blue baby syndrome) which may be linked to stomach cancer.
(vi) pH	-	5.5 - 9.5	

21.5 **SOIL POLLUTION**

The top layer of the earth's crust is known as **soil**, which is the most vital part of the lithosphere. The term 'soil' is derived from the Latin word 'solum' which means the earthly material on which the plants grow. It provides support for all terrestrial organisms. The process of formation of soil involves the weathering of rocks and subsequent changes due to the action of micro organisms like bacteria, fungi by secretion of organic acids, enzymes, CO_2 , production and addition of organic matter upon their death. In an average soil, inorganic matter, organic matter, soil water and air present by 40, 10, 25 and 25% respectively. Soil is the soul of biosphere which provides nutrients, water and minerals for the growth of the plants on which all the animals

depend. But unfortunately population explosion, rapid urbanisation, industrialization, increase in the use of automobiles etc. are damaging the quality of soil and resulting into soil pollution.

21.5.1 Sources of soil pollution :

Soil pollution mainly results from the following sources :

(i) Industrial water :

The rapid growth of industries has resulted in the release of a lot of industrial wastes containing toxic acid disastrous chemicals which are usually non-biodegradable. These are mainly discharged from pulp and paper mills, oil refineries, sugar factories, textiles, drugs, glass industries etc.

The industrial wastes affect and alter the chemical and biological characteristics of soil which finally enter into food chain, disturb the biochemical processes and finally induce serious hazards to living organisations.

(ii) Urban wastes :

Urban wastes commonly known as *refuse* contains garbage and rubbish materials like plastics, glasses, fibres, polyethene bags, food wastes, fuel residues, abandoned vehicles etc.

These wastes emit poisonous gases, toxic hydrocarbons and pathogenic bacteria causing various diseases.

(iii) Agricultural wastes :

Agricultural wastes include farm wastes which include roots and stems of crops, straw, hay etc and also the excess fertilizers, pesticides, herbicides etc. These enter the food chain, thus affecting the health of human beings causing serious metabolic and physiological disorders.

Agricultural pollutants are :

- (a) **Fertilizers** : Fertilizers act as nutrients, but excess nitrates and phosphates have hazardous effects.
- (b) **Pesticides** : Common pesticides used are
 1. **Insecticides** like DDT, Gammexane, Aldrin etc.
 2. **Herbicides** - Triazines, Sodium chlorate and Sodium arsenite.
 3. **Fungicides** - Organo mercury compounds.

- (c) **Soil conditioners :** Though used to protect the soil fertility, these contain several toxic metal like, Pb, As, Hg, Cd, Co etc.
- (d) **Farm wastes :** Farm wastes from dairies poultries are usually collected as a wet slurry on the land which may seep through the soil and pollute the ground water.

(iv) Radioactive wastes :

Radioactive substances produced from nuclear explosion, nuclear reaction and from nuclear testing laboratories enter into the soil and accumulate there causing land pollution. These wastes are highly dangerous and cause cancer in living organisms and also degrade genetic materials like DNA and RNA inducing mutation.

(v) Pollution by Biological agents :

Soil pollution is also due to biological agents present in the excreta of human beings, animals and birds. The sewage sludges contain a number of viruses and viable intestinal worms which take shelter in soil and cause a number of diseases by attacking the living organisms.

21.5.2 Effect of soil pollution :

Detrimental effects of soil pollution are :

- (i) Industrial wastes containing toxic metals like Hg, Pb, Cd, As, Cu etc. kill bacteria and beneficial micro-organisms in the soil.
- (ii) Direct discharge of industrial effluents through sewage system causes several soil borne and water borne diseases.
- (iii) The dumped urban wastes spread several chronic diseases becoming a serious threat to mankind.
- (iv) The fertilizers though increases the yield, inhibit the synthesis of vitamin-C and carotene in vegetables and fruits.
- (v) Entry of polychlorinated biphenyl (PCB) into human body causes deformities in foetus, nervous disorders, liver and stomach cancer.
- (vi) Pesticides being non-biodegradable by nature seep into ground water through soil and contaminate the entire public water supply system.
- (vii) Pathogenic bacteria in soil act as carrier of a number of chronic diseases like cholera, typhoid, dysentery etc from soil to man and vice versa.
- (viii) The radioactive wastes enter into the food chain and causes the disruption of physiological process and metabolic change.

21.5.3 Control of soil pollution :

Since soil is vital for the living organisms to exist, protective measures must be adopted to keep soil pollution free, some of which are:

- (i) Organic measure should be used instead of agro-chemicals.
- (ii) The effluents released should be subjected to proper treatment before their release into soil.
- (iii) The garbage produced should be burnt in a closed chamber.
- (iv) Integrated pest control method should be applied.
- (v) Proper care must be taken for the planned disposal of radioactive wastes.

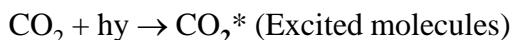
21.6 CHEMICAL REACTIONS IN ATMOSPHERE

Atmosphere is the thick multilayered gaseous envelope that surrounds the earth, protecting the living organisms from the unfriendly environment of the outer space. It can be divided mainly into four zones or spheres of varying temperature, density and chemical composition. These are troposphere, stratosphere, mesosphere and thermosphere containing gases which undergo photochemical reactions.

(a) Reactions in troposphere :

Troposphere is the lowest zone of the atmosphere lying just above the earth surface where all biological activity takes place. The most important reaction in troposphere are those involving CO_2 and H_2O .

- (i) CO_2 molecules present absorb sunlight and get excited.



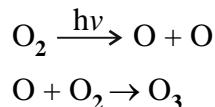
Due to collision of the excited CO_2^* molecules excess energy present in them is converted into heat, hence increasing the temperature of the atmosphere.

- (ii) Similarly, water vapour present in the troposphere absorb the solar energy reaching the earth and when the earth cools, the energy is re-emitted as infrared radiation.

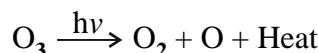
Some of this re-emitted radiations is absorbed by H_2O vapour and CO_2 and again radiated back to the surface of the earth. Such warming of the earth by absorption and re-emission of solar radiation is called “**Green House Effect**” or **Global Warming**.

(b) Reactions occurring in the stratosphere :

- (i) The upper stratosphere contains a considerable amount ozone which is a product of UV radiations acting on oxygen molecule splitting into two free oxygen atoms. These combine with molecular oxygen to form ozone.



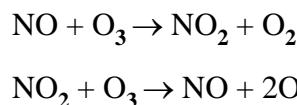
Ozone is unstable and breaks down absorbing UV radiation to form oxygen molecule and an oxygen atom. Heat is released warming up the stratosphere.



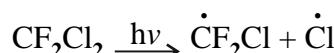
Thus, ozone cycle is completed in the stratosphere.

- (ii) Ozone layer in the stratosphere protects us from the harmful UV radiation acting as a protective layer for life on the earth, otherwise humans will have to suffer from skin cancer. But ozone layer is being depleted due to human activities releasing oxides of nitrogen and chlorofluoro carbons (CFCs) or freons into the atmosphere.

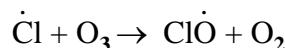
NO can react with O_3 thus decreasing its amount.



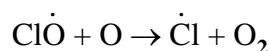
- (iii) Freons are nonreactive, nonflammable, nontoxic organic molecules being used in refrigerators, air conditioners and in the production of plastic foam. Once they are released in the atmosphere, they alongwith the other atmospheric gases reach the stratosphere where they are decomposed by UV radiation to form chlorine free radical.



Chlorine free radical then react with O_3 to form chlorine monoxide radicals and molecular oxygen.



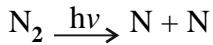
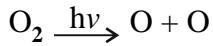
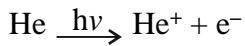
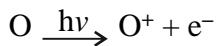
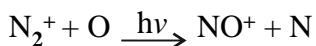
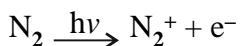
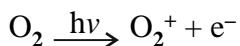
Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.



In this way the reaction is continued causing the depletion of O_3 layer.

(c) Reaction occurring in the mesosphere and thermosphere :

Due to photochemical reactions free ions and electrons are generated in these regions.



Since free ions and electrons are unstable they will collide with each other to form neutral species. However they may stay free in the thermosphere i.e. ionosphere where pressure and density are very low.

21.7 **SMOG**

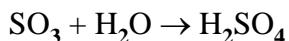
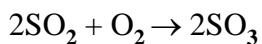
The word **smog** is a combination of two words *smoke* and *fog*. It was named so because for the first time it was observed to be formed by the condensation of some kind of fog on the carbon particles present in the smoke produced by the combustion of fuels like coal and petroleum.

Smog, the most common example of pollution, is mainly of two types. These are :

A. Classical smog or London smog or sulphurous smog :

It is a mixture of fog, smoke and sulphur dioxide (SO_2) gas, which was first observed in London in 1952 killing about 4000 people and for this reason it is called '**London Smog**'.

Its formation is initiated by a mixture of SO_2 , particulates and high humidity in the atmosphere. SO_2 being oxidized to SO_3 combines with water to form sulphuric acid (H_2SO_4) droplets, which causes bronchitis and respiratory problems, pneumonia and eye diseases. Since it is a mixture of reducing pollutants, it is also known as **reducing smog**.

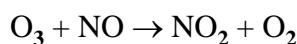
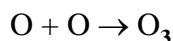
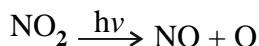


B. Photochemical smog or Los Angeles smog :

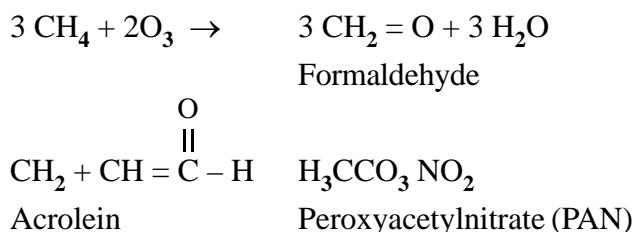
This type of smog was so named because it was first observed in Los Angeles in 1950. This type of smog occurs in warm, dry and sunny climate. The main components of photochemical smog result from the action of sunlight on nitrogen dioxide and hydrocarbons released by automobiles and factories. Since it is having high concentration of oxidising agents and is therefore called as **oxidising smog**.

(a) Formation of photochemical smog :

NO_2 and hydrocarbons are produced in large amount due to heavy vehicular traffic during the day time. In the presence of sunlight NO_2 undergoes photolysis to form NO and atomic oxygen, which in turn combines with oxygen molecule to form ozone (O_3). The ozone thus formed reacts with NO to regenerate NO_2 and O_2 . Thus, NO_2 cycle is completed.



Ozone is a toxic gas and both NO_2 and O_3 are strong oxidizing agents and can react with unburnt hydrocarbons in the polluted air producing chemicals like formaldehyde, acrolein and peroxyacetyl nitrate (PAN).



(b) Harmful effects of photochemical smog :

High concentration of ozone, PAN, aldehydes and ketones in the atmosphere is quite destructive influencing both the physiological and metabolic activities of the living beings.

- (i) Both ozone and PAN act as powerful eye irritants.
- (ii) Presence of NO_2 in smog causes nose and throat irritation and chronic diseases in lungs and hearts.
- (iii) PANs cause dizziness and headache.

- (iv) Photochemical smog leads to cracking of rubber and causes extensive agricultural and forestry damages.
- (v) It also damages metals, stones, building materials and painted surfaces.

C. Control of photochemical smog :

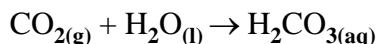
It can be controlled by the following measures :

- (i) Emission of nitrogen oxides and hydrocarbons by the automobiles into the atmosphere can be prevented by using catalytic converters in the automobiles.
- (ii) Plantation of certain plants like Pinus, Juniperus, Pyrus and Vitis can metabolise nitrogen oxide and check the formation of photochemical smog.

21.8 ACID RAIN

Acid rain may be defined as the rain water containing sulphuric acid and nitric acid being formed from the oxides of sulphur and nitrogen present in the air as pollutants having a lower pH than that of normal rain water.

Normal rain water has a pH of 5.6 i.e. slightly acidic due to the presence of H^+ ions formed by the reaction of CO_2 gas present in the atmosphere with rain water giving carbonic acid (H_2CO_3) which is a weak acid.



When the pH of the rain water drops below 5.6 it is called **acid rain**.

A. Sources of acid rain :

Acid rain is due to the presence of various pollutants like oxides of nitrogen, oxides of sulphur and halogen radicals or molecules in the atmosphere which are discharged by the following two factors.

(i) Natural sources :

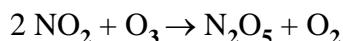
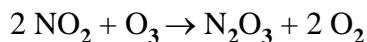
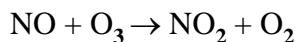
Natural phenomena like volcanic eruptions, forest fires, lightning, burning of fossil fuel, decomposition of organic matters etc. release large quantities of these pollutants into the atmosphere.

(ii) Human activities :

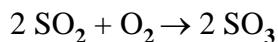
Due to human activities mainly involving combustion of fuels like coal, wood, petroleum products or from chemical industries release large quantities of oxides of nitrogen and sulphur into the atmosphere.

B. Formation of acid rain :

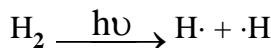
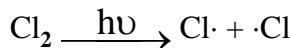
- (i) After the release of the pollutants, oxides of nitrogen undergo oxidation reaction followed by reaction with water vapour present in the atmosphere to form HNO_3 .



- (ii) The oxidation of SO_2 to SO_3 is catalysed by aerosol containing metal ions like Cu(II), Fe (II) etc which subsequently reacts with water vapour to form H_2SO_4 .



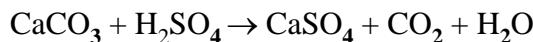
- (iii) A little percentage of HCl is also formed.



All these acids mixing with rain water form acid rain and pH falls below 5.6, at times pH can also fall to 2.0. The concentration of these acids as well as the quantity of water in which the acids are dissolved determines the pH of rain water.

C. Harmful effects of acid rain :

- (i) Acid rain causes extensive damages to buildings, statues and sculptural material especially those made up of limestone, marble, slate etc. Acid rain attacks CaCO_3 (marble) as follows :



This is the main reason for which the wonderful monuments Taj Mahal at Agra is being slowly disfigured, discoloured and lustreless. In order to save Taj Mahal, Govt. of India has announced an action plan aiming at clearing the air in Taj Trapezium i.e. area which includes the towns of Agra, Firozabad, Mathura and Bharatpur. Measures taken are :

- (a) All industries in these areas would switch over to the use of natural gas or LPG instead of coal or oil.
- (b) People will be encouraged to use LPG instead of coal, kerosene or firewood.
- (c) Vehicles in the nearby area would be advised to use low sulphur content fuel.
- (ii) Acid rain increase the soil acidity affecting land flora and fauna.
- (iii) It damages iron and steel structures.
- (iv) It corrodes water pipes . As a result heavy metal like iron, lead and copper are leached into drinking water which have toxic effects.
- (v) Diseases caused by bacteria and pathogens can be spread by acid rain.
- (vi) Acid rain may cause respiratory and skin diseases.
- (vii) It causes acidification of aquatic bodies which lead to the killing of aquatic plants and animals.
- (viii) It retards the growth of plants and reduces the productivity of crops like potato, peas, beans etc.

D. Control measures :

Acid rain can be controlled by implementing certain measures. These are:

- (i) Fuels, devoid of sulphur or having low sulphur content should be used.
- (ii) The leakage chlorine or its discharge should be stopped.
- (iii) The vehicular exhaust should be minimised by using control valves in the outlet of the exhaust pipeline of the automobiles.
- (iv) SO_2 gas released can be removed as calcium sulphate (CaSO_4) by spraying with lime water.

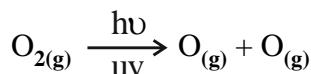
21.9 OZONE LAYER

Ozone layer serves as the earth's protective umbrella as it protects us from the harmful ultraviolet (UV) radiations coming from the sun to reach the surface of the earth which is responsible for skin cancer (*melanoma*) in humans. In the upper stratosphere at an altitude of 25–30 km, the concentration of ozone is about 10 ppm forming ozone layer.

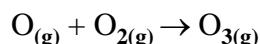
A. Formation of ozone layer :

Ozone, a light bluish gas, is formed in the stratosphere by the action of highly energetic ultraviolet radiation coming from the sun on dioxygen (O_2) molecules.

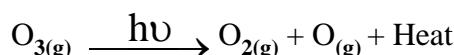
In the first step, UV radiations split apart molecular oxygen into free oxygen (O) atoms.



In the second step, the oxygen atoms combine with molecular oxygen to form ozone.



Ozone thus formed again absorbing UV radiation breaking into dioxygen and an oxygen atom.



Heat is given out warming up the stratosphere. In this way ‘ozone cycle’ goes on in the stratosphere. Thus a dynamic equilibrium exists between the production and decomposition of ozone molecules.

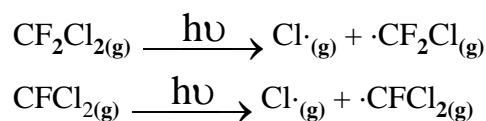
B. Depletion of ozone layer :

Due to continuous and non-interrupted release of chlorofluorocarbons and oxides of nitrogen the ozone layer is constantly depleted. These two ozone depleting agents are:

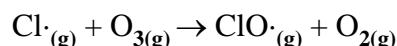
(i) Chlorofluorocarbons (CFC) :

CFC, commonly known as **freons** are the compounds containing chlorine, fluorine and carbon. These compounds are chemically unreactive, nonflammable, non-toxic and adourless, for which these are used in refrigerators, air-conditioners, in the production of plastic foams as blowing agents and by the electronic industry for cleaning computer parts etc.

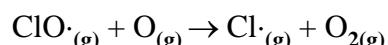
Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and ultimately reach the stratosphere where they start decomposing in the presence of UV radiation coming from the sun releasing chlorine free radical.



The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

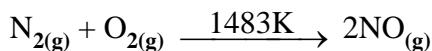


Then chlorine monoxide radical react with atomic oxygen producing chlorine radical again repeating the decomposition of ozone and thus depleting the ozone layer.

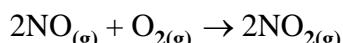


(ii) Nitric oxide (NO) :

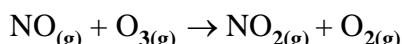
When fossil fuel is burnt in an automobile engine nitrogen molecule and oxygen molecule combine at high temperature to yield nitric oxide (NO) and nitrogen dioxide (NO₂)



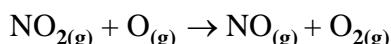
NO reacts immediately with oxygen to form NO₂.



Production of NO₂ is accelerated when NO reacts with ozone in the stratosphere, thereby decreasing the amount of ozone.



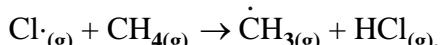
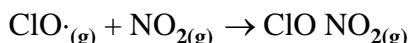
NO₂ in turn reacts with oxygen atoms available in the stratosphere due to decomposition of ozone and oxygen producing back NO. Thus, there is no loss of NO but ultimately O₃ gets depleted.



C. The Ozone Hole :

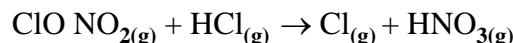
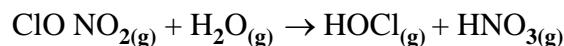
Due to depletion of ozone especially by CFCs taking place in all parts of stratosphere, a large ozone hole has been reported mainly in the stratosphere over Antarctica in 1980s where ozone level dropped by 30 percent.

This is because in other parts of the stratosphere, chlorine monoxide radicals combine with the oxides of nitrogen and chlorine free radicals combine with the methane present in the stratosphere thus ceasing the chain reaction and preventing much ozone depletion.



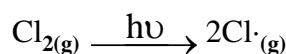
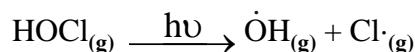
But in Antarctica, the climatic conditions are quite different. In winter special type of clouds called polar stratospheric clouds (PSC) are formed over Antarctica which are of two types :

- (i) Type I Clouds** are those which are formed at -77°C containing solidified nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$)
- (ii) Type II Clouds** are those which are formed at -85°C containing some ice. These clouds provide surface on which chlorine nitrate formed gets hydrolysed to form hypochlorous acid and reacts with hydrogen chloride to form molecular chlorine.



HOCl and Cl₂ thus formed are easily converted back into reactive chlorine atoms even under mild conditions thus starting the chain reaction leading to depletion of ozone.

Depletion of ozone over Antarctica takes place during spring when sunlight returns and the sun's warmth breaks up the clouds and HOCl and Cl₂ are photolysed by sunlight to form reactive chlorine atoms which destroy the ozone layer.



A tight whirlpool of wind surrounds Antarctica due to the presence of PSC, which is called **Polar Vertex**. It is so rigid that it keeps Antarctica separated from the surrounding ozone rich air of non-polar regions. Ultimately ozone hole remains unfilled. But when spring passes away, the intensity of sunlight increases and the Polar Vertex breaks down, thus helping the ozone hole to be filled up.

D. Effect of depletion of ozone layer :

Due to the depletion of ozone layer in the stratosphere, the harmful UV radiation will reach the surface of the earth causing the following destructive effects.

- (i) It can cause skin burns and skin cancer (melanoma).
- (ii) Exposure of eye to UV radiation damages the cornea and lens of eye and may cause cataract or even blindness.
- (iii) It injures plant proteins and causes depletion of chlorophylls and harmful mutations of cells.
- (iv) It causes killing of many phytoplanktons and damage to fish productivity.
- (v) It increases evaporation of surface water through the stomata of the leaves and decreases the moisture content of the soil.
- (vi) Ozone depletion brings about significant changes in the climate.
- (vii) UV radiation damage paints and fibres, causing them to fade faster.

E. Protection of ozone layer :

Ozone layer can be protected by taking some controlling measures as follows :

- (i) Use of CFC must be either restricted or completely banned by finding out some alternatives.

- (ii) Use of plastic foam has to be boycotted.
- (iii) Suitable methods should be adopted to recapture CFC released from the air-conditioners and refrigerators.

21.10 **GREEN HOUSE EFFECT AND GLOBAL WARMING**

The Green house is that body which allows short wavelength solar radiation to pass through it but does not allow the long wavelength infrared radiation to escape.

Due to rapid industrialization, gases like CO_2 , chlorofluorocarbons (CFCs), methane, nitrogen oxides, ozone etc are accumulated in the atmosphere which behave like wall of a green house and transmit short wave solar radiations but does not allow the longer wavelength heat radiations to be reflected back into outer space. This means green house is transparent to solar radiation but not to heat radiation.

Thus, the **green house effect** may be defined as the progressive warming up of the atmosphere at the surface of the earth due to blanketing of infrared radiation from the earth's surface by the green house gases, which is otherwise termed as **Global Warming**.

The green house effect was initially essential for older climates to grow few plants in winter, which require higher temperature for their growth and survival. But now-a-days our atmosphere is enriched with green house inducing gases causing global warming. The fundamental principles underlying green house effect are :

- (i) Absorption of infrared radiation by the green house inducing gases.
- (ii) Re-emission back towards the earth's surface which results in heat trap and increases the mean global temperature.

A. **Consequences of Green House effect :**

- (i) Average global level of CO_2 has been reported to have increased by 26 percent between 1960 and 1986 leading to an average increase of global temperature by 1.5°C to 4.5°C .
- (ii) Increase in temperature is more prominent in polar region which will lead to melting of glaciers and polar ice caps raising the level of sea water by about 1.5 meter and flooding of low lying areas all over the earth.
- (iii) Global warming causes evaporation of terrestrial water content leading to shortage of drinking water.
- (iv) It may decrease the crop productivity due to reduction of soil moisture.
- (v) Increase in the global temperature increases the incidence of infectious diseases like malaria, dengue, yellow fever and sleeping sickness.

B. Control of Green House effect :

Following measures are to be adopted to control the Green house effect.

- (i) To minimise the use of automobiles by using bicycle, public transport system or go for carpool, so that consumption of fossil fuels can be drastically reduced.
- (ii) Banning of deforestation and developing greenery by massive plantations.
- (iii) Banning of the use of chlorofluorocarbons (CFCs)
- (iv) To avoid burning of dry leaves and wood.
- (v) To avoid smoking in public places.

21.11 POLLUTION DUE TO INDUSTRIAL WASTES

The industries use raw materials, process them and produce finished products along with some by-products which are thrown into the environment as industrial wastes in the form of gas, liquid or solid, thus polluting either the air or water or soil.

Industrial wastes may be classified as :

1. Biodegradable and non-biodegradable wastes :

- (i) Biodegradable wastes are generated by cotton mills, food processing units, paper mills and textile factories.
- (ii) Non-biodegradable wastes are generated by iron and steel plants, thermal power plants, fertilizer industries which pose a serious threat to humankind.

2. Process waste and chemical wastes :

- (i) Process waste is produced during washing and processing of raw materials which may be organic or inorganic in nature, but both are toxic to living organisms. Organic wastes are liberated from food processing units, distilleries, breweries, sugar mills etc. Inorganic process wastes may be generated by caustic soda industry, paint industry, petroleum industry, iron and steel plants, thermal power plants etc.

Fly ash from thermal power plants contaminate atmospheric tract causing respiratory tract disorder. Fertilizer industries produce gypsum. Iron and steel plants produce slag. The industries may also cause thermal pollution and noise pollution.

- (ii) Chemical wastes includes heavy metals and their ions, detergents, acids, alkalis and various other toxic substances, produced by fertilizer industries, paper and pulp industries, sugar mills etc. These are usually liberated into nearby water bodies like rivers, lakes etc. which may alter the pH, BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand).

The aquatic animals and plants absorb, accumulate the chemical wastes destroying the trophic levels and food chain of the ecosystem.

The disposal of non-biodegradable industrial solid wastes may be done by the following ways in order to control environmental pollution.

- (a) Fly ash and slag from the steel industry are to be utilized by the cement industry.
- (b) Toxic water can be destroyed by controlled incineration.
- (c) Wastes should be subjected to proper treatment before their discharge.

21.12 GREEN CHEMISTRY AS AN ALTERNATIVE TOOL FOR REDUCING POLLUTION

A. Introduction :

Green chemistry or Sustainable chemistry may be defined as the sustainable, safe and non-polluting chemical science which enables man to manufacture products with minimum consumption of materials and energy and also production of minimum waste.

Important principles of Green Chemistry are :

- (i) Minimizing or eliminating the need for waste clean-up by emphasizing waste preventions.
- (ii) Minimizing energy consumption.
- (iii) Planning and using chemical products with minimum toxicity.
- (iv) As far as possible, use and production of hazardous substances which cause harm to man and environment should be avoided.
- (v) Materials and the involved process which may lead to explosions, high temperatures or pressure should be avoided.

B. Use of environmental friendly reagents :

In ideal case green chemistry helps in avoiding feedstock and catalysts, toxic reagents or solvents and drastic conditions eliminating generation of hazardous intermediates and byproducts. It involves the use of mild and environmental friendly reagents such as sunlight, microwaves, sound waves and enzymes.

(i) Use of sunlight and microwaves :

Recently many photochemical reactions are being carried out using microwave ovens where no toxic solvents are used, but only the reactants in appropriate ratios are mixed on a solid support such as alumina. The use of microwaves have not only reduced the time of reaction, but have also increased the yields.

(ii) Use of sound waves :

The branch of chemistry where sound waves have been used to carry out certain known chemical reactions instead of microwaves is called *sonochemistry*.

(iii) Use of enzymes :

Now many biochemical methods have been utilized to prepare precursors and intermediates of certain medicines and antibiotics using enzymes which work in aqueous solution at mild conditions. For example, antibiotics like ampicillin and amoxycillin have been prepared using this method.

C. Achievements of Green chemistry :

Some of the recent achievements of green chemistry are :

(i) Catalytic dehydrogenation of diethanolamine :

Herbicide can be synthesized by the catalytic dehydrogenation where the reactants and the products are eco-friendly unlike the old classical reactions in which cyanide and formaldehyde were used.

(ii) Synthesis of ibuprofen :

Ibuprofen is now synthesized by a new technique giving 99% yield using smaller quantities of solvents and being associated with no waste products.

(iii) Replacement of chlorofluorocarbons (CFCs) by CO₂ as blowing agent :

CFCs are responsible for ozone depletion, global warming and formation of smog. Now CFCs have been replaced by CO₂ as blowing agent.

(iv) Replacement of organotins by ‘Sea-nine’ as antifouling compound in sea marines :

Previously organotins were used as antifouling agents in sea marines, which are highly stable persisting for a longer time causing pollution. Now these have been replaced by safer compounds called ‘sea-nine’.

21.13 STRATEGY FOR CONTROL OF ENVIRONMENTAL POLLUTION

The human activities such as the rapid growth of population, industrialization, urbanization etc. play a vital role for environmental pollution, which has become a global problem. In order to check environmental pollution and to save our earth from the future destructive situation the following measures should be adopted and implemented by each individual in addition to Government and NGO’s co-operation.

- (i) Public awareness must be created through meetings and trainings how to control pollution.
- (ii) Individuals should learn three R's i.e. Recycle, Recovery and Reuse about the waste materials.
- (iii) Waste materials should not be thrown into the water bodies or sewer.
- (iv) Instead of using chemical fertilizers and pesticides in the agriculture, traditional manures e.g. cow dung and compost manures are to be used.
- (v) Every one must take care of waste management.
- (vi) Waste materials must be put in waste containers or at selected places.
- (vii) Deforestation must be checked and massive plantation programmes are to be encouraged at the road sides, on the river bank, on the sea shore and unused lands.
- (viii) All of us should accept the famous slogan 'Think Globally, Act Locally'.

21.14 WASTE MANAGEMENT :

Waste management is the process by means of which the wastes are converted into valuable resources by means of the improved techniques without producing any sort of environmental problems.

Since the waste materials create many environmental problems including health hazards to humanbeings if not properly disposed of, it is now highly essential to properly implement the waste management. Main sources of waste materials are :

- (i) Domestic waste includes sewage and municipal garbage.
- (ii) Industrial waste which includes toxic materials
- (iii) Construction sites, medical etc.

Environmental pollution due to these wastes can be substantially reduced by applying the following methods.

A. Recycling : Recycling is based on the principle that waste is considered as a resource, where the waste materials can be used as raw material to manufacture some useful products again e.g.

- (i) Used glass bottles as well as broken pieces of glass.
- (ii) Iron scrap for manufacture of steel.
- (iii) Plastic wastes and polyethene bags.
- (iv) Used newspapers and magazines for making papers again.

- B.** **Composting :** It is a biological degradation or breaking of organic materials such as cow dung, garbage, residues of plants and animals through biochemical process. This process takes place under aerobic conditions giving rise to manure, which increases the soil nutrients and improve crop yields.
- C.** **Land fills :** In this method, solid wastes are dumped into low lying areas in layers with insecticides like DDT being sprayed on the top to prevent breeding of mosquitoes , flies etc.
- D.** **Incineration :** Incineration involves the burning of combustible wastes including household wastes, chemical wastes and biological wastes at high temperature leaving the ash which can be used as a land-filling material. But the gases produced must be suitably treated before they escape into the atmosphere and cause pollution. Disposal of polychlorinated biphenyls (PCBs) is possible by this method as high temperature breaks the C–Cl bonds. However, the ash produced might contain toxic heavy metal causing serious health hazards.
- E.** **Pyrolysis :** This is the combustion of waste in the absence of oxygen, where the end products obtained are the combustible gases, tar, charcoal etc. and are used as resource materials in industries.
- F.** **Sewage treatment :** Treatment of sewage can be carried out through the following steps:
- Bigger materials are filtered through screens, which can be used to fill low lying land.
 - It is allowed to stand in tanks, so that heavy solids settle down (called sludge) while oils and grease float on the surface which can be easily removed.
 - The organic materials present in it are allowed to undergo microbial oxidation.
 - Finally the waste water is treated to remove phosphate followed by coagulation, filtration and disinfecting it by adding chlorine.
- G.** **Digesting :** By this method the waste is disposed by microorganisms in the absence of oxygen releasing mainly CO_2 and CH_4 .
- $$2 [\text{CH}_2\text{O}] \rightarrow \text{CO}_{2(\text{g})} + \text{CH}_{4(\text{g})}$$
- Methane can be used as a fuel.
- H.** **Disposal into ocean :** The oceans are the vast, natural sink for waste materials. The types of waste disposed into the oceans are sewage sludge, dredgs spoils, solid waste, construction and demolition materials. Although it is a simple and cheap method, it has certain disadvantages, e.g.
- It causes water pollution leading to marine pollution and causing health hazards.
 - The lighter solid waste float and return to the beach creating environmental problems.

CHAPTER (21) AT A GLANCE

1. **Environmental Chemistry** deals with the chemical reaction in the environment where the reacting species are generated either naturally or by human activities.
2. **Environmental Pollution** may be defined as the process involving the addition of any undesirable material to air, water and soil naturally or due to human activities to such a level of concentration adversely affecting the quality of environment and having harmful effects on plants, animals and humanbeings.
3. Troposphere and Stratosphere are the two important zones of atmosphere mainly affected by pollution. Ozone layer present in stratosphere protects our earth from harmful UV ray coming from the sun. But now ozone layer is being depleted by mainly CFCs, increasing the chance of occurrence of skin cancer.
4. The lowest region of atmosphere i.e. troposphere where usually the living organisms live is polluted by oxides of sulphur, nitrogen and carbon mainly responsible for acid rain.
5. Increased concentration of green house gases, mainly CO_2 is responsible for **Global Warming** due to re-emission of sun's energy absorbed by the earth followed by its absorption by CO_2 molecules and H_2O vapour present near the earth surface and then its radiation back to the earth. If not timely controlled it may submerge the coastal land due to melting of polar ice caps.
6. **Rapid urbanisation**, excessive industrialisation and use of excessive pesticides, fertilizers in agriculture are the main source of air, water and soil pollution.
7. It is now high time to think seriously to adopt and implement very strong controlling measures to save our earth from environmental pollution. Most important measures include
(i) Waste management (ii) Green chemistry as an alternative tool for reducing pollution.
(iii) Individual awareness.

QUESTIONS**A. VERY SHORT ANSWER QUESTIONS (1 mark)**

1. Ozone is present in which region of the atmosphere ?
2. Give an example of non-biodegradable waste.
3. Which gas is mainly responsible for ozone layer depletion ?
4. What is the colour of ozone gas ?
5. Unpolluted rain water contains which acid ?
6. In the absence of ozone layer which rays will enter into atmosphere ?
7. Which gas can remove oxygen from oxyhaemoglobin ?
8. What is the other name of Los Angeles smog ?
9. What is CFC ?
10. What is PAN ?
11. What is BOD ?
12. What COD ?
13. Which disease is caused due to hole in the ozone layer ?
14. Why photochemical smog is so called ?
15. Which acids are present in the acid rain ?
16. Name two natural sources of air pollution.
17. What is the nature of photochemical smog ?
18. What are polar stratospheric clouds ?
19. Name any two methods for waste management.
20. Which national monument is now being corroded by acid rain ?
21. Which is more poisonous CO or CO₂ ?
22. Which gas is used during photosynthesis by the plants ?

B. SHORT ANSWER QUESTIONS (Carrying 2 marks)

1. What do you mean by environmental chemistry ?
2. Define environmental pollution.
3. What are pollutants ?
4. Define green house effects.
5. What causes ozone to break down ?
6. Explain how CO is harmful to a person exposed to it.
7. What are the effects of soil pollution ?
8. How sulphuric acid and sulphurous acids are formed in the atmosphere ?

9. What are biodegradable and non-biodegradable pollutants ?
10. What is Los Angeles smog ? How is it produced ?
11. How ozone layer is formed and acting as a protecting umbrella ?
12. Write down the difference between London smog and photochemical smog.
13. How plant nutrients and pesticides act as water pollutants ?
14. Why ozone hole has been observed only in Antarctica ?

C. SHORT ANSWER QUESTIONS (Carrying 3 marks)

1. Give two examples from each of solid, liquid and gaseous pollutants.
2. What is CFC ? How does it destroy ozone ?
3. Define acid rain ? Name any one acid and its formation which causes acid rain ?
4. What are the pollutants attacking Taj Mahal and how ?
5. What is smog ? How Los Angeles smog is produced ?
6. What do you know by depletion of ozone layer ? How it is caused ?
7. What are air pollutants ? Give two examples.
8. What do you know by incineration ? How is it helpful for waste management ?
9. What do you mean by global warming ? Suggest one method to control it.
10. Which one is more dangerous, carbon monoxide or carbon dioxide and why ?

D. LONG ANSWER QUESTIONS :

1. What is smog ? How is classical smog different from photochemical smog ? How can they be controlled ?
2. What do you mean by green chemistry ? How will it be helpful to decrease environmental pollution ?
3. What are the major causes of water pollution ? What measures can you suggest to control it ?
4. Explain the reactions occurring in the atmosphere.
5. What is soil ? What are the sources of soil pollution ? Can it be controlled ?
6. What do you mean by acid rain ? How it is formed and what are its consequences ?
7. Define green house effect. Discuss its causes and effects. Suggest some remedial measures to control it.
8. Write short notes on.
 - (a) Global warming
 - (b) Smog
 - (c) Acid rain
 - (d) Pollutants

- (e) Waste management
- (f) Industrial wastes
- (g) Ozone hole

E. MULTIPLE CHOICE QUESTIONS :

1. Which is true for photochemical smog ?
 - (a) is reducing in nature
 - (b) It is formed in winter
 - (c) It is a mixture of smoke and fog
 - (d) It causes irritation in eyes
2. Ozone layer is present in
 - (a) Troposphere
 - (b) Stratosphere
 - (c) Mesosphere
 - (d) Exosphere
3. Which of the following is not a green house gas ?
 - (a) CO_2
 - (b) CH_4
 - (c) Chlorofluorocarbons
 - (d) O_2
4. Which of the following is present in maximum amount in acid rain ?
 - (a) HNO_3
 - (b) H_2SO_4
 - (c) HCl
 - (d) H_2CO_3
5. Which is not considered as a pollutant ?
 - (a) NO_2
 - (b) O_3
 - (c) CO_2
 - (d) CH_4
6. Depletion of ozone layer causes
 - (a) Breast cancer
 - (b) Lung cancer
 - (c) Skin cancer
 - (d) Blood cancer
7. Which is not involved in formation of photochemical smog ?
 - (a) NO
 - (b) Hydrocarbon
 - (c) SO_2
 - (d) O_3
8. Which has the greatest affinity for haemoglobin ?
 - (a) CO
 - (b) NO
 - (c) O_2
 - (d) CO_2

ANSWERS

1. (a) 2.(b) 3.(d) 4. (b) 5. (c) 6. (c) 7. (c) 8. (a)



