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HIGHER SECONDARY (+2)

CHEMISTRY

VOL. - II

Dr. A. K. Das
Former Chairman, CHSE, Odisha
Bhubaneswar.

Dr. S. Behera
Former Principal, D. D. College,
Keonjhar.

Dr. A. K. Panigrahi
Former Director, Odisha State Bureau of
Textbook Preparation and Production,
Bhubaneswar.

Dr. B. C. Singh
Former Professor of Chemistry,
Ravenshaw College, Cuttack.

Dr. B. K. Mohapatra
Former Chairman, CHSE, Odisha,
Bhubaneswar.

Dr. J. N. Kar
Former Principal, Govt. College, Phulbani.

Dr. H. K. Patnaik
Former Principal, Govt. College,
Rourkela.

Dr. G. C. Dash
Former Principal,
S.C.S. (Autonomous) College, Puri.

Dr. Hrushikesh Mohanty
Associate Professor & HOD, Chemistry,
B.J.B. Autonomous College, Bhaubaneswar.

Dr. Santosini Patra
Associate Professor in Chemistry
R.D. Women's University, Bhubaneswar

Dr. Panchanan Gouda
Associate Professor & H.O.D., Chemistry,
Khallikote University, Berhampur.

Dr. I. B. Mohanty
Deputy Director
Department of Higher Education, Odisha

Dr. Sakuntala Jena
Asst. Professor, Department of Chemistry,
Govt. Women's College, Dhenkanal.

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FOREWORD

(New Edition - 2017)

The Council of Higher Secondary Education, Odisha has revised the Courses of Studies in Chemistry for its Examination, 2018 and onwards. It is really heartening to know that the Chemistry, Vol-II is an exclusive textbook of CHSE and 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.

I would like to express my thanks to Dr. Jibanananda Kar, Dr. Akhil Krishna Panigrahi, Dr. Gobinda Chandra Dash, Dr. Hrushikesh Mohanty, Dr. Panchanan Gouda, Dr. Santosini Patra and 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.

Improvement has no limit especially when one aims at excellence. The Bureau welcomes constructive suggestions from the students as well as the teachers to make the book more purposeful.

Sri Umakanta Tripathy
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.

Bhubaneswar
14.3.2017

Board of Writers

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

SECOND YEAR

Course Structure

Unit	Title	Marks
I	Solid State	23
II	Solutions	
III	Electrochemistry	
IV	Chemical Kinetics	
V	Surface Chemistry	
VI	Isolation of Elements	19
VII	p-Block Elements	
VIII	d- and f- Block Elements	
IX	Coordination Compounds	
X	Haloalkanes and Haloarenes	28
XI	Alcohols, Phenols and Ethers	
XII	Aldehydes, Ketones and Carboxylic Acids	
XIII	Organic Compounds containing Nitrogen	
XIV	Biomolecules	
XV	Polymers	
XVI	Chemistry in Everyday Life	
		Total : 70

Unit - I : Solid State

Classification of solids based on different binding forces: molecular, ionic, covalent and metallic solids, amorphous and crystalline solids (elementary idea). Unit cell in two dimensional and three dimensional lattices, calculation of density of unit cell, packing in solids, packing efficiency, voids, number of atoms per unit cell in a cubic unit cell, point defects, electrical and magnetic properties.

Band theory of metals, conductors, semiconductors and insulators and n & p type semiconductors.

Unit II : Solutions

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, colligative properties - relative lowering of vapour pressure, Raoult's law, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, van't Hoff factor.

Unit III : Electrochemistry

Redox reactions, electrolytes and non-electrolytes, conductance in electrolytic solutions, specific and molar conductivity, variation of conductivity with concentration, Kohlrausch's law, electrolysis and laws of electrolysis (elementary idea), dry cell electrolytic cells and Galvanic cells, lead accumulator, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and emf of a cell, fuel cells, corrosion.

Unit IV : Chemical Kinetics

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst, order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment). Activation energy, Arrhenius equation.

Unit V : Surface Chemistry

Adsorption - physisorption and chemisorption, factors affecting adsorption of gases on solids, catalysts, homogenous and heterogenous activity and selectivity; enzyme catalysis, colloidal state, distinction between true solutions,colloids and suspension; lyophilic, lyophobic, multimolecular and macromolecular colloids; properties of colloids; Tyndall effect, Brownian movement, electrophoresis, coagulation, emulsion - types of emulsions.

Unit VI : General Principles and Processes of Isolation of Elements

Principles and methods of extraction - concentration, oxidation, reduction - electrolytic method and refining; occurrence and principles of extraction of aluminium, copper, zinc and iron.

Unit VII : p - Block Elements

Group15 Elements: General introduction, electronic configuration, occurrence, oxidation states, trends in physical and chemical properties; Nitrogen : preparation properties & uses; compounds of nitrogen, preparation and properties of ammonia and nitric acid, oxides of nitrogen (Structure only); Phosphorus - allotropic forms, compounds of phosphorus: preparation and properties of phosphine, halides PCl_3, PCl_5 and oxoacids (elementary idea only).

Group 16 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties, dioxygen: Preparation, Properties and uses, classification of oxides, Ozone, Sulphur: allotropic forms; compounds of sulphur: Preparation properties and uses of sulphur dioxide, sulphuric acid: industrial process of manufacture, properties and uses; oxoacids of sulphur (Structures only).

Group 17 Elements: General introduction, electronic configuration, oxidation states, occurrence, trends in physical and chemical properties; compounds of halogens, Preparation properties and uses of chlorine and hydrochloric acid,interhalogen compounds, oxoacids of halogens (structure only).

Group 18 Elements : General introduction,electronic configuration, occurrence, trends in physical and chemical properties, uses.

Unit VIII : d and f Block Elements

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first row transition metals - metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2 Cr_2O_7$ and $KMnO_4$.

Lanthanoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

Actinoids - Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

Actinoids - Electronic configuration, oxidation states and comparison with lathanoids.

Unit IX : Coordination Compounds

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's therory, VBT and CFT; structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X : Haloalkanes and Haloarenes

Haloalkanes : Nomenclature, nature of C-X bond, physical and chemical properties, mechanism of substitution reactions, optical rotation.

Haloarenes : Nature of C - X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only.

Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT, BHC.

Unit XI : Alcohols, Phenols and Ethers

Alcohols : Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols : Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers : Nomenclature, methods of preparation, physical and chemical properties uses.

Unit XII : Aldehydes, Ketones and Carboxylic Acids

Aldehydes and Ketones : Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes uses.

Carboxylic Acids : Nomenclature, acidic nature, methods of preparation, physical and chemical properties, uses.

Unit XIII : Organic compunds containing Nitrogen

Amines : Nomenclature, classification, structure, methods of preparation, physical and chemical proporties, uses, identification of primary, secondary and teritary amines.

Cyanide and Isocyanides - will be mentioned at relevant places in context

Diazonium salt - Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit XIV : Biomolecules

Carbohydrates - Classification (aldoses and ketoses) Monosaccharides (glucose and fructose), D-L configuration, oligosaccharides (sucrose, lactose, maltose) polysaccharides (starch, cellulose, glycogen), importance.

Proteins - Elementary idea of α - amino acids, peptide bond, polypeptide, proteins, structure of proteins-primary secondary, tertiary structure and quaternary structure(qualitative idea only), denaturation of proteins, enzymes.

Hormones - Elementary idea excluding structure

Vitamins - Classification and functions

Nucleic Acids : DNA and RNA

Unit XV : Polymers

Classification-Natural and synthetic, methods of polymerization(addition and condensation)co polymerization, some important polymers : natural and synthetic like polythene, nylon, polyester, bakelite, rubber. Biodegradable and non-biodegradable polymers.

Unit XVI : Chemistry in Everyday life

Chemicals in medicines - Analgesics, tranquilizers antiseptics, disinfectants, antimicrobials, antifertility, drugs, antibiotics, antacids, antihistamines.

Chemicals in food - Preservations, artificial sweetening agents, elementary idea of antioxidants

Cleansing agents - Soap and detergents, cleansing action.

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UNIT - XV

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………

UNIT - I

CHAPTER - 1

THE SOLID STATE

The study of solids is mainly the study of crystals since most of the naturally occurring solids are crystalline in nature. Solids are characterised by definite shape, definite volume and fixed melting point.Besides compressibility, rigidity and high-mechanical strength are the properties of a solid. The molecules, atoms or ions that constitute a solid are closely packed and held by strong cohesive forces. So the solids have well ordered molecular arrangement.

1.1 CHARACTERISTIC PROPERTIES OF SOLIDS :

1. **Shape :** A solid has a definite shape.

2. **Volume :** A solid possesses a definite volume. It does not depend upon the size or shape of the container.

3. **Rigidity :** Solids are highly rigid. This is due to the fact that the molecules have definite positions and they cannot slide over each other to take up different positions. The interparticle attractions in them tend to arrange the particles in an orderly manner.

4. **Compressibility :** Solids are mainly incompressible. This is because the particles which constitute the solid are in close contact with one another.

5. **Diffusion :** The diffusion in case of solids is extremely small. This is due to the fact that the intermolecular forces of attraction holding the particles are very strong in solids which result in a close packing of particles in it. Thus movement of particles in a solid is very limited.

6. **Melting point :** The process of transformation of a solid into the liquid state at a particular temperature is called melting. The constant temperature at which a solid is transformed into the liquid state is called the melting point of the solid. At the melting point there is an equilibrium between the solid and liquid phases.

7. **Crystalline state :** Solids possess a crystalline structure. This is due to orderly arrangement of particles in solids.

1.2 CLASSIFICATION OF SOLIDS :

A. Solids are broadly classified into two categories : (a) crystalline solids (b) amorphous solids.

Crystalline solids : Crystalline solids are not only rigid and incompressible but also possess a regular orderly arrangement of atoms or molecules or ions which constitute the crystals. Some examples of crystalline solids are sodium chloride, sugar, alum and diamond.

A crystal of sodium chloride is cubic. In sodium chloride, Na^+ and Cl^- ions are arranged in the crystal lattice at alternate sites. Each Na^+ is surrounded octahedrally by six Cl^- ions and each Cl^- is surrounded octahedrally by six Na^+ ions. This arrangement exists throughout the crystal.

There are some crystalline solids whose crystalline structure contains few molecules of water. Such crystals are called **hydrates**. The water of hydration is called **water of crystallisation**. Examples of such crystalline solids are Blue vitriol ($CuSO_4 . 5H_2O$), Green vitriol ($FeSO_4 . 7H_2O$), Glauber's salt ($Na_2SO_4 . 10H_2O$), White vitriol ($ZnSO_4 . 7H_2O$), Washing soda ($Na_2CO_3 .10\ H_2O$). There are some crystalline solids which do not contain water of crystallisation. Such salts are called **anhydrous**. Some examples of such salts are sodium chloride (NaCl), potassium nitrate (KNO_3), ammonium chloride (NH_4Cl) etc.

Amorphous solids : Amorphous solids are rigid and incompressible and possess some ordered arrangement around a particular atom or ion which lasts only upto short distances. Examples of such solids are glass, fused silica, rubber and plastic.

DISTINCTION BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline	Amorphous
1. **Geometry :** Crystalline solids have regular and definite geometry which extends throughout the crystal.	**1.** Amorphous solids do not have regular geometry. The ordered arrangement extends only upto a short distance.
2. **Melting point :** Crystalline solids possess sharp melting points.	**2.** Amorphous solids do not possess sharp melting points.
3. **Isotropy and Anisotropy :** Crystalline solids are **anisotropic** i.e. their physical properties such as conductivity, refractive index etc. are different along different directions.	**3.** Amorphous solids are **isotropic** i.e. their physical properties such as conductivity, refractive index are the same along all directions.
4. **Cleavage :** When a crystalline solid is cut with a sharp edged tool, it is readily cut into smaller crystals with plane surface.	**4.** When an amorphous solid is cut with a sharp edged tool, it gives smaller pieces with irregular surfaces.
5. **Symmetry :** Crystalline solids possess crystal symmetry.	**5.** Amorphous solids do not possess symmetry.

Classification of Crystalline solids :

Crystalline solids may be further classified into following types according to the nature of particles constituting them and the binding forces between them.

a. Ionic solids.	b. Covalent solids.
c. Molecular solids.	d. Metallic solids.

a. **Ionic solids :** In ionic solids, the constituent particles are ions which are held together by electrostatic forces. The arrangement of these ions is such that cations have an ions as their nearest neighbours and vice versa. Examples of ionic solids are salts like Sodium chloride (NaCl), Lithium fluoride (LiF), Barium sulphate ($BaSO_4$), Sodium nitrate ($NaNO_3$), Sodium sulphate (Na_2SO_4) etc.

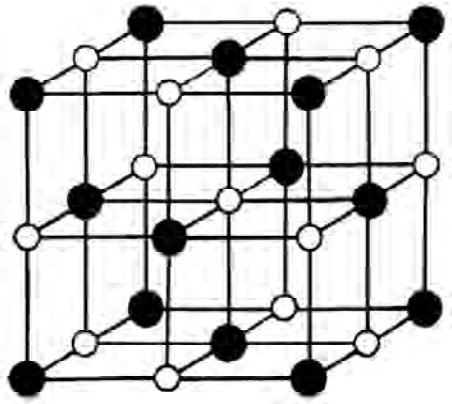


Fig. 1.1 Sodium chloride crystal

Because of stronger and non-directional electrostatic interactions the ionic solids are hard, brittle, and possess high melting and boiling points. They are bad conductors in the solid state but good conductors in the molten state.

b. **Covalent solids :** In covalent solids the constituent particles are the atoms which are held by covalent bonds. The bonds in covalent solids extend throughout the crystal and this results in the formation of a giant three dimensional structure. Some examples of covalent solids are diamond, graphite, quartz (SiO_2). Covalent solids are hard, non-volatile and possess high melting points. They are bad conductors of heat and electricity.

c. **Metallic solids :** In metallic solids, the constituent particles are positive ions immersed in a sea of electrons. The positively charged metal ions are held together by the cloud of negative electrons. The cloud of electrons belong to the entire net work of crystals. Some examples of metallic solids are common metals like copper, silver, aluminium and sodium and some alloys. Metallic solids are malleable and ductile. They have metallic lustre and are good conductors of heat and electricity.

d. **Molecular solids :** In molecular solids, the constituent particles are small molecules which are held together by weak van der Waals forces. Some examples of molecular solids are solid carbon dioxide, ice, sugar, iodine etc. Molecular solids are soft and volatile. They possess low melting points and are bad conductors.

1.3 CRYSTAL LATTICES AND UNIT CELLS :

Crystal lattice :

A crystal lattice (or space lattice) is a general term of an arrangement of points in space representing the atoms, ions or molecules forming the crystal which if extended in all directions throughout the crystal forms a repeating unit giving a shape of the crystal. In otherwords, a crystal lattice is a regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.

Lattice points :

The positions which are occupied by the atoms, ions or molecules in the crystal lattice are called lattice points or lattice sites.

Unit cell :

It is the smallest repeating unit in crystal lattice which when repeated over and over again produces the complete crystal lattice.

Such units are repeated over and over again in three dimensions and represents the shape of the entire crystal. The collection of points in the unit cell indicate the crystal coordination number and are in consistence with the formula of the compound.

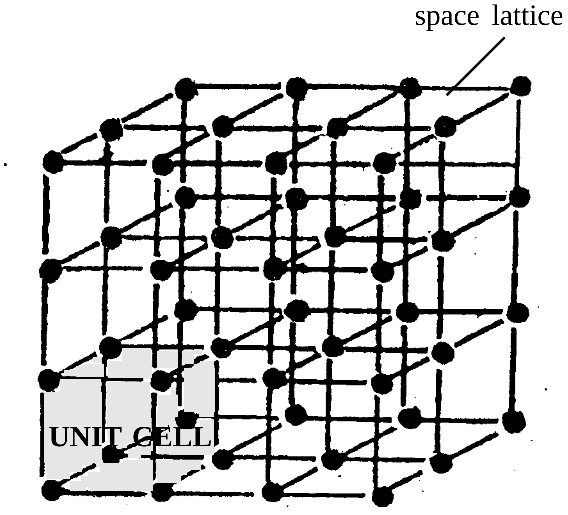


Fig. 1.2 Space lattice and a unit cell

Close packing in Crystalline solids :

In the formation of crystals the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which the maximum available space is occupied. The closer the packing, the greater is the stability of the packed system. The packing will also vary according to the shape and size of the constituent particles of crystals.

(i) Close packing in two dimensions :

To understand the packing of constituent particles let us consider the packing of hard spheres of equal size. The spheres can be arranged side by side touching each other in a row. The rows can be combined in the following two ways with respect to the first row to build a crystal plane.

1. The spheres are packed in such a way that the rows have a horizontal as well as vertical alignment. In this arrangement the spheres are found to form squares. This type of packing is also called **square close packing. (scp)**
2. The spheres are packed in such a way that the spheres in the second row are placed in the depressions between the spheres of the first row. Similarly, the spheres in the third row are placed in the depressions between the spheres of the second row and so on. This gives rise to **hexagonal close packing of spheres (hcp)**

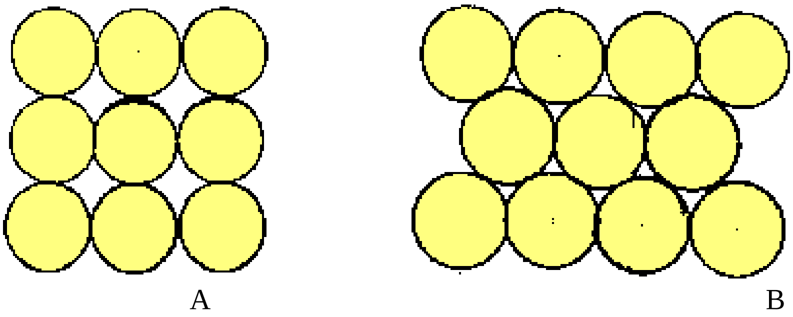


Fig 1.3 (A) A sphere in square close packing is in contact with four spheres.
(B) A sphere in hexagonal close packing is in contact with six spheres.

Arrangement I **(Less closely packed)**

Arrangement II **(More closely packed)**

Fig. 1.4 Packing of Spheres

(ii) Close packing in three dimensions :

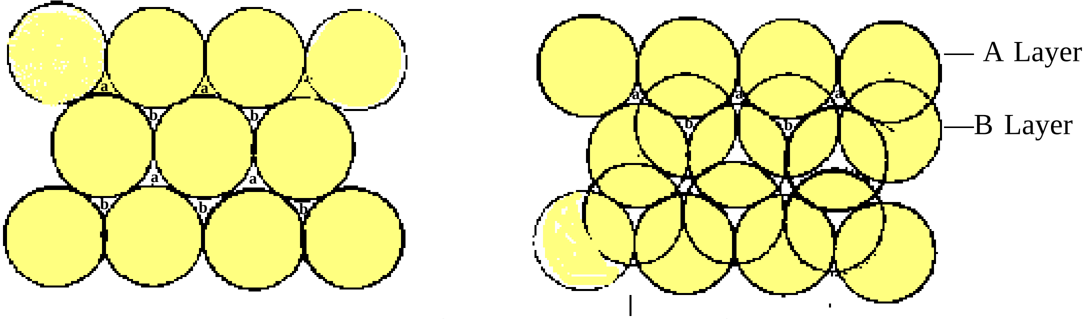


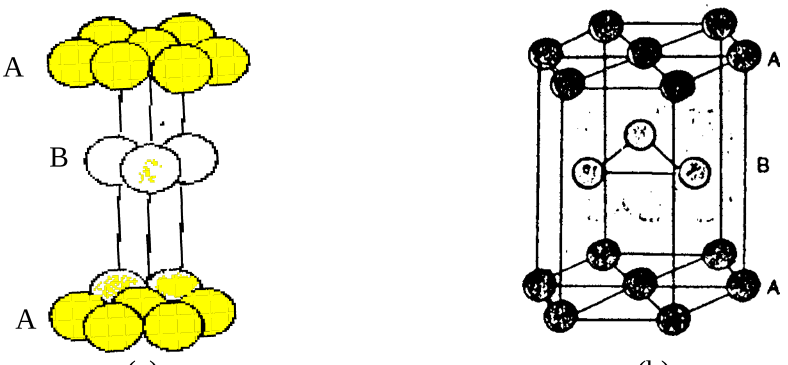
Fig. 1.5 Packing of second layer (B) on first layer (A)

Consider the above arrangement. Let us mark the spheres in the first layer as A. It is clear from the above arrangement that there are two types of voids of hollows in the first layer. These are marked as a and b. All the hollows are equivalent but the spheres of second layer may be placed either on hollows which are marked 'a' or on other set of hollows marked 'b'. It is to be noted that it is not possible to place spheres on both type of hollows.

Let us place the spheres on hollows marked 'b' to make the second layer which may be labelled as B layer. Obviously the holes marked 'a' remain unoccupied while building the second layer. The second layer is indicated as dotted circles.

When a third layer is to be added, again there are two types of hollows available. One type of hollows marked 'a' are unoccupied hollows of first layer. The other type of hollows are hollows in the second layer marked 'c'. Thus two alternatives are available to build the third layer.

1. In this case, the spheres of the third layer lie directly above those in the first layer. This type of packing is referred to as ABABA .... arrangement .

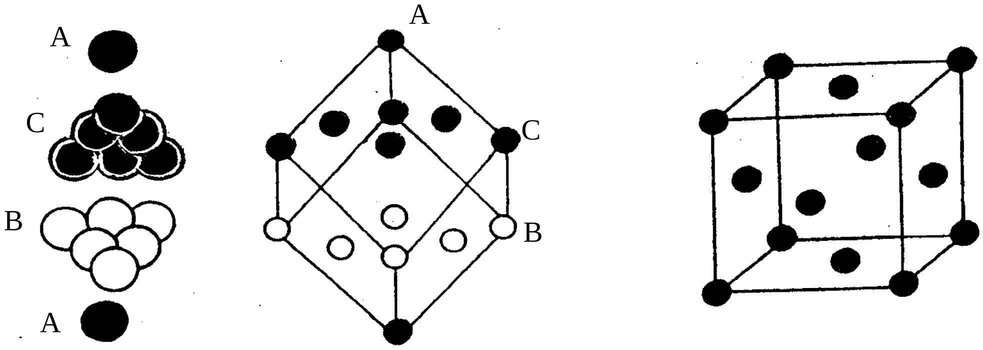


(a) (b)

Fig. 1.6 ABABA... or hcp arrangement of spheres.

It is also known as **hexagonal close packing (hcp)**

2. The second way to pack spheres in the third layer is to place them over hollows marked 'a'. This gives rise to a new layer labelled as 'C'. However it can be shown that the spheres in the fourth layer will correspond to those in the first layer. This gives rise to A B C A B C A ....type of arrangement. It also known as **cubic close packing. (ccp)**.



(a) (b) (c)

Fig. 1.7 ABCABCA... or ccp arrangement of spheres.

1.4 TYPES OF CUBIC CRYSTALS :

It is a fact that cubic system is the simplest system. There are three common types of cubic system.

1. Simple cubic.
2. Body centred cubic (bcc)
3. Face centred cubic (fcc) or
   Cubic close packing (ccp)

1. Simple cubic : In this arrangement the points (atoms, ions or molecules) are present at all the corners of a cube.

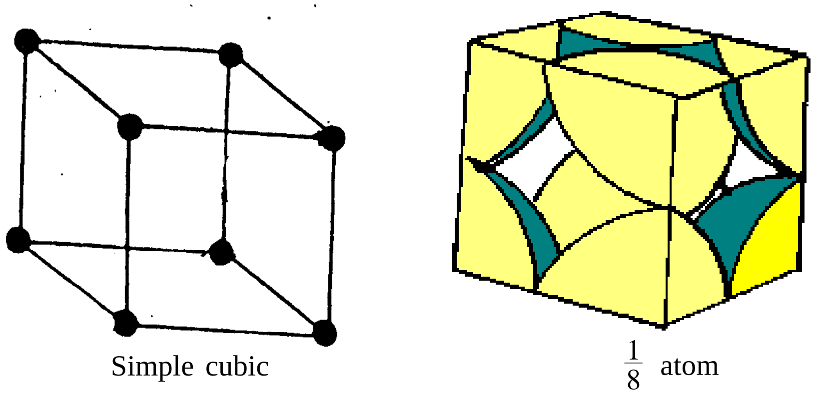


Fig. 1.8 Simple cubic arrangement and number of spheres per unit cell.

From the figure it is clear that the atom present at each corner contributes $\frac{1}{8}$ to each cube because it is shared by 8 cubes. Now there are 8 atoms at the corners. Thus the number of atoms present in each unit cell = 8 corner atoms x $\frac{1}{8}$ atoms per unit cell = 1 atom.

2. Body centred cube (bcc) : It has points at all the corners as well as at the centre of the cube.

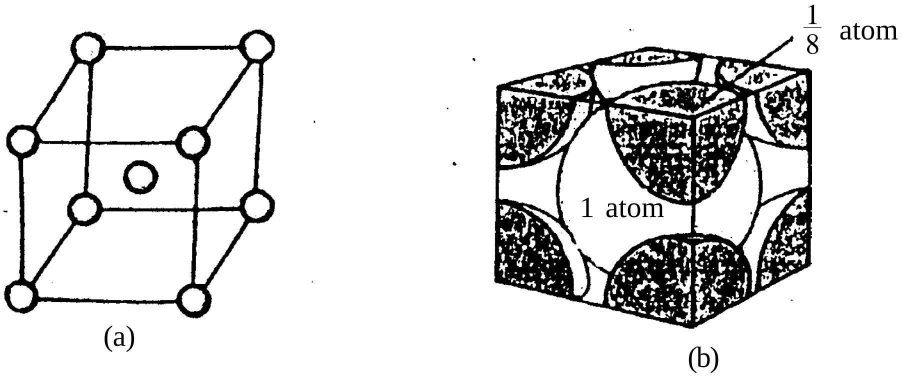


Fig. 1.9 Body centred cubic arrangement.

It is clear from the figure that there are eight atoms at the corners and each is shared by 8 unit cells so that the contribution of each atom at corner is $\frac{1}{8}$. In addition there is one atom in the body of the cube which is not shared by any other cube.

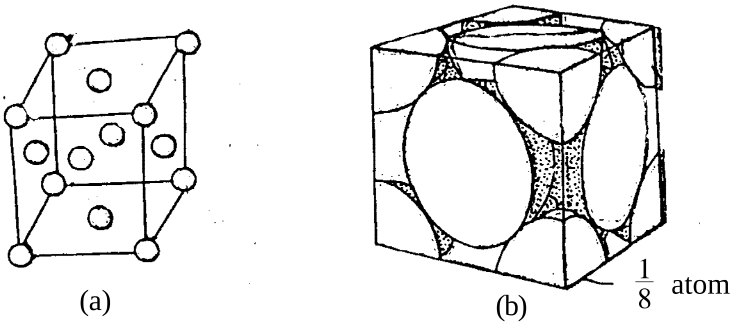
Therefore, the number of atoms present at the corners per unit cell = 8 corner atoms x $\frac{1}{8}$ atom per unit cell = 1

The number of atoms present at the centre of the cube = 1

∴ Total number of atoms in **bcc** arrangement = 1 + 1 = 2.

Thus, a body centred cube has two atoms per unit cell.

3. **Face centred cube (fcc).** This is also called cubic close packed arrangement. It has points at all the corners as well as at the centre of each of the six faces.



(a) (b)

Fig. 1.10 Cubic close packed or face centred cubic arrangement and share of each atom per unit cell.

In this arrangement, there is one atom at each of the eight corners.

From the above figure it is quite clear that atom present at each corner contributes $\frac{1}{8}$ to each cube because it is shared by 8 cubes. In addition, there are six atoms at the faces of the cube and each is shared by two unit cells. Therefore the contribution of each atom at the face per unit cell is $\frac{1}{2}$.

∴ The number of atoms present at corner per unit cell = 8 corner atoms x $\frac{1}{8}$ atoms per unit cell =1

The no. of atoms present at faces per unit cell

= 6 atoms at faces x $\frac{1}{2}$ atoms per unit cell = 3

∴ The total no of atoms in **ccp** or **fcc** arrangement = 1 + 3 = 4

The following table (1.1) depicts the total no. of atoms present per unit cell in different types of crystals.

Table 1.1 No. of atoms per unit cell in different crystals

Unit cell	No. of atoms at corners	No. of atoms at faces	No. of atoms in centre	Total No. of atoms
Simple cubic	8 x $\frac{1}{8}$	0	0	1
Body centred	8 x $\frac{1}{8}$	0	1	2
Face centred	8 x $\frac{1}{8}$	6 x $\frac{1}{2}$	0	4

1.5 CALCULATION OF DENSITY OF UNIT CELLS :

The density of unit cell can be calculated knowing the type of crystal structure and the edge length of the unit cell.

Let the edge length of unit cell = x pm

Volume of unit cell = $(x\ \text{pm})^3 = (x \times 10^{-10}\ \text{cm})^3 = x^3 \times 10^{-30}\ \text{cm}^3$

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{\text{No. of atoms in the unit cell} \times \text{Mass of each atom}}{\text{Volume of unit cell}}$$

$$\frac{n \times {}^{M}\!/_{N}}{x^3 \times 10^{30}\ \text{cm}^3}$$

$$= \frac{nM}{Nx^3 10^{30}}\ \text{g. cm}^{3}$$

where n = No. of atoms in the unit cell

M = Atomic mass

N = Avogadro Number

Thus, knowing the density of unit cell, the atomic mass as well as number of atoms or Avogadro number can be determined. n = 1, 2, and 4 for simple cubic lattice, bcc and fcc lattice respectively.

1.6 INTERSTICES OR INTERSTITIAL VOIDS :

In close packing spheres, certain hollows are left vacant. These hollows or voids in the crystals are called **interstital sites**, or **interstitial voids** or simply **interstices**. Two such voids are quite important.

1. Tetrahedral 2. Octahedral.

1. Tetrahedral void :

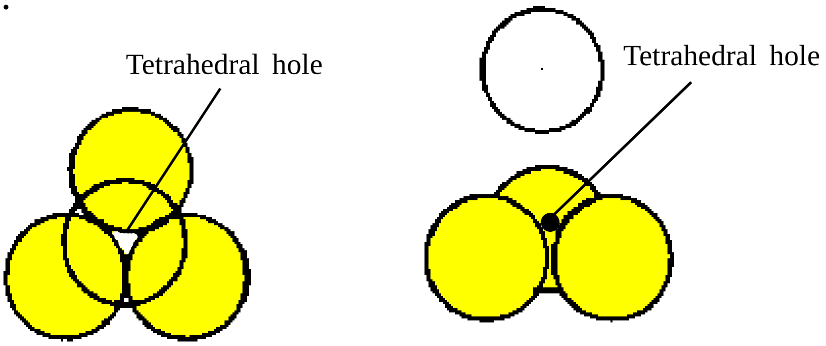


Fig. 1.11 Tetrahedral void.

The above arrangement of four spheres shows that their centres lie at the apices of a tetrahedron. But the shape of the void is not tetrahedral. Thus the vacant space among four spheres having tetrahedral arrangement is called **tetrahedral site or tetrahedral hole**.

2. Octahedral void :

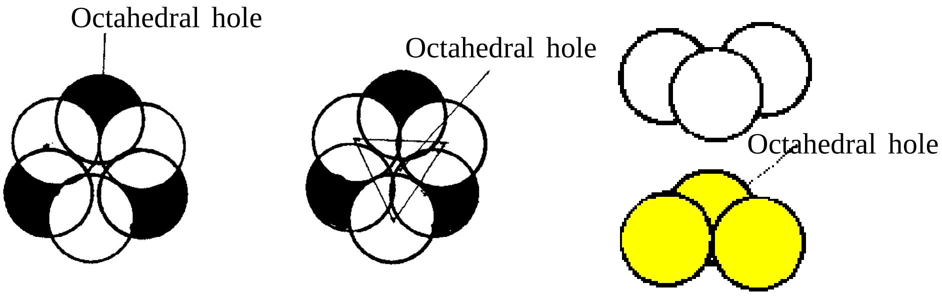


Fig. 1.12 Octahedral site

This type of void is formed at the centre of six spheres. In the above arrangement, each octahedral site is produced by two sets of equilateral triangles which point in opposite directions. Thus the void formed by two equilateral triangles with apices in opposite direction is called octahedral site or octahedral hole or simply **octahedral void**. This site is therefore surrounded by six spheres lying at the vertices of a regular octahedron.

1.7 CO-ORDINATION NUMBER :

The number of nearest neighbours with which a given sphere is in contact is called co-ordination number. For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio. The radius ratio for a given co-ordination number is fixed.

To understand it better, let us consider ionic solids. Each ionic solid is made up of cations and anions which have definite arrangements. Each ion is surrounded by a number of ions of opposite charge. For example, in A^+B^-, A^+ ions are surrounded by a definite number of B^- ions. This number is called co-ordination number of A^+. Similarly, the number of A^+ions which are surrounding a B^- ion is called co-ordination number of B^- ions.

Since the arrangement of ions in a crystal and the co-ordination number of ions depend upon the ratio of its radius with respect to the radius of the ions or atoms surrounding it, the radius ratio can be represented as :

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r^+}{r^-}$$

Radius ratio plays very important role in determining the structures of ionic solids. We know that the cations and anions in the ionic compound are held together by strong electrostatic forces. As a result, the ions try to arrange themselves in such geometrical arrangements where the attractions between the oppositely charged ions are maximum and the repulsions between the similar charged ions are minimum.

Example - Consider an ionic crystal AB in which a cation is surrounded octahedrally by six anions. For simplification, let us take any four B^- ions. There will be two more B^- ions, one above and the other below A^+ ion which have been omitted for clarity. The most stable arrangement is one in which anions are touching each other and the cation simultaneously.

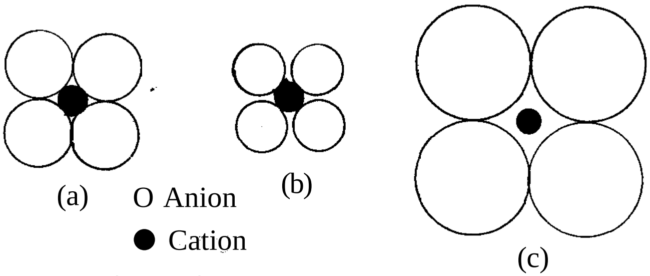


Fig. 1.13 Effect of change of size of anion (same cation) and the stability of structure. The cation is octahedrally surrounded by six anions but only four are shown. The anions above and below the cation are not shown for simplicity.

This arrangement will be most stable. However, if the size of the anion is less (cation same) the anions will no longer touch other anions and the structure will be unstable.

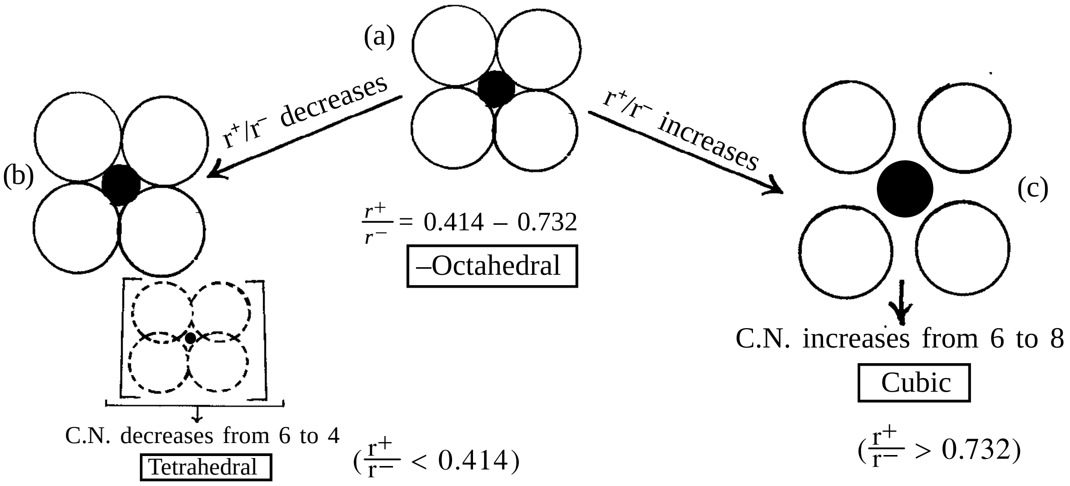


Fig 1.14 Effect of radius ratio on co-ordination number.

Similarly, if the size of anions is large (cation same) all the anions will not be able to touch the cation simultaneously. The structure will be unstable.

Therefore, if we decrease or increase the radius of the anion, keeping the cation same, the co-ordination number may increase or decrease to get stable arrangement. This means that the co-ordination number of a compound depends upon the radius of the cations and anions.

Radius ratio versus possible co-ordination number :

The possible co-ordination numbers and structural arrangements of anions around cations for different $\frac{r^+}{r^-}$ values are given below in table 1.2.

Table 1.2 Radius ratio versus co-ordination number with examples

Radius ratio	Possible Co-ordination number	Structural arrangement	Examples
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS, SiO_4^{4-}
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1.0	8	Cubic	CsCl

Example :

The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict whether the co-ordination number of Na^+ ion is 6 or 4. (pm = picometer = 10^{-12}m)

Solution :

Radius of Na^+ = 95 pm

Radius of Cl^- = 181 pm.

$$\text{Radius ratio}, \frac{r^+}{r^-} = \frac{r^+(Na^+)}{r^-(Cl^-)} = \frac{95}{181} = 0.524$$

The radius ratio lies between 0.414 – 0.732. Hence, Na^+ ions prefer to occupy octahedral holes having co-ordination number 6.

Structure of substances related to close packed lattices :

Example :

1. **Structure of sodium chloride :** A unit cell representation of sodium chloride is shown in fig. 1.15

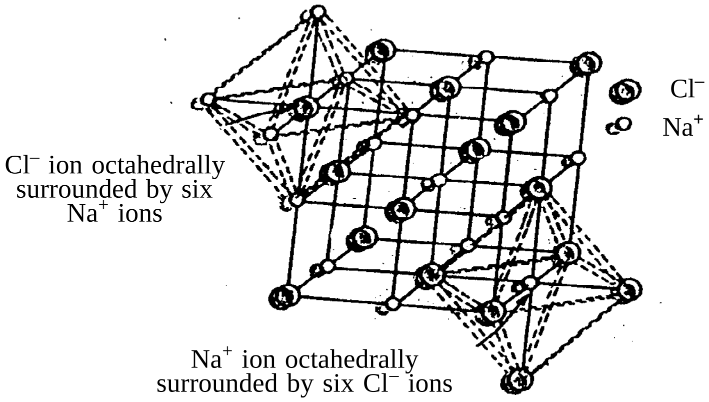


Fig. 1.15 Representation of unit cell of NaCl.

The salient features of the structure are :

i. The Cl^- ions adopt cubic close packed arrangement. Therefore, Cl^- ions are present at all the corners and at the centre of each face of the cube. This arrangement is also regarded as fcc arrangement of Cl^- ions.

ii. The Na^+ ions occupy all the octahedral sites.

iii. Since there is an octahedral site per atom in closed packed arrangement, there will be one Na^+ ion for every Cl^- ion. Thus the ratio of Na^+ and Cl^- ions in this structure is 1 : 1 and the formula of the compound is $Na^+ Cl^-$.

iv. In this structure, each Na^+ ion is surrounded by 6 Cl^- ions which are disposed towards the corners of a regular octahedron. (Fig 1.16). Similarly each Cl^- ion is surrounded by six Na^+ ions. Thus the co-ordination numbers of Na^+ and Cl^- in NaCl structure are 6 and 6.

2. Structure of Zinc sulphide (Zinc blend)

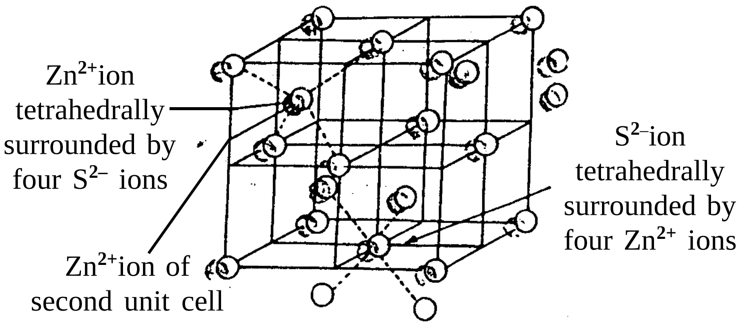


Fig. 1.16 Representation of zinc blend (ZnS) structure.

The salient features of the structure are :

i. The S^{2-} ions form cubic close packed arrangement. In this arrangement the S^{2-} ions are present at the corners of the cube and at the centre of each face.

ii. The zinc ions (Zn^{2+}) occupy half of the tetrahedral sites.

iii. There are two tetrahedral sites per atom in a closed packed lattice. That means there are two tetrahedral sites available for every S^{2-} ions. In this arrangement, any half of the tetrahedral sites is occupied by Zn^{2+} ions. Therefore, there is one Zn^{2+} ion for every S^{2-} ion and the formula is ZnS.

iv. In this structure each Zn^{2+} ions is surrounded by four sulphide ions which are disposed towards the corner of a regular tetrahedron. Similarly each S^{2-} ion is surrounded by four Zn^{2+} ions which are also disposed towards the corners of a regular tetrahedron.

3. Structure of CaF_2 (Calcium fluoride) :

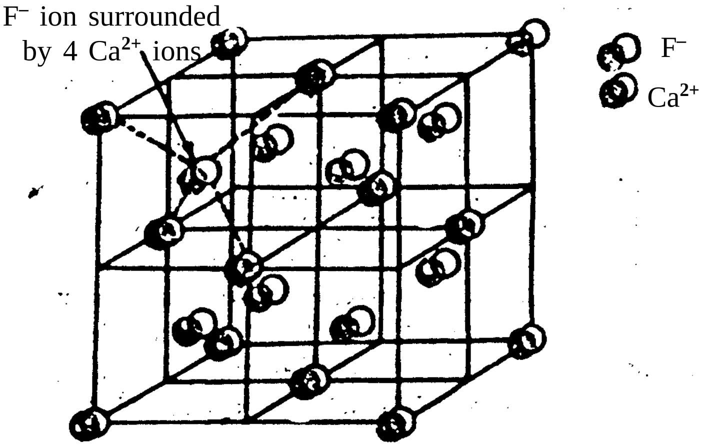


Fig. 1.17 Representation of CaF_2 structure.

The salient features of the structure are :

i. The Ca^{2+} ions are arranged in ccp arrangement. In this arrangement Ca^{2+} ions are present at all the corners and at the centre of each face of the cube.

ii. The fluoride ions occupy all the tetrahedral sites.

iii. There are two tetrahedral sites per atom in a closed packed lattice. This means there are two tetrahedral sites for every Ca^{2+} ion. Since F^- ions occupy all the tetrahedral sites, there will be two F^- ions for each Ca^{2+} ion.

Thus the formula of the substance is CaF_2.

iv. In this structure, each F^- ion is surrounded by four Ca^{2+} ions, while each Ca^{2+} ion is surrounded by eight F^- ions. Thus the co-ordination numbers of Ca^{2+} & F^- ions are 8 & 4.

4. Structure of Cesium chloride (CsCl)

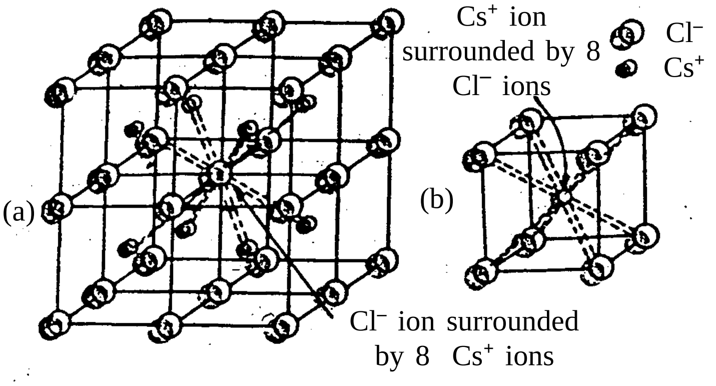


Fig. 1.18 Representation of CsCl structure.

The salient features are :

i. The Cl^- ions are arranged in a simple cubic arrangement. In this arrangement the Cl^- ions are present at all the cornes of the cube.

ii. The Cs^+ ions occupy the cubic site. That is Cs^+ ions are present at the body centre of the cube.

iii. From the above figure, it is clear that there are 8 Cl^- ions at the corners of the cube. Since each ion at the corner is shared by eight unit cells, its contribution per unit cell is 1/8. Therefore 8 Cl^- ions at the corners = $8 \times \frac{1}{8}$ = 1 Cl^- ion per unit cell.

There is also one Cs^+ ion in the body centre and its contribution per unit cell is 1. Thus there is one Cl^- for each Cs^+ ion and the compound has the formula CsCl.

iv. In this structure, each Cs^+ ion is surrounded by 8 Cl^- ions which are disposed towards the corners of a cube. (see the fig. 1.18) When the unit cell is extended, it can be seen that each Cl^- ion is also surrounded by 8 Cs^+ ions.

Thus, the co-ordination number of Cs^+ and Cl^- ions are 8 and 8.

1.8 POINT DEFECTS :

The crystal which is made up of same unit cells and contains the same lattice points throughout the crystal is said to be an ideally perfect crystal. Any deviation of the ideally perfect crystal from the periodic arrangement of its constituents is known as defect or imperfection of the crystal.

The imperfection or defect which arises due to missing atoms, displaced atom or extra atom within the crystals in known as **Point defect**. Point defects are thus due to imperfect packing during original crystallisation or they may arise due to thermal vibration of atoms at elevated temperature. The common point defects one **Schotty defect** and **Frenkel defect**. The less common point defects includes **metal excess defect** and **metal deficiency defects**.

Defects in stoichiometric solids - Stoichiometric compounds are those in which the number of +ve and –ve ions are in the same ratio as indicated by their chemical formulae. The defects which do not disturb the stoichiometry of the compound are known as stoichiometric defects. These are of the following types.

(1) Schottky Defects

(i) These defects arise due to missing of equivalent number of cations and anions from their respective positions in the crystal lattice thereby forming pair of holes.

(ii) These defects are more common in ionic compounds with high co-ordination number and having both positive and negative ions with almost equal size.

(iii) The crystal, as a whole, is electrically neutral since the number of missing +ve and –ve ions is the same.

(iv) Examples of ionic crystal showing Schottky defect include NaCl, KCl, KBr, CsCl etc.

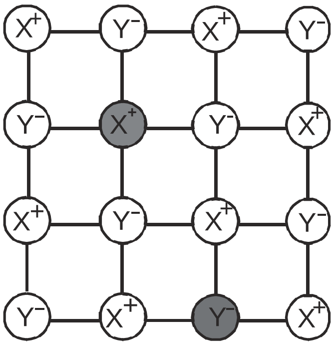


Fig. 1.19 Schottky Defect

Consequences of Schottky defects.

(i) Due to Schottky defect there is an increase in volume of the crystal with no increase in mass.

(ii) The density as well as the covalent character of the crystalline solid decreases.

(iii) The crystal becomes capable of conducting a small amount of electricity through ion jump mechanism.

(iv) The movement of atoms or ions in the crystal is induced due to existence of a vacancies. This accounts for the phenomenon of diffusion solids.

(v) The number of Schottky defects increase with increase in temperature.

(vi) The lattice energy of the crystal in lowered due to presence of holes. Thus, stability of crystal is lowered.

(2) Frenkel Defects

(i) This defect arises due to shifting of an ion from its normal position to interstitial site in the crystal lattice between the lattice points thereby causing a vacancy in the original position.

(ii) This defect is more common in ionic compounds having low co-ordination number and having large difference in size between positive and negative ions.

(iii) The crystal remains neutral since the number of +ve ions is equal to the number of –ve ions.

(iv) In an ionic crystal generally the cation moves since it is smaller than the anion and can easily fit into the vacant space in the lattice.

(v) Examples of ionic crystals showing Frenkel defect include ZnS, AgCl, AgBr, AgI etc.

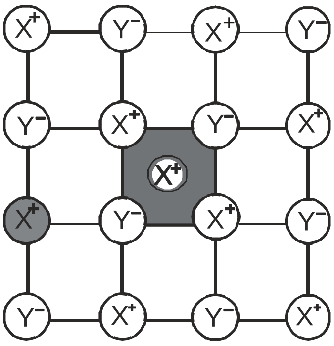


Fig. 1.20 Frenkel Defect

Consequences of Frenkel Defects

(i) The crystals are made good electrical conductors due to these defects.

(ii) These defects also account for the phenomenon of diffusion in solids.

(iii) These defects bring about closeness of similar charges which tend to increase the dielectric constant of the crystal.

(iv) The number of Frenkel defects increase with temperature.

(v) The stability of the crystal is lowered due to presence of the holes.

Defects in Non-stoichiometric solids

Non-stoichiometric solids are those in which the ratio of +ve and –ve ions differs from that represented by chemical formulae. These compounds do not strictly obey the law of constant proportions. Examples include $Fe_{0.94}O$ or VO_x , where x is between 0.6. and 1.3, In such type of compounds the balance of +ve and –ve charge is made by having either extra electrons or extra +ve charge. As a result the crystal structure becomes irregular and defective. These defects are of two types.

(i) Metal excess defects

When the metal ions are in excess as compared to –vely charged ion, the solid is said to have metal excess effect. There defect are due to two phenomena.

(a) Anion vacancies

(i) This defect arises due to removal of anions or nonmetal ions from the lattice sites resulting in the increase in concentration of metal ion or cation.

(ii) The vacancy caused by the loss of anion is occupied by electron so that electrical neutrality is maintained

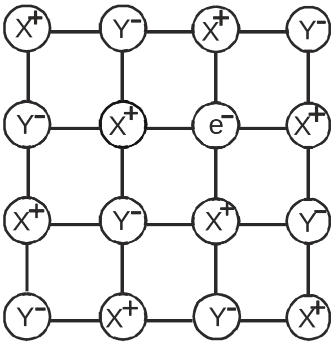


Fig. 1.21 Metal excess defect

(iii) This type of defect is observed in crystals which are likely to exhibit Schottky defect. Alkali metal halides are heated in a medium of alkali metal vapour so that anion vacancies are created. Alkali metals get deposited over alkal halide crystal. The halide ions move towards the surface and combine with metal ions.

(iv) On the otherhand when metals are converted into metal ions electrons are produced and the electron diffuse into the crystal and occupy the vacant positions in the lattice sites.

(v) The electrons occupy the holes known as F- Centres or Coloured centres (German word 'Farbe' meaning colour). F-centre is responsible for colour of the compound. For example, NaCl is yellow due to presence of excess Na^+ ion. KCl is violet due to presence of excess K^+ ion.

Consequences of Metal excess deffect due to anion vacancies

(a) The solids havings metal excess deffect act as semiconductors. This is due to presence of electrons at the F-centres.

(b) The electrons present at F- centres are excited to higher energy level and when they return to the ground state they do so by emitting certain radiation. This radiation falls is the visible region, so a colour is visualised. For example, ZnO gets yellow on heating.

(c) The solids having F-centres with unpaired electrons are paramagnetic.

(b) Extra cations in interstitial sites.

(i) This defect arises due to presence of extra cations in the interstitial sites.

(ii) To maintain electrical neutrality equivalent number of electrons are placed in the interstital sites.

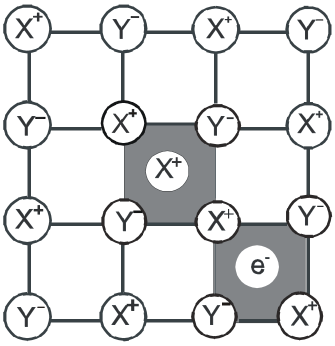


Fig. 1.22 Metal excess defect due to interstitial cations.

(iii) This type of defect is observed by the crystals which are likely to exhibit Frenkel defect. For example, when ZnO is heated, oxygen is lost reversibly and the interstitial sites accomodate excess metal ion. The electrons are trapped in the neighbourhood.

(iv) The electrical conductivity and the yellow colour in hot condition are due to these trapped electrons.

2. Metal deficiency defect

If the number of metal ions is less than the number of –vely charged ions, the solid is said to have metal deficiency defect. These defects are of two types.

(a) Cation vacancies

(i) This arises due to loss of cations from normal lattice site.

(ii) When a cation is missing, an extra electron must be present in the crystal and the extra negative charge in balanced by neighbouring metal ion (X^+) acquiring two +ve charges (X^{++}) instead of one.

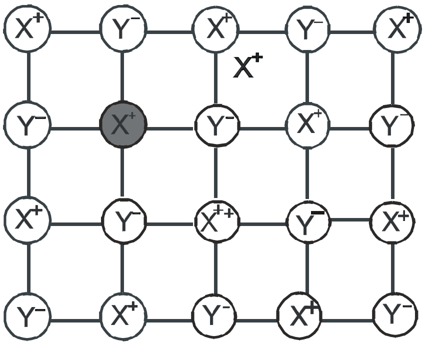


Fig. 1.23 Metal deficiency defect due to cation vacancy

(iii) The movement of +ve hole is caused due to apparent movement of X^{2+} ions is due to movement of an electron from X^+ ion.

(iv) Transition metal compounds having metals with variable valencies exhibit this type of defect. Some specific examples are crystals of FeO, NiO and FeS.

(b) Extra anions in the interstitial sites

(i) This effect arises due to presence of extra anions in the interstial spaces of the crystal.

(ii) The cations carrying additional charge are helpful in maintaining electrical neutrality.

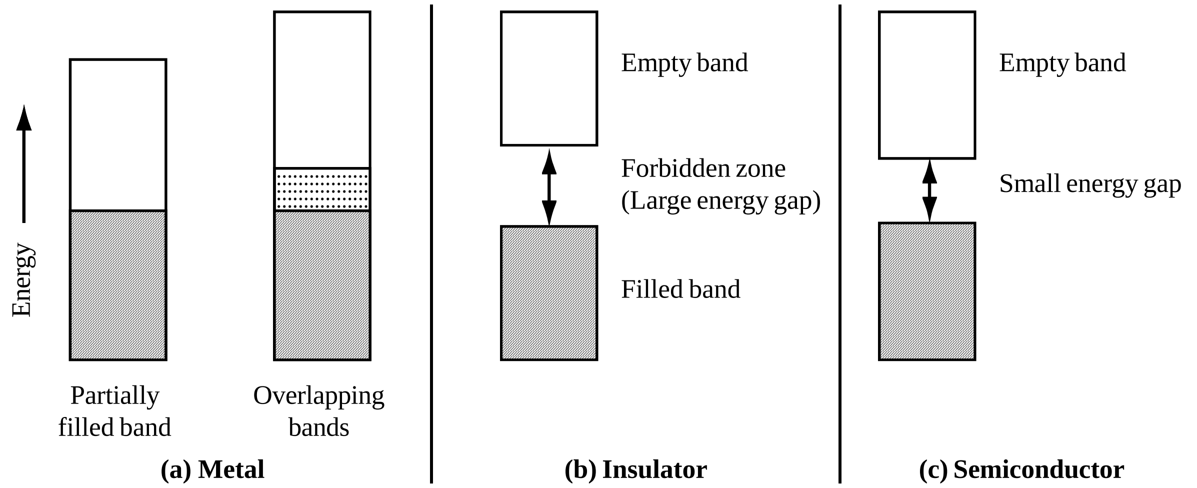
(iii) Anions are much larger than cation therefore do not fit well into interstitial sites. Hence this defect is usually not seen.

1.9 ELECTRIC AND MAGNETIC PROPERTIES OF METALS :

Metals conduct electricity due to the movement of electrons or ions when a potential difference is created. The conduct of electricity by metals takes place in solid as well as in molten state. The conductivity of metals depends upon the number of valence electrons present in it and the binding energy. The atomic orbitals of atoms linearly overlap to form molecular orbitals which are very close to each other in energy to form a band. If this band is partially filled in it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and metal behaves as good conductor. (Fig. 1.24a)

If the energy gap between filled valence band and the next higher unoccupied band is large, electrons cannot jump to the unoccupied band. Such a substance cannot conduct electricity and behaves as insulator. (Fig. 1.24b)

When the energy gap between the filled valence band and the next higher unoccupied band is small, some electrons can jump to the conduction band and show some conductivity, such substances are called **semiconductors**. Electrical conductivity of semiconductors increases with the rise of tempreraturе because electrons acquire more energy and can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**. The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**.



(a) Metal **(b) Insulator** **(c) Semiconductor**

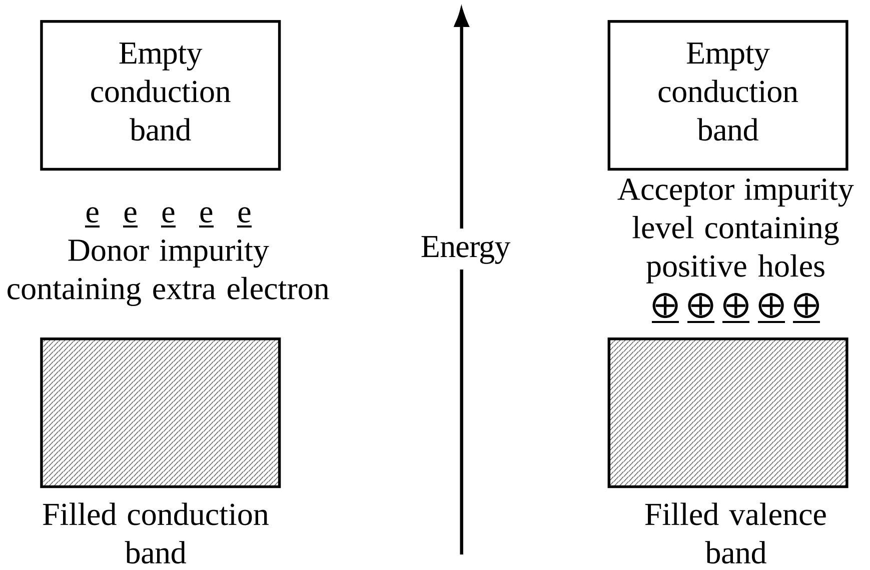
Fig. 1.24 Electronic Bands of (a) Metal (b) Insulator and (C) Semiconductor

Such substances are called *extrinsic* or *impurity semiconductors*. Depending on the nature of impurity added extrinsic semiconductros are of two types : (a) n-type extrinsic semiconductors and p-type extrinsic semiconductors.

(a) n-Type extrinsic semiconductors :

These are obtained by adding impurity atoms having more external electrons than the parent insulator atoms. Silicon and Germanium are insulators which belong to group 14 of the periodic table and have four valence electrons each. When phophorous, arsenic and antimony (all containing five valence electrons) atoms are added to pure silicon or germanium, we get n-type extrinsic semiconductors. Each of these atoms occupy some of lattice stites in silicon or germanium crystal. Four out of five electrons are engaged in formation of four covalent bonds with the four neighbouring silicon atoms. The fifth extra electron is free to occupy the lattice points. Such extra electrons occupy delocalised level, called donor impurity level which remains just below the empty conduction band of silicon or germanium crystal.

These extra electrons can easily be excited to the empty conduction band by the application of electric field or by increase in the thermal energy. Thus silicon or germanium become semiconductors by doping. Here the increase of conductivity is due to the negatively charged electron of the electron-rich impurity, hence the name **n-type** semiconductor. (Fig. 1.25a)



(a) n-type semiconductor **(b) p-type semiconductor**

Fig. 1.25 (a) n-type semiconductor, (b) p-type semiconductor

(b) p-Type semiconductors :

These are obtained when an impurity atom to be added has fewer external electrons than the parent insulator atoms. Silicon or Germanium can also be doped with a group 13 element like boron, aluminium or gallium which contains only three valence electrons. The place where the fourth valence electron is missing is called electron hole or electron vacancy. This electron vacancy creates a positive hole in the valence band of silicon or germanium.

There are as many positive holes as there are impurity atoms. These positive holes occupy the level, called acceptor impurity level which exists close to the filled valence band of the acceptor crystal. Electrons from the filled valence band can thermally be promoted to this empty acceptor impurity level of positive holes.

Under the influence of an applied potential an electron from an adjacent atom moves into the hole and in turn is replaced by an electron from another atom. In this way the molecule move across the crystal in a direction which is opposite the direction of electron migration. The conduction takes place due to the migration of the positive holes. Hence the name p-type is given to these extrinsic semiconductors. (Fig. 1.25b)

Various combination of n-type and p-type semiconductors are used for making electronic components. Diode is a combination of n-type and p-type semiconductors and is used as rectifier. Transistors are made by placing one type of semiconductor between two other type, such as npn or pnp semiconductors. These are used to detect or amplify radio or audio signals. Solar cell is an efficient photodiode used for coversion of light energy into electrical energy.

Magnetic properties of solids :

Magnetic properties of solids generate due to the movement of electrons in an atom. An electron has two types of motion (i) revolution around the nucleus and (ii) spinning along its own axis. Since electron is a charged body its movement generates magnetic field. It behaves like a tiny bar magnet and possesses magnetic moment. The magnitude of the magnetic moment is very small and is measured in the unit called Bohr magneton. It is equal to 9.27×10^{-24} Am^2.

On the basis of the magnetic properties, substances can be classified into five categories : (a) paramagnetic (b) diamagnetic (c) ferromagnetic (d) anti-ferromagnetic and (e) ferrimagnetic.

(a) **Paramagnetism :** Paramagnetism is due to presence of unpaired electrons which are attracted by the magnetic field. They are magnetised in a magnetic field in the same direction and lose their magnetism in the absence of the field. Some examples of paramagnetic substances are O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} etc.

(b) **Diamagnetism :** Diamagnetism is due to the presence of all paired electrons in a substance. These substances are weakly repelled by magnetic field. H_2O, NaCl and benzene are some examples of such substances. They are weekly magnetised in a magnetic field in opposite direction. Pairing of electrons cancels their magnetic moment and they lose their magnetic character.

(c) **Ferromagnetism :** Ferromagnetic substances are strongly attracted by magnetic field. Besides strongly attracted these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together in small regions called domains which act as tiny magnets. In an unmagnetised ferromagnetic substance these domains remain randomly oriented and their magnetic moments are cancelled. When the substance is placed in a magnetic field all the domains get oriented along the direction of the magnetic field and a strong magnetic effect is produced. This order of the domains remains as such even after the magnetic field is withdrawn and the ferromagnetic substance becomes permanently magnetic. Iron, cobalt, nickel, gadolinium and CrO_2 are examples of ferromagnetic substances.

(d) **Anti-ferromagnetism :** Substances like MnO have their magnetic domain structure similar to ferromagnetic substances, but their domains are oppositely oriented and cancel out each others magnetic moment.

(e) **Ferrimagnetism :** Ferrimagnetism is observed when the magnetic moments of the domains in the substance are alligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances. Magnetite (Fe_3O_4) is such a substance. These substances lose ferrimagnetism on heating and become paramagnetic.

(a) Ferromagnetic ⟶ ↑ ↑ ↑ ↑ ↑ ↑
(b) Anti-ferromagnetic ⟶ ↑ ↓ ↑ ↓ ↑ ↓
(c) Ferrimagnetic ⟶ ↑ ↑ ↓ ↑ ↑ ↓

CHAPTER (1) AT A GLANCE

1. Solids are characterised by definite shape, definite volume and fixed melting point. Compressibility, rigidity, high mechanical strength are the properties of a solid.
2. Solids are classified as crystalline and amorphous solids.
3. Crystalline solids have definite geometry, sharp melting point and crystal symmetry. They are anisotropic an nature.
4. Amorphous solids have neither definite geometry nor sharp melting point. They do not possess symmetry and are isotropic in nature.
5. Crystalline solids are classified as ionic, covalent, molecular and metallic solids.
6. Ionic solids are hard, brittle, possess high melting point. Covalent solids are hard, nonvolatile, bad conductors of heat and electricity. Metallic solids are malleable and ductile, have metallic lusture and are good conductors. Molecular solids are soft and volatile and bad conductors.
7. A crystal lattice is regular arrangement of the constituent particles (atoms, ions or molecules) of a crystalline solid in three dimensional space.
8. The positions that are occupied by the atoms, ions or molecules in the crystal lattice are called lattice points or lattice sites.
9. Unit cell is the smallest repeating unit in crystal lattice which when repeated over and over again produces the complete crystal lattice.

10. Close packing in two dimensions in crystalline solids may be square close packing (scp) or hexagonal close packing (hcp).

11. In three dimension close packing ABABA ... arrangement is known as **Hexagonal Close Packing** (hcp), whereas ABCABCA... is known as **Cubic Close Packing** (ccp)

12. There are three common types of cubic systams. They are **Simple Cubic, Body Centred Cubic** (bcc) and **Face Centred Cubic** (fcc).

13. The no. of atoms per unit cell in simple cubic, body centred cubic and face centred cubic crystals are 1, 2 and 4 respectively.

14. The hollows or voids in the crystal are known as **interstitial voids.** These voids may be tetrahedral or octahedral.

15. The number of nearest neighbours with which a given sphere is in contact is known as the **co-ordination number.**

16. Radius ratio $= \frac{\text{Radius of cation}}{\text{Radius of anion}}$

17. On the basis of electrical conductivity, solids are divided into three categories :

    (i) Metals (ii) Insulators (iii) Semiconductors. Free electrons in the metals are responsible for conduction of electricity. Conductivity of semiconductors is intermediate between metals and insulators. Semiconductors are of two types : Intrinsic and Extrinsic. Extrinsic semiconductors are either n-type or p-type. Their combinations are used in making electronic components.

18. On the basis of magnetic properties, solids are classified into five categories : Paramagnetic, Diamagnetic, Ferromagnetic, Anti-ferromagnetic and Ferrimagnetic.

QUESTIONS

A. Very short answer type (One mark each) :

1. Diamond and graphite are ——————. (allotropes, isomorphous)
2. Diamond is —————— solid. (co-valent, ionic, molecular)
3. What is the number of atoms present per unit cell in a face centred cubic and a body centred cubic arrangement.
4. What is the radius ratio for an ion to occupy tetrahedral site.
5. Explain isotropy.
6. Define Anisotropy.
7. Define a unit cell of a crystal.
8. What are interstitials ?
9. What are the types of lattice imperfections found in crystals ?

10. What do you mean by crystal lattice ?
11. How many types of close packing are known in crystals ?
12. Define co-ordination number of a crystal.
13. Explain interstitial voids.
14. How many types of lattice points occur in diffrent cubic unit cells ?
15. What is the number of atoms in a body centred cubic unit cell of a monoatomic substance ?
16. What is a polycrystalline solid ?
17. What are crystallites ?
18. Calculate the number of atoms contained in body centred cubic cell.
19. Give two examples of ionic solids.
20. Diamond, Graphite and Quartz are ―――――― solids.
21. Define metallic solids.
22. What is meant by molecular solids ?
23. What is meant by radius ratio ?
24. Why carbon tetrachloride is immiscible in water ?
25. The solubiltiy of a solid ―――――― by increase of pressure. (increased, not changed, decreased)
26. What is the effect of pressure on the solubility of a solid ?
27. What happens to the solubility of calcium acetate if temperature increases
28. Give two examples of molecular solid.
29. Give an example of hcp and bcc crystals.
30. What is the commercial name of SiC ?
31. What are the coordination numbers of Cs^+ & Cl^- in CsCl lattice ?

B. Short Answer Type (Two marks each) :

1. Give two points of difference to distinguish between crystalline and amorphous solids.
2. If the radii of the cation and anion are 95 pm and 181 pm respectively, what would be coordination number and the type of crystal geometry?
3. Explain how hcp or ccp for the some element give the same identity?
4. What should be the ideal radius of the anion in a NaCl type of structure if the radius of the cation is r ?
5. Calculate the radius ratio $\left(\frac{r^+}{r^-}\right)$ and the condition number of Li^+ and F^- in LiF crystal from the given data $r_{Li^+} = 60$ pm and $r_{F^-} = 136$ pm.
6. Silver crystallises in fcc lattice with all the atoms at the lattice points. The length of the edge of the unit cell as determined by x-ray diffraction studies is found 408.6 pm. the density of silver is 10.5g cm^{-3}. Calculate the atomic mass of silver.

7. Explain the difference between conductor and insulator.
8. Explain the difference between conductor and semiconductor.
9. Explain the following :
   (i) Ferromagnetism
   (ii) Paramagnetism
   (iii) Antiferromagnetism
   (iv) Ferrimagnetism
10. What are interstitials and interstitial voids ?

C. Short answer type (Three marks each) :

1. Write four important characteristics of solids.
2. Write two points to distinguish between Crystalline and Amorphous solids.
3. What are chief characteristics of ionic crystals ?
4. Describe a few general characteristics of covalent crystals.
5. What are molecular crystals ? How many types of molecular crystals are known ?
6. Explain metallic crystals and their properties ?
7. What do you understand by the terms space lattice and unit cell. ?
8. Define co-ordination number in crystals. Is the co-ordination number of a sphere in ccp and hcp arrangement same or different ?
9. Discuss the following types of cubic structures :
   a. Simple cubic
   b. Body centred cubic.
   c. Face centred cubic.
10. How does radius ratio help in determining the structures of compounds ?
11. What are interstitial sites ? Discuss tetrahedral and octahedral interstitial sites in a closed packed arrangement.
12. Explain why diamond is hard while graphite is soft.

D. Long answer type (Seven marks each) :

1. Describe various characteristics of solids.
2. What do you understand by close packing of spheres ? Discuss briefly hexagonal close packing and cubic close packing of spheres.
3. Describe fcc, bcc and hcp crystals of simple ionic compounds.
4. Discuss the characteristics of solids. Give the classification of solids into ionic, covalent, molecular and metallic solids.
5. Explain the crystal defects and their origin in the crystal.

E. Multiple choice answer type (One mark each) :

1. The number of atoms in bcc arrangement is

   (a) 1 (b) 4 (c) 2 (d) 6

2. In hcp mode of stacking, a sphere has co-ordination number.

   (a) 4 (b) 6 (c) 8 (d) 12

3. If edge of a bcc crystal of an element is 'a' cm, M is the atomic mass and 'N' is the Avogadro number, then density of the crystal is

   (a) $\frac{4M}{a^3N}$ (b) $\frac{2N}{Ma^3}$ (c) $\frac{2M}{Na^3}$ (d) $\frac{Ma^3}{2N}$

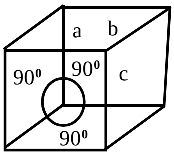
4. The unit cell with crystallographic dimensions a = b F c, $\alpha = \beta = \gamma = 90^0$ is

   (a) cubic (b) tetragonal (c) monoclinic (d) hexagonal

5. The structure of sodium chloride is

   (a) Hexagonal (b) Octahedral (c) Rhombohedral (d) Tetrahedral.

6. The unit cell with the structure below refers to ————— crystal system.



   (a) cubic, (b) orthorhombic (c) tetragonal (d) trigonal

7. The arrangement ABC ABC...... is referred to as

   (a) Octahedral close packing (b) Hexagonal close packing

   (c) Tetrahedral close packing (d) Cubic close packing

8. Which among the following will show anisotropy ?

   (a) glass (b) barium chloride (c) wood (d) paper.

9. For an octahedral arrangement the lowest radius ratio limit is

   (a) 0.155 (b) 0.732 (c) 0.414 (d) 0.225

10. The number of octahedral voids in a unit cell of a cubic close packed structure is

    (a) 2 (b) 3 (c) 4 (d) 6

ANSWER TO MULTIPLE CHOICE TYPE QUESTION

1. c
2. d
3. c
4. b
5. b
6. a
7. d
8. b
9. c
10. c

* * *

UNIT - II

CHAPTER - 2

SOLUTIONS

A solution is a homogeneous mixture of two or more substances whose composition can be varied within certain limits. Depending upon the total components present in the solution, it is called binary (two components), ternary (three components), quaternary solution (four components) etc.

2.1 CHARACTERISTICS OF A SOLUTION :

1. It has no surface of separation. As a result the various constituents in it can not be distinguished.
2. The constituents can neither be separated by filtration nor do they settle down under the effect of gravity.
3. The constituents in it can be obtained by processes like crystallisation, distillation, evaporation etc.
4. The various constituents in a mixture show the properties to prove their presence.

Example :

When sodium chloride dissolves in water, the solution will show the properties of both NaCl and water.

Solute, Solvent and Solution :

Solute : It is a substance that dissolves in a solvent.

Solvent : It is a substance in which dissolution takes place.

Therefore, **solute + solvent = solution.**

Further, the components of a binary solution are generally referred to as solute and the solvent.

Types of solutions :

Depending upon the physical states of the solute and the solvent the solutions can be classified into the following nine types.

Table 2.1 Types of Solutions

Solvent	Solute	Example
Gas	Gas	Mixture of gases, air
Gas	Liquid	Water vapour in air (humidity)
Gas	Solid	Sublimation of a solid into gas, dust particles in air.
Liquid	gas	CO_2gas dissolved in air
Liquid	Liquid	Mixture of miscible liquids (alcohol in water)
Liquid	Solid	Salt in water, sugar in water
Solid	Gas	Adsorption of gases over metal (H_2 over palladium)
Solid	liquid	Mecury in copper
Solid	Solid	Alloys (copper in gold), zinc in copper.

The solutions in which water is a solvent are called **aqueous solutions** while those in which water is not the solvent are called **non-aqueous solutions**.

Examples of non-aqueous solvents are ether, benzene, carbon tetrachloride etc.

Unsaturated, Saturated and Supersaturated solutions :

When the quantity of the solute is very small as compared to the solvent, it is called **dilute** solution. It can dissolve more of the solute at that temperature. Such solutions are called **unsaturated** solutions.

Unsaturated solution :

The solution in which more quantity of the solute can dissolve at that temperature is called **unsaturated solution**.

When more solute is added it will also dissolve. If the addition of solute is continued, a stage will reach, when the solvent refuses to dissolve the solute at that temprature. That stage of the solution is termed as **saturated solution**.

Saturated solution :

The solution in which no more quantity of the solute can dissolve at room temprature is called as **saturated solution**.

When a saturated solution is heated slowly, the solvent starts evaporating from it. In other words, the quantity of solvent starts decreasing while that of the solute remains the same. After sometime, stop heating the solution. At this stage, a solution is obtained which contains more solute than needed for preparing a saturated solution at that temperature. This solution is called **super saturated solutions**.

2.2 SOLUBILITY :

Definition : The weight in grams of a substance (solute) which when dissolved in 100 gms of a solvent forms a saturated solution at a particular temperature, is called **solubility** of the substance (solute) at that temperature.

$$\text{Hence, solubility} = 100 \times \frac{\text{wt (in grams) of solute}}{\text{wt (in grams) of solvent}}$$

Let 'm' grams of a solid be present in M grams of its saturated solution at t^0C. Then taking 'X' as the solubility of the solid at t^0C, we find that

$$X = \frac{100m}{(M - m)}$$

Solubility Rules :

It is a fact that polar solids are soluble in polar solvents while non-polar solids are soluble in non-polar solvents. Further, the following generalisations are also true.

(i) An ionic solid is soluble in polar solvent :

Ionic solids contain oppositely charged ions and held by electrostatic force of attraction in the crystal. Example : In NaCl, Na^+ and Cl^- are present. When such substance is added to water, attraction of water molecules for the ions is greater than the electrostatic attraction.

(ii) Ionic solids are insoluble in non-polar solvents :

In non-polar solvents like CCl_4, benzene etc, the attractive force between the molecules is very weak. Hence molecules of non-polar solvents can not pull an ion form the ionic solid. Thus ionic solids like NaCl, KCl etc are not soluble in non-polar solvents.

(iii) Non-polar covalent solids are soluble in non-polar solvents :

The molcules of both non-polar covalent solutes and solvents are held by weak attractive forces. As the attractive forces between the molecules of non-polar solutes and solvents are of the same order, covalent solids are readily soluble in non-polar solvents. Iodine, wax etc are freely soluble in benzene, carbon tetrachloride etc.

Determination of solubility of a solid like common salt in water at the temperature of the laboratory :

It involves the following steps.

(a) Preparation of a saturated solution :

Take about 100 ml of water in a beaker and warming a little, go on adding the salt with constant stirring till some of the salt remains undissolved and settle down without going into solution. Cool the saturated solution thus prepared to room temperature. Filter it and note the temperature of the filtrate (t^0C).

(b) Estimation of the masses of the salt and solvent :

Take a clear and dry procelain basin and weigh it accurately. Take about 10 ml of the solution in it by a pipette and weigh again. Then evaporate the solution on a water bath carefully. When the salt is left in the basin, dry the basin with the residue in an air oven. Cool it in a desiccator and weigh again. Repeat the process of heating cooling and weighing till the final weight is constant.

(c) Calculation :

Room temperature = t^0C

Mass of the empty porcelain basin = W_1 gms.
Mass of the basin + saturated solution = W_2 gms.
Mass of the basin + residue = W_3 gms.
∴ Mass of residue = $(W_3 - W_1)$ gms.
Mass of water = $(W_2 - W_3)$ gms.

∴ Solubility = $\frac{(W_3 - W_1)}{(W_2 - W_3)} \times 100$ at t^0C.

Problem :

28 gms of a saturated solution of a substance contain 3 gms of the solute at 300K. Calculate the solubility of the solute at the temperature.

Solution : Mass of solution = 28 gms.
Mass of solute = 3 gms.
∴ Mass of solvent = (28–3) = 25 gms.
∴ Solubility = $\frac{3}{25} \times 100 = 12$
∴ Solubility of the solute at 300K = 12

Effect of temperature and pressure on solubility :

(a) Effect of temperature :

When the temperature of a saturated solution is raised, it is observed that more solute can be dissolved in the same solution. Solute separates out from it on cooling. Thus, it can be said that solubility of a substance depends on the temperature. (Fig. 2.1)

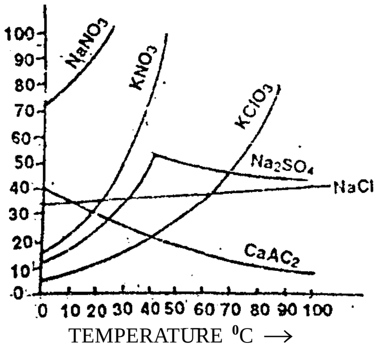


Fig. 2.1 Solubility versus Temperature

Again solubility of a substance may increase or decrease with temperature depending on the heat of solution. If the heat of solution is negative (m H = – ve) or heat is evolved, the solubility decreases with increase in temperature. Similarly, if m H is +ve i.e. heat is absorbed in solution, then the solubility increases with increase in temperature.

Salts like KNO_3, KCl, NH_4Cl, NH_4NO_3 etc show increase in solubility with increase in temperature. In those cases, m H is +ve. A few substances like Na_2SO_4, calcium acetate Ca $(CH_3COO)_2$ etc dissolve in water with evolution of heat i.e. m H is –ve. In all those cases, the solubility decreases with the increase in temperature.

(b) Effect of pressure :

It is known that if the solute is a solid or a liquid, pressure has no effect on solubility. But if the solute is a gas, the pressure influences solubility according to **Henry's law**. The law states that **the amount of gas dissolved in a given volume of liquid at constant temperature is directly proportional to the pressure of the gas.** The law is strictly applicable to slightly soluble gases at low pressure but for highly soluble gases such as ammonia, HCl etc, the law does not hold good.

2.3 CONCENTRATION OF A SOLUTION :

The strength of a solution also called as the **concentration** can be defined as the *quantity of the solute in a given quantity of the solvent or solution.*

Standard solution is a solution whose strength is known. Thus, 8 g of NaOH present in 500 ml of the solution is a standard solution.

There are various ways in which the concentration of a solution can be expressed. The common types are :

1. Grams per litre
2. Normality **(N)**
3. Molarity **(M)**
4. Molality **(m)**
5. Mole fraction **(X)**
6. Per cent solution.
7. Formality **(F)**

1. Grams per litre : Here, the strength of the solution is expressed as the amount of solute in grams present in a litre of the solution.

If 4.9 g of H_2SO_4 is present in one litre of the solution, then the strength is written as 4.9 g/litre. Similarly, if 1g. of NaOH is present in 250 ml of the solution, then the strength is written as 4g/litre. (1g/250 ml = 4g / litre).

Thus, if W g of the solute is present in V ml of the solution, the strength is written as $\left(\frac{W}{V} x 1000\right)$ g per litre.

2. **Normal solution and normality :** A **normal** solution of a substance (acid, base or salt) is one which contains one gram - equivalent of the substance in one litre of the solution. Thus, **Normality** *is the number of gram - equivalent of the solute present in a litre of the solution.* It is denoted by N. If one gram equivalent of the solute is present in one litre of the solution, it is called (N) solution. Thus, 1000 ml of (N) H_2SO_4 shall contain 49.g. of H_2SO_4, 1000 ml of (N) Na_2CO_3 shall contain 53g of Na_2CO_3 and 1000 ml of (N) $BaCl_2 . 2H_2O$ shall contain 122 g of $BaCl_2 . 2H_2O$.

Sometimes, a normal solution becomes stronger for analytical purpose and diluted solutions like one-half (semi), one - tenth (deci) or one - hundredth (centi) of a normal solution are used.

Thus, 1000 ml. of (N) H_2SO_4 (one normal) solution shall contain 49g of H_2SO_4

1000 ml of $(\frac{N}{2})$ H_2SO_4 (semi - normal) solution shall contain $\frac{49}{2}$ = 24.5g of H_2SO_4

1000 ml of $\frac{N}{10}$ H_2SO_4 (deci - normal) solution shall contain $\frac{49}{10}$ = 4.9 g of H_2SO_4.

1000 ml of $(\frac{N}{100})$ H_2SO_4 (centi - normal) solution shall contain $\frac{49}{100}$ = 0.49 g of H_2SO_4.

and 1000 ml of 2(N) H_2SO_4 shall contain 2 x 49 = 98g of H_2SO_4 .

Therefore, the '**normality**' or '**normality factor**' of the above solution will be 1, 1/2, 1/10, 1/100 and 2 respectively. Hence, if W grams of the solute with equivalent mass Z are present in Vml of the solution, then

$$\text{Normality factor} = \frac{W}{Z} \times \frac{1000}{V} = \frac{\text{Grams per litre}}{\text{Equivalent mass of the solute}} .$$

Therefore, **Grams/litre = Normality x Equivalent mass.**

It will be seen that 1000ml of (N) H_2SO_4 will contain 49 g of H_2SO_4 and 500ml of a 2(N) H_2SO_4 will contain 49g of H_2SO_4.Therefore, both the solutions are equivalent. This is written as

1000 ml of (N) $H_2SO_4 \equiv$ 500 ml of 2(N) H_2SO_4.

Similarly. 250 ml of (N) $H_2SO_4 \equiv$ 1000 ml of (N/4) H_2SO_4.

We find that

250 ml. of (N) H_2SO_4 $\equiv$ 50 ml of 5(N)H_2SO_4.
$\equiv$ 25 ml of 10(N)H_2SO_4.
$\equiv$ 500 ml of (N/2)H_2SO_4.
$\equiv$ 1000 ml of (N/4)H_2SO_4.

In general. V ml of x(N) $H_2SO_4 \equiv$ (V x x) ml of (N) H_2SO_4.

Problem 1. How much NaOH is present in 100 ml of (N) solution ? (CHSE, 1990A)

Solution : Equivalent mass of NaOH = 40

1000 ml of (N) NaOH will contain 40g of NaOH

100 ml of (N) NaOH will contain $\frac{40}{1000}$ x 100 = 4g of NaOH.

Problem 2. Find out the weight of NaOH required to prepare 2 litres of N/10 solution.

Solution : Equivalent mass of NaOH = 40

1 litre of (N) solution of NaOH will contain 40 g of NaOH.

2 litres of (N/10) solution will contain $\frac{40 \text{ x } 2}{10}$ = 8 g of NaOH.

Hence, 8g of NaOH will be required to prepare 2 litre of (N/10) solution.

Problem 3. 12 g of H_2SO_4 is dissolved in water to make 1200 ml of solution. Find out the normality of the solution.

Solution : Equivalent mass of H_2SO_4 = 49

49 g of H_2SO_4 in 1000 ml will give (N) solution.

12 g of H_2SO_4 in 1000 ml will give $\frac{12}{49}$ (N) solution.

12 g of H_2SO_4 in 1200 ml will give $\frac{12 \text{ x } 1000}{49 \text{ x} 1200}$ = 0.204 (N) solution.

Hence, the normality of the solution is 0.204.

3. Molar solution and Molarity : A **molar** solution is one which contains one gram mole of the solute in a litre of the solution. Thus, **Molarity (M)** *is the number of moles of the solute present per litre of the solution.*

If Wg of the solute having the molecular mass m is present in V ml of the solution, then

$$\text{Molarity } \mathbf{(M)} = \frac{\text{No of moles of the solute}}{\text{Volume of the Solution in ml}} \times 1000$$

$$= \frac{W}{m} \times \frac{1}{V} \times 1000$$

(Mass of the solute / mol. mass of the solute gives the number of moles of solute)

$$\text{or, Molarity } \mathbf{(M)} = \frac{\text{Grams per litre}}{\text{Molecular mass of the solute}}.$$

Molarity is extensively followed in practice since it is a convenient measure of concentration. Molarity of the solution changes with temperature because the volume of the solution expands or contracts with the increase or decrease in temperature.

NOTE : Grams/litre = Normality × Equivalent mass = Molarity × Molecular mass.

Hence, **Normality/Molarity = Molecular mass/Equivalent mass.**

Problem 1. 4g of NaOH is present in 200 ml of a solution. Find out the molarity.

Solution **:** Molecular mass of NaOH = 40.

40 g of NaOH in 1000 ml of the solution give 1M solution.

4 g of NaOH in 200 ml will give ($\frac{1}{40} \times \frac{4}{200} \times 1000$) M = 0.5 (M) solution.

Hence, molarity of the solution is 0.5.

Problem 2. How many grams of Na_2CO_3 is required to make 600 ml. of 0.04 (M) solution ?

Solution **:** Molecular mass of Na_2CO_3 = 106

1000 ml of 1 (M) Na_2CO_3 will contain 106 g of Na_2CO_3

600 ml of 0.04 (M) Na_2CO_3 will contain $\frac{106 \times 600 \times 0.04}{1000}$ g = 2. 544 g of Na_2CO_3.

Hence. 2.544 g of Na_2CO_3 is required.

Problem 3. What will be the molarity of sulphuric acid if 0.8 g of sulphur trioxide is dissolved in 100 ml of water ? (At mass of S = 32)

Solution : Mol. mass of $SO_3 = 32 + (3 \times 16) = 80$

0.8 g of SO_3 will contain $\frac{0.8}{80}$ = 0.01 mole of SO_3

$SO_3 + H_2O \rightarrow H_2SO_4$

1 mole of SO_3 = 1 mole of H_2SO_4

1 mole of SO_3 in 1000 ml of water will produce 1(M) H_2SO_4

0.01 mole of SO_3 in 100 ml of water will produce 0.1 (M) H_2SO_4

Hence, molarity of sulphuric acid is 0.1.

Problem 4. Calculate the molarity of water in pure water. (IIT, 1976 A)

Solution : Molarity is the number of moles of H_2O per litre of pure water. Since one mole of H_2O = 18g and 1 litre of pure water ≈ 1000 g (Roughly 1 ml = 1g)

Hence, molarity of H_2O in pure water = $\frac{1000}{18}$ = 55.55.

4. **Molal solution and Molality :** A **molal** solution is one which contains one gram mole of the solute in 1000 g of the solvent. Thus, **molality (m)** is *the number of moles of the solute in 1000 g of the solvent.*

If W_1 g of the solute having molecular mass M_1 is present in W_2 g of the solvent, then

$$\text{Molality } \mathbf{(m)} = \frac{W_1}{M_1} \times \frac{1}{W_2} \times 1000 = \frac{1000\,W_1}{M_1 \times W_2}$$

The molality of the solution does not change with the change in temperature of the solution.

Problem 1 . Calculate the molality of sodium carbonate solution which is formed by dissolving 1.325 g of it in 250 g of water.

Solution : Molecular mass of Na_2CO_3 = 106

106 g of Na_2CO_3 in 1000 g of water gives 1 m solution

1.325 g of Na_2CO_3 in 250 g of water will give $\frac{1.325}{106} \times \frac{1000}{250}$ (m) = 0.05 (m) solution.

Hence, molality of the solution = 0.05

5. **Molefraction : Molefraction** *of the solute (X_{solute}) or solvent ($X_{solvent}$) is the ratio of the number of moles of the solute or solvent to the total number of moles of solute and solvent in the solution.*

Thus.

$$X_{\text{solute}} = \text{molefraction of the solute} = \frac{\text{no. of moles of the solute}}{\text{no. of moles of solute + no. of moles of solvent}}$$

$$\text{and } X_{\text{solvent}} = \text{molefraction of the solvent} = \frac{\text{no. of moles of the solvent}}{\text{no. of moles of solute + no. of moles of solvent}}$$

If W_1 g of solute of molecular mass M_1 is present in W_2 g of solvent having molecular mass M_2 then molefraction of the solute,

$$X_{\text{solute}} = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2} = \frac{W_1/M_1}{\frac{W_1M_2 + W_2M_1}{M_1M_2}} = \frac{W_1}{M_1} \times \frac{M_1M_2}{W_1M_2 + W_2M_1} = \frac{W_1M_2}{W_1M_2 + W_2M_1}$$

Smilarly, the molefraction of the solvent

$$X_{\text{solvent}} = \frac{W_2/M_2}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} = \frac{W_2M_1}{W_1M_2 + W_2M_1}$$

[Note - Molefraction of solute + Molefraction of solvent = 1]

Problem 1 : Calculate the molefraction of NaOH is an aq. NaOH solution which contains 2.0 g of it in 150 ml of solution. (Density of the solution = 1.25 g/ml)

Solution Mass of NaOH = 2 g

Molecular mass of NaOH = 40

$\therefore$ No. of mole of NaOH = $\frac{2}{40}$ = 0.05

Volume of the solution = 150 ml. and

Density of the solution = 1.25 g / ml.

$\therefore$ Mass of the solution = Volume x density = (150 x 1.25)g = 187.5 g

Mass of solvent (water) = 187.5 g – 2 g = 185.5 g

$\therefore$ No. of moles of solvent = $\frac{185.5\text{g}}{18\text{g}}$ = 10.3

$$\text{Molefraction of NaOH} = \frac{\text{no.of moles of NaOH}}{\text{no.of moles of NaOH + no.of moles of } H_2O}$$

$$= \frac{0.05}{0.05 + 10.3} = 4.83 \times 10^{-3}.$$

6. **Per cent solution :**

This way of expressing concentration can be of four types :

(a) *Mass to mass percentage :* The number of grams of solute in 100 grams of the solution determines the percentage of a solution (w/w). = $\frac{\text{mass of solute in g}}{\text{Mass of solution in g}} \times 100.$

(b) *Mass to volume percentage :-* The number of grams of solute in 100 ml of the solution determines the percentage of a solution (w/v) = $\frac{\text{mass of solute in g}}{\text{volume of solution in ml}} \times 100.$

(c) *Volume to volume percentage (for liquids) : -* The number of ml. of solute in 100 ml of the solution determines the percentage of a solution (v/v) = $\frac{\text{volume of solute in ml}}{\text{volume of solution in ml}} \times 100.$

(d) *Volume to mass percentage :-* The number of ml of solute in 100 g of the solution determines the percentage of a solution (v/w) = $\frac{\text{volume of solute in ml}}{\text{mass of solution in g}} \times 100$

Thus, 5% solution (w/w) of NaOH will mean 5 g of NaOH in 100 g of NaOH solution. Similarly, 80% H_2SO_4 solution (v/v) will mean 80 ml of H_2SO_4 in 100 ml of H_2SO_4 solution and so on.

7. Formality :

Formality **(F)** is defined as the number of formula mass of the solute per litre of the solution.

$F = \frac{W \times 1000}{M \times V}$ where W = mass of solute in g.

M = Formula mass of solute in g.

V = Volume of solution in ml.

Thus, 5.85g of NaCl in 500 ml of the solution will give $\frac{5.85 \times 1000}{58.5 \times 500}$ = 0.2 F solution of NaCl

(formula mass of NaCl is 58.5)

In most of the cases *formality* is same as *molarity*.

8. Parts per million : When a solute is present in a very small amount (trace amount) in a solution, its concentration is expressed in terms of **parts per million** (ppm). It is defined as the number of parts by mass of the solute present in one million (10^6) parts by mass of the solution. Thus,

$$\text{ppm} = \frac{\text{mass of the solute}}{\text{mass of solution}} \times 10^6$$

Dissolved oxygen in sea water is 5.8 ppm, which means that 5.8g of oxygen is dissolved in 10^6 g of sea water.

Atmospheric pollution in cities is expressed in terms of ppm by volume. It refers to the volume of pollutant in 10^6 units of volume. 15 ppm SO_2 in air means 15mL of SO_2 is present in 10^6 mL of air.

Interrelations between various concentration terms

We have already found that

Grams per litre = Normality × Equivalent mass of solute

= Molarity × Molecular mass of solute

$$\frac{\text{Nomality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Relationship between Molality and Molarity

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{Vol. of solution (in L)}}$$

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{moles of solute}}{\text{Vol. of solution (in L)}} \times \frac{\text{mass of solvent (in kg)}}{\text{moles of solute}}$$

$$= \frac{\text{mass of solvent (in kg)}}{\text{Vol. of solution (in L)}} = \frac{\text{mass of solvent (in g)}}{\text{Vol. of solution (in mL)}} = \frac{W_2}{V}$$

where W_2 = mass of solvent in grams and

V = volume of solution in mL.

If the density of the solution is d gmL^{-1}

Mass of solution = d × V

Mass of solute = No. of moles ×mol. mass of solute = $n \times M_1$

Mass of the solvent = W_2 = mass of solution – mass of solute

= $d \times v - n\, M_1$

Thus, $-\frac{\text{Molarity}}{\text{Molality}} = \frac{\mathbf{M}}{\mathbf{m}} = \frac{V \times d \quad nM_1}{V}$

Hence, Molality (**m**) = $\frac{\text{Molarity} \times V}{V \times d \quad nM_1} = \frac{\text{molarity}}{d \quad \frac{n}{V} M_1} = \frac{\text{molarity}}{d \quad \text{molarity} \times M_1}$

Relationship between molefraction and molality

Suppose X_A = mole fraction of the solute and

X_B = mole fraction of the solvent.

$$X_A = \frac{\text{No. of moles of solute}}{\text{No. of moles of solute} + \text{No. of moles of solvent}}$$

and $X_B = \frac{\text{No. of moles of solvent}}{\text{No. of moles of solute} + \text{No. of moles of solvent}}$

$$\frac{X_A}{X_B} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

If W_1 = mass of solute with molecular mass M_1 and

W_2 = mass of solvent with molecular mass M_2

$$\frac{X_A}{X_B} = \frac{W_1 \times M_2}{W_2 \times M_1}$$

$$\frac{X_A \times 1000}{X_B \times M_2} = \frac{W_1 \times 1000}{W_2 \times M_1} = \mathbf{m}$$

or, $$\frac{X_A \times 1000}{\left(1 \quad X_A\right) \times M_2} = \mathbf{m}$$

Miscellaneous problems involving determination of concentration :

Problem 1 : What is the molarity and molality of a 13% solution (by mass) of H_2SO_4 ? Its density is 1.02 g / ml. To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 (N) solution ? (I.I.T., Adm. Test, 1978 B)

Solution : 13% H_2SO_4 (by mass) means

Mass of H_2SO_4 = 13 g

Mass of solution = 100 g

Molecular mass of H_2SO_4 = 98

Volume of the solution = $\frac{\text{mass}}{\text{density}} = \frac{100\text{g}}{1.02\text{g / ml}}$ = 98.04 ml.

Thus, 98.04 ml of H_2SO_4 contain 13 g of H_2SO_4

$\therefore$ 1000 ml of H_2SO_4 will contain $\frac{13 \times 1000}{98.04}$ g of H_2SO_4 =132.6 g of H_2SO_4

132.6 g H_2SO_4 = $\frac{132.6}{98}$ moles = 1.35 moles of H_2SO_4.

$\therefore$ 1000 ml of H_2SO_4 will contain 1.35 moles of H_2SO_4.

Hence. molarity = 1.35

Mass of 1000 ml of H_2SO_4 soln.= 1000 × 1.02 = 1020 g

Mass of H_2SO_4 in 1000 ml of H_2SO_4 soln = 132.6 g

$\therefore$ Mass of solvent = (1020 – 132.6) g = 887.4 g

887.4 g of solvent contain 132.6g of H_2SO_4 or 1.35 moles of H_2SO_4 .

$\therefore$ 1000 g of solvent will contain $\frac{1.35 \times 1000}{887.4}$ = 1.52 moles of H_2SO_4 .

Hence, molality = 1.52

Equivalent mass × Normality = g/litre

or, Normality = $\frac{\text{g / litre}}{\text{Equivalent mass}} = \frac{132.6}{49}$ = 2.71

Hence, Normality of the solution = 2.71.

100 ml of 2.71(N) will be diluted to give 1.5(N) H_2SO_4.

Suppose V ml = Volume of the diluted acid.

Then, 100ml × 2.71 (N) = V ml × 1.5(N)

or, V = $\frac{100\text{ml} \times 2.71(\text{N})}{1.5(\text{N})}$ = 180.67 ml.

Therefore, 100 ml of this acid must be diluted to 180.67 ml or 180.7ml.

Problem 2 : Calculate the molefraction of a 90% ethyl alcohol (by mass) solution.

Solution : 100 g of ethyl alcohol solution will contain 90 g of ethyl alcohol and 10g of water.

Mol. mass of ethyl alcohol (C_2H_5OH) = 24 + 6 + 16 = 46

and of water (H_2O) = 2 + 16 = 18.

∴ No of moles of C_2H_5OH per 100 g of solution = $\frac{90}{46}$ =1.96

and No. of moles of H_2O per 100 g soln = $\frac{10}{18}$ = 0.56

Hence. mole fraction of ethyl alcohol = $\frac{1.96}{1.96 + 0.56}$ = 0.78

and mole fraction of water = $\frac{0.56}{1.96 + 0.56}$ = 0.22

Problem 3 : Calculate the normality of the resulting solution obtained by mixing 10cc of N/2 HCl with 30cc of N/10 H_2SO_4 and 40cc of N/20 HNO_3.

Solution : Total volume of the acid = (10 + 30 + 40)cc = 80 cc.

10cc of N/2 HCl ≡ 5cc of (N) HCl

30cc of N/10 H_2SO_4 ≡ 3cc of (N) H_2SO_4

and 40cc of N/20 HNO_3 ≡ 2cc of (N) HNO_3

Suppose the normality of the resulting solution = x

∴ 80cc of x (N) ≡ 10 cc of (N) acids

or, x = $\frac{10}{80}$ = 0.125

Hence, the normality of the solution = 0.125

Alternately, N = $\frac{\Sigma VS}{\text{Total volume}} = \frac{10}{80}$ = 0.125

Hence, the strength of the resulting acid solution is 0.125 (N)

2.4 SOLUBILITY OF GASES IN LIQUIDS :

Most of the gases are soluble in water as well as in other liquids to a more or less extent. The solubility of a gas in liquids depends upon

(i) Nature of the gas
(ii) Nature of the solvent
(iii) Temperature of the gas- liquid system
(iv) Pressure of the gas

Generally, the gases which are easily liquified, are more soluble in common solvents. Thus CO_2 is more soluble in water or in any other solvent than hydrogen or oxygen. The gases which are capable of forming ions in aqueous solutions are more soluble in water than in any other solvent. Gases like HCl and NH_3 are highly soluble in water, but not in organic solvents in which they do not ionise.

The solubility of most of the gases decreases with increase in temperature at constant pressure. When the temperature increases gas is expelled. However, some gaes are more soluble at higher temperature.

The solubility of a gas in liquid is considerably influenced by **presure**. William Henry, in 1805 found that at a given temperature the solubility of a gas increases directly as the pressure. This is known as Henry's law, which states that **the mass of a gas dissolved by a given volume of liquid at constant temperature, is proportional to the pressure of the gas**.

Therefore, if m be the mass of gas dissolved per unit volume of the liquid and P is the pressure of the gas in equilibrium with the solution, then according to Henry's law.

$m \alpha P$ at constant temperature.

or, $m = kP$ where, k is the proportionality constant.

or, $\frac{m}{P} = k$

It has been found that most of the gases obey Henry's law provided

(i) the pressure is not too high
(ii) the temperature is not too low
(iii) the gas is not highly soluble and does not chemically combine with the solvent.
(iv) the gas does not dissociate.

Henry's law may also be stated in terms of the volume of gas dissolved instead of mass. Suppose m grams of a gas occupying a volume VmL is dissolved in a given volume of the solvent at an equilibrium pressure of the gas (P). Keeping the temperature constant, if the pressure is increased to 2P, the mass of gas dissolved in the same volume of solvent will be 2m, which corresponds to a volume 2V at pressure P. But the new volume of the gas passing into the solution at pressure 2P will be $\frac{1}{2} \times 2V = V$, since according to Boyle's law, volume varies inversely as the pressure. Thus the volume of the gas dissolved will remain same as before inspite of increase in pressure. Henry's law, therefore, may also be stated as **the volume of gas dissolved in a solvent at a given temperature is independent of the pressure**.

2.5 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.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

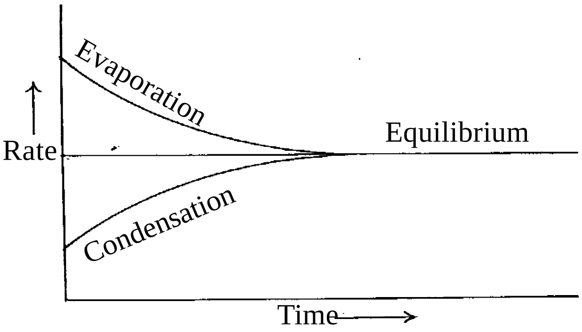


Fig. 2.2 Equilibrium curve for evaporation and condensation

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.

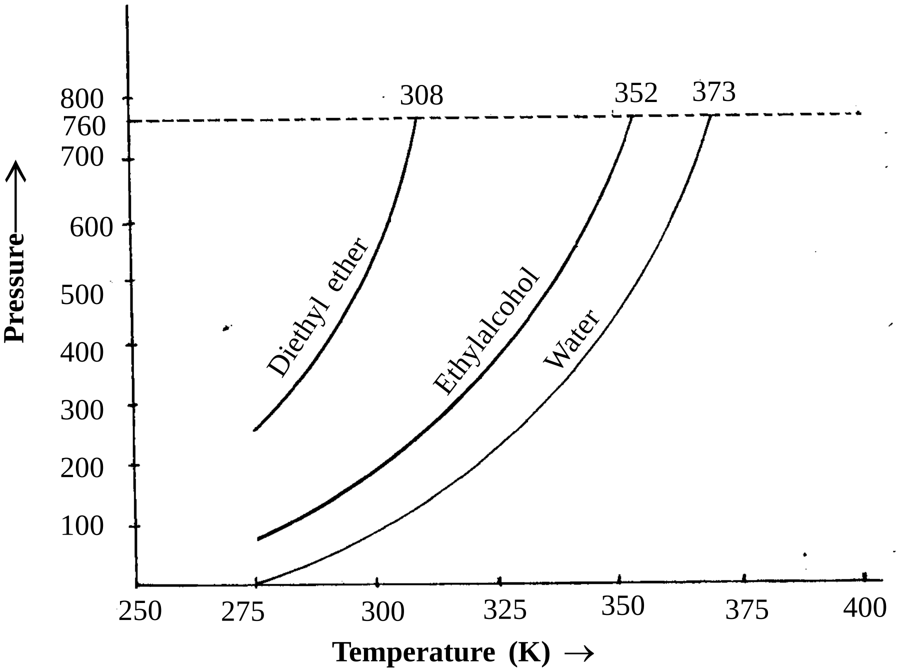


Fig. 2.3 Plot showing variation of vapour pressure of liquids with temperature

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.

2.6 IDEAL AND NON-IDEAL SOLUTIONS :

Ideal solutions

An ideal solution of component A and B means that the force of attraction between A and B molecules (i.e. A – B molecular interaction forces) will be the same as those for the A – A or B – B molecules. For such a situation to occur, the component should have identical structure and polarity. As there is no change in interaction forces between two components when they are mixed to form ideal solution, heat change on mixing (ΔH_{mixing}) will be zero. Moreover, in such cases, the volume of the solution is the sum of the volumes of the components before mixing. Thus volume change on mixing (ΔV_{mixing}) is zero. To sum up, the conditions for an ideal solution formation are

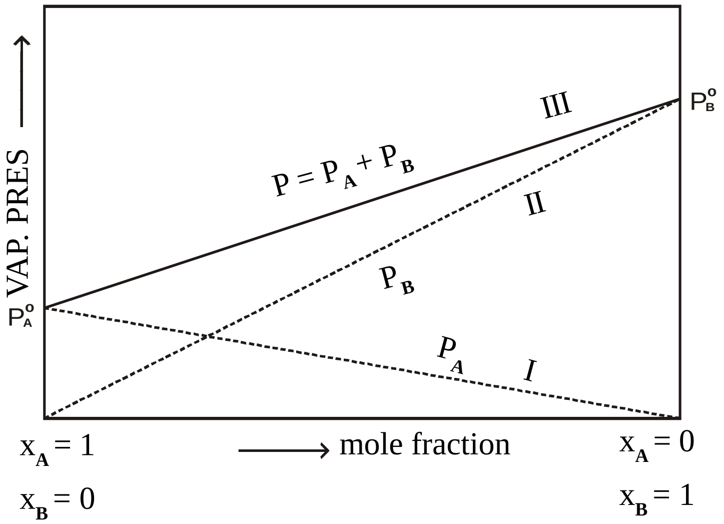


Fig. 2.4 Vapour pressure versus mole fraction curve of an ideal solution

(i) Raoult's law should be obeyed.

(ii) ΔH_{mixing} should be zero

(iii) ΔV_{mixing} should be zero

Examples of ideal solution are

(i) Ethyl chloride + Ethyl bromide

(ii) Benzene + Toluene

(iii) Chloro benzene + Bromobenzene

(iv) n-Hexane + n - Heptane

According to Raoult's law, a plot of P_A or P_B against x_A and x_B for a solution should give a straight line I & II (Fig. 2.4) passing through the points P_A^O or P_B^O when x_A and x_B equals unity. The total vapour pressure P exerted by the solution as a whole at any composition is given by the sum $P_A + P_B$, indicated by the line III in Fig. 2.4 (as required by Dalton's law of partial pressure), joining points P_A^O & P_B^O

Vapour pressure at any point on the graph is the same as calculated from Raoult's law,

$$P_A = x_A . P_A^O$$

and $$P_B = x_B . P_B^O$$

Non-ideal solutions

It has been found that most of the pairs of miscible liquids form non-ideal solutions. Non-ideal solutions (i) do not obey Raoult's law (ii) ΔV_{mixing} is not equal to zero (iii) ΔV_{mixing} is not equal to zero. There is difference in the structures and polarity of the molecules of the components. Depending upon the nature of solute and solvent, non-ideal solutions may exhibit positive or negative deviations from the ideal behaviour.

(a) Non-ideal solutions exhibiting positive deviation

Let us consider a liquid solute and a liquid solvent constituting a solution where the solute-solvent interactions are weaker than the solute-solute or solvent-solvent interactions. In such a solution, the total vapour pressure of the solution is greater than that corresponding to an ideal solution of the same composition. The boiling points of such solutions are relatively lowered. Such behaviour of solutions is said to have a positive deviation from Raoult's law (Fig. 2.5) For such solutions

$P_A > P_A^O x_A$ and $P_B > P_B^O x_B$ and $\Delta V_{\textbf{mixing}} > 0$ and

heat is absorbed which means $\Delta H_{\textbf{mixing}} > 0$

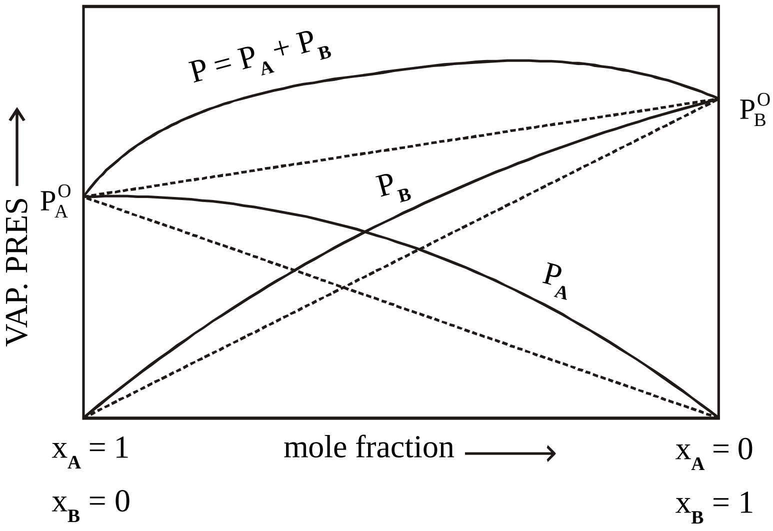


Fig. 2.5 Vapour Pressure versus mole fraction curve for non-ideal solution exhibiting positive deviation

In Fig. 2.5 the thick lines show actual behaviour whereas the dotted lines show the ideal behaviour. The total vapour pressure of such a solution will be the highest and the boiling point will be the lowest for one of the intermediate compositions. This solution has now the property of boiling at a constant temperature without any change in composition. Liquid mixtures which can distil without any change in composition are termed as **azeotropes** or **azeotropic mixtures**. In case of positive deviations, **minimum boiling point** azeotropes are obtained. A few examples of solutions showing positive deviations are

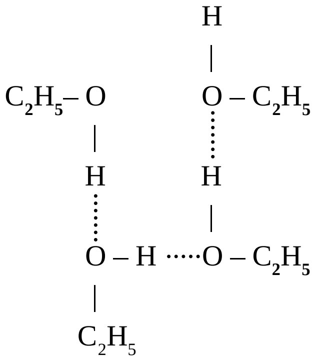
(i) Ethanol (polar) and cyclohexane (non-polar)

(ii) Benzene (non-polar) and acetone (polar)

(iii) Benzene and carbon tetrachloride

(iv) Carbon tetrachloride and chloroform.

In pure ethanol, a considerable fraction of the molecules are hydrogen bonded.



When cyclohexane is added, these molecules enter into the hydrogen bonded ethanol molecules breaking up the hydrogen bonds and reduce the ethanol-ethanol intermolecular attraction. The liquid pair shows a slight increase in volume and heat is absorbed.

(b) Non-ideal solutions exhibiting negative deviation

Let us consider a solution of a liquid solute and liquid solvent where the solute-solvent interactions are stronger than solute-solute or solvent-solvent interactions. In such a solution, the total vapour pressure of the solution is less than that corresponding to an ideal solution of the same composition at the same temperature. These solutions are said to exhibit negative deviations from **Raoult's law**. They also show an increase in boiling point on adding more of the solute. For such solutions, $P_A < P_A^O x_A$ and $P_B < P_B x_B$, $\Delta H_{mixing} < 0$, $\Delta V_{mixing} < 0$

The total vapour pressure of such a solution will be the least and the boiling point will be the highest for one of the intermediate compositions.

The solution has now the property of boiling at a constant temperature without any change in composition and can distil over at a constant temperature without any change in composition. Such mixture are termed as **azeotropes** or **azeotropic mixture**. In case of negative deviations, *maximum boiling point azeotropes* are obtained.

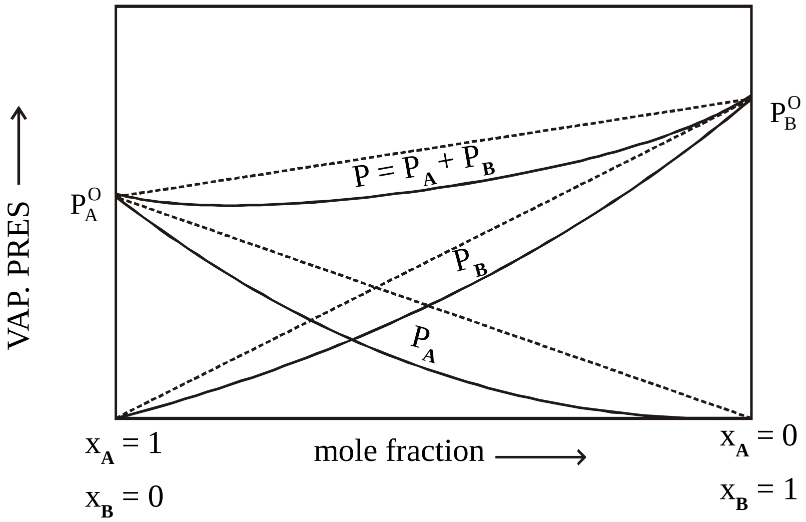


Fig. 2.6 Vapour Pressure versus mole fraction curve for non-ideal solution exhibiting negative deviation

A few examples of solutions showing negative deviation are

(i) Chloroform and acetone

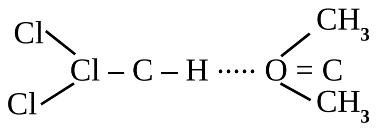
(ii) Acetic acid and pyridine

(iii) Chloroform and benzene

(iv) Water and nitric acid

(v) Diethyl ether and chloroform

When chloroform and acetone are mixed, the hydrogen bonding occurs between the two molecules.



$$\mathrm{(Cl)_2\,Cl-C-H \cdots\cdots O=C(CH_3)_2}$$

This decreases the escaping tendency of the molecules from each component and results in the increase in the boiling point of the solution. In case of negative deviation, contraction in volume on mixing along with evolution of heat is expected.

2.7 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS :

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions behave ideally. Dilute solutions obey Raoult’s law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend upon the number of solute particles irrespective of their nature. These properties are known as **colligative properties** and since they are properties of dilute solutions, the properties are often called **colligative properties of dilute solutions**. These properties are inter-related, since if one is measured, other can be calculated. Thus **the properties of the dilute solutions which depend upon the number of solute particles irrespective of their nature are called colligative properties**. A few colligative properties are

(i) Relative lowering in vapour pressure

(ii) Elevation in the boiling point

(iii) Depression in the freezing point

(iv) Osmotic pressure

These properties provide excellent method for the determination of the molecular masses of dissolved solutes. For best results the following conditions must be satisfied.

(a) the solution should be very dilute

(b) the solute should be non-volatile

(c) the solute should not undergo association or dissociation in solution.

Lowering of vapour pressure : Whenever we add a nonvolatile solute e.g. sodium chloride to a solvent i.e water, the solute occupies a certain surface area of the solvent. As a result, the solvent molecules which are more volatile than the solute molecules get lesser opportunity to change to the vapour state. In other words, the vapour pressure of the solution. becomes lesser than that of pure solvent i.e. there is lowering of vapour pressure.

Relative lowering of Vapour pressure : The vapour pressure of a liquid is lower when a non-volatile solute is dissolved in it and the lowering is proportional to the amount of solute dissolved. Suppose a pure liquid has a vapour pressure P^0 and the solution has vapour pressure P_S. Hence the lowering wiill be $P^0 – P_S$. The ratio of the lowering of vapour pressure to the vapour pressure of pure solvent $\frac{P^0 - P_S}{P^0}$ is known as the **relative lowering of vapour pressure**.

Raoult's Law states that the vapour pressure of the solution is directly proportional to the molefraction of the solvent at a given temperature.

Mathematically, $P_S \propto x_1$

where $P_S \rightarrow$ vapour pressure of solution.

$x_1 \rightarrow$ mole fraction of solvent

or, $P_S = P^0 x_1$,

where P^0 is the vapour pressure of pure solvent.

We know, $x_1 + x_2 = 1$

where x_2 is the mole fraction of solute.

or, $x_1 = (1 - x_2)$

or, $P_S = P^0(1 - x_2)$

or, $$\frac{P_S}{P^0} = (1 - x_2)$$

or, $$\frac{P_S}{P^0} - 1 = - x_2$$

or, $$1 - \frac{P_S}{P^0} = x_2$$

or, $$\boxed{\frac{P^0 - P_S}{P^0} = x_2}$$

Thus, Raoult's law may be stated in another form :

"The relative lowering of vapour pressure is equal to the mole fraction of the solute."

$$\frac{P^0 - P_S}{P^0} = \frac{n}{n+N}$$

where n and N are the number of moles of solute and solvent respectively.

Since the solution under consideration is dilute, the molar concentration of the solute is very small as compared to the solvent and can be neglected.

$$\frac{P^0 - P_S}{P^0} = \frac{n}{N}$$

Relative lowering in vapour pressure is a colligative (interlinked) property, since it relates to the molar concentration of solute and solvent in the solution.

Determination of molecular mass :

We know that, $$\frac{P^0 - P_S}{P^0} = \frac{n}{N}$$

or, $$\frac{P^0 - P_S}{P^0} = \frac{w_1/M_1}{w_2/M_2}$$

Where w_1 is the mass of the solute

M_1 is the molecular mass of the solute.

w_2 is the mass of the solvent.

M_2 is the molecular mass of the solvent

$$\frac{P^0 - P_S}{P^0} = \frac{w_1 M_2}{w_2 M_1}$$

or, $$\frac{P^0}{P^0 - P_S} = \frac{w_2 M_1}{w_1 M_2}$$

or, $$\boxed{M_1 = \frac{P^0 w_1 M_2}{(P^0 - P_S) w_2}}$$

All other values, being known, the molecular mass of the solute can be calculated.

Raoult’s Law for Volatile Solutes

Let us consider a solution of two miscible liquid components A and B having mole fractions x_A and x_B respectively. Let their partial vapour pressures be P_A and P_B respectively. The partial vapour pressures in the solution will be proportional to the respective mole fractions in the solution. Therefore,

$$P_A \, \alpha \, x_A \text{ and } P_B \text{ and } x_B$$

Basing on the experimental data, Raoult showed that in case of mixtures of two miscible liquids, the above relation can be written as

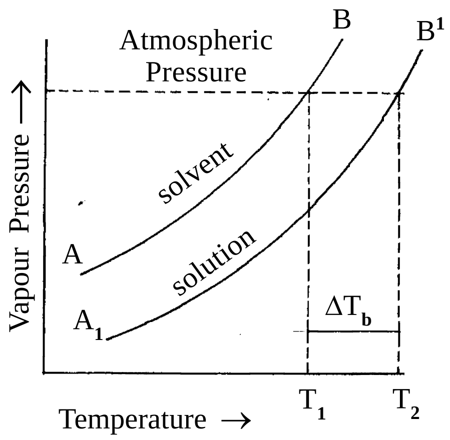
$$P_A = P^O_A x_A \text{ and } P_B = P^O_B x_B$$

where P^O_A and P^O_B are the vapour pressures of pure components A and B. This is **Raoult's law** which states that **for a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction**. It may be remembered that this will not hold good if a mixture of volatile liquids does not form a solution.

2.8 ELEVATION OF BOILING POINT (EBULLIOSCOPY) :

A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. But as the vapour pressure of the solvent is lowered by addition of non-volatile solute, it is apparent that the boiling point of the solution will be higher than that of the pure solvent. In other words the boiling point of the solvent is elevated by the addition of non-votatile solute to it. This is known as **elevation of boiling point.** (ΔT_b)

If we plot graphs between the different values of temperature and the vapour pressure for the pure solvent as well as for its solution, the two curves that are formed may be given as follows.



It 'P' represents the atmospheric pressure, then the boiling point temperature of the pure solvent is T_1 and that of the solution is T_2. The elevation in boiling point, ΔT_b may be given as,

$$\Delta T_b = T_2 - T_1$$

Mathematically, $\Delta T_b = K_b \times m$. where K_b is the molal elevation constant obtained by dissolving one moles of solute in 1000 gm of the solvent. As K_b is constant,

$$\Delta T_b \propto m.$$

Fig 2.7 Plot of vapour pressure versus temperature

Since elevation of boiling point is dependent upon the molar concentration of the solute, it is a colligative property.

Determination of molecular mass of solute : The elevation of boiling point ΔT_b is useful in determining the molecular mass of the solute (M).

The mass of the solute = W_1 gm.
The mass of the solvent = W_2 gm.
The molecular mass of the solute = M

$$\therefore \quad \text{Molality of the solution} = \frac{\text{mass of the solute per 1000gms of the solvent}}{\text{molecular mass of the solute}}$$

$$= \frac{W_1 \times 1000}{W_2 \times M}$$

$$\therefore \quad \Delta T_b = K_b.m$$

$$\text{or,} \quad \Delta T_b = K_b \frac{W_1 \times 1000}{W_2 \times M}$$

$$\text{or,} \quad \boxed{M = \frac{K_b.W_1 \times 1000}{\Delta T_b.W_2}}$$

2.9 DEPRESSION OF FREEZING POINT (CRYOSCOPY) :

Freezing point of a liquid is defined as the temperature at which the solid and liquid state of a substace have the same vapour pressure. In other words, it is that temperature at which the solid and the liquid states of a substance coexist; the liquid and solid are in equilibrium state.

Vapour pressure of a solution is lower than that of the pure solvent. Hence the freezing point of a solution is lower than that of pure solvent. Hence the freeezing point of a solution is lower than that of pure solvent.

If we plot graphs between different values of temperature and the corresponding vapour pressure for the solid and the liquid states of pure solvent as well as for its dilute solution, the curves formed may be represented as follows.

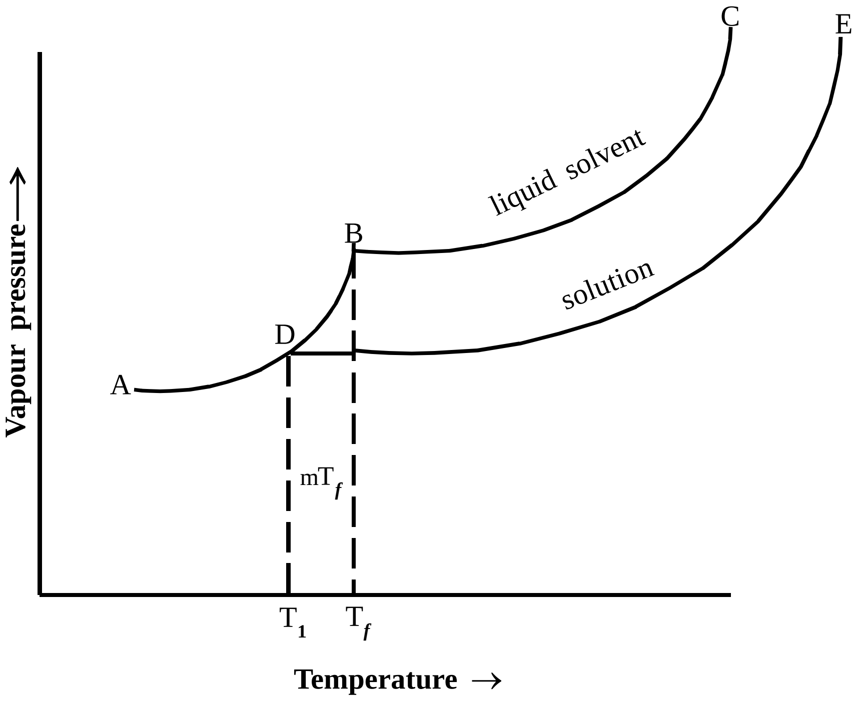


Fig. 2.8 Plot of V.P. against temperature

According to the definition of freezing point temperature, freezing point of the solvent is T_f and that of solution is T_1. Since T_f is greater than T_1 there is lowering or depression in freezing point temperature, ΔT_f

$\therefore\ \Delta T_f = T_f - T_1$

Mathematically, $\Delta T_f = K_f \times m$.

where K_f is the molal depression constant obtained by dissolving 1 mole of the solute in 1000 gm of the solvent.

As K_f is a constant, $\Delta T_f \propto m$.

Since the depression in freezing point is dependent upon the molal concentration of the solute, it is a colligative property.

Determination of molecular mass of solute : The depression in freezing point value ΔT_f is useful in determining the molecular mass of the solute (M).

Let the mass of the solute be W_1 gm.

The mass of the solvent be W_2 gm.

Molecular mass of the solute be M.

$$\text{Molality of the solution} = \frac{\text{mass of the solute per 1000 gm of the solvent}}{\text{molecular mass of the solute}}$$

$$= \frac{W_1 \times 1000}{W_2 \times M}$$

By substituting the value of M in the relation, $\Delta T_f = K_f \times m$,

$$\text{we have, } \Delta T_f = \frac{K_f . W_1 \times 1000}{W_2 \times M}$$

$$\text{or} \quad \boxed{M = \frac{K_f . W_1 \times 1000}{\Delta T_f . W_2}}$$

2.10 OSMOSIS :

When a solution is separated from its solvent by a semipermeable membrane, the solvent molecules pass through it into solution to have uniform concentration of both sides of the membrane.

"The spontaneous flow of solvent into a solution or from a more dilute to a concentrated solution through a semipermeable membrane is known as OSMOSIS"

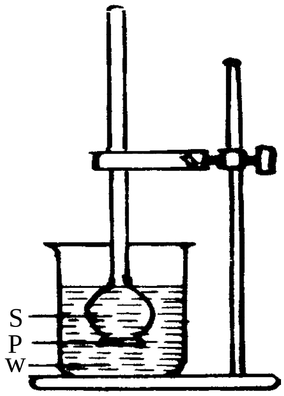


Fig 2.9 Abbe Nollet's experiment

Abbe Nollet's Experiment : The passage of solvent through membranes was first observed by Abbe Nollet (1784). He used an animal membrane (Pig's bladder) as the semipermeable membrane, which was stretched across the mouth of a thistle funnel P. (Fig.10.5). The funnel was filled with a strong sugar solution, S, and inverted over a trough of water, W. The water gradually rises in the stem of the thistle funnel and position of equilibrium ultimately reached when the hydrostatic pressure equalises the pressure of the water. This pressure developed as a result of osmosis is the osmotic pressure of the solution and is measured by the difference in water levels inside and outside.

Illustration of OSMOSIS : Take two eggs of equal size, whose outer shells have been removed by dissolving in hydrochloric acid. Put one of them in distilled water and the other in saturated salt solution. After a few hours, it will be noticed that the egg placed in distilled water swells and the one in salt solution shrinks. It is due to the fact that in the former case, water enters the concentrated egg fluid while in the latter water comes out of the egg in order to have equal concentration on both sides.

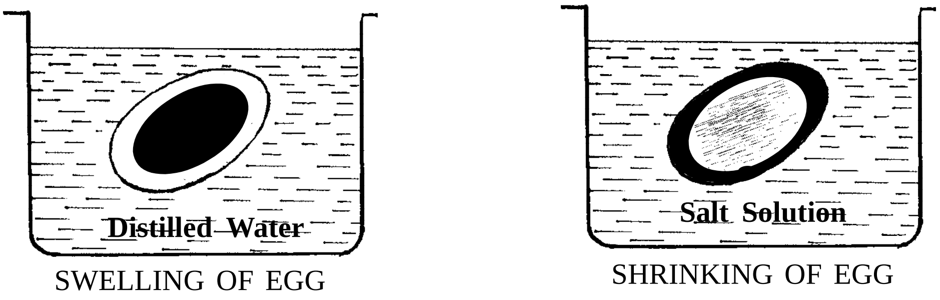


Fig. 2.10 Illustration of osmosis

Difference from diffusion :

(i) In osmosis, the presence of semipermeable membrane is essential.

(ii) In osmosis it is only the solvent molecules which flow out whilst in diffusion both the solute as well as the solvent molecules flow out in opposite direction.

Osmotic Pressure : The flow of solvent into solution may be stopped by the application of pressure on the solution side. This extra pressure which must be applied to a solution to stop the flow of solvent molecules through the semipermeable membrane is known as **osmotic pressure.** This is represented by the symbol π.

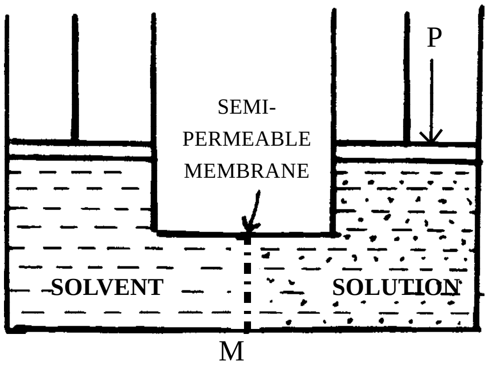


Fig. 2.11 Osmotic pressure

Isotonic Solution : The solutions having same osmotic pressure are known as isotonic solutions.

Molecular mass and osmotic pressure : van't Hoff (1887) made a thorough study of the osmotic pressure of dilute solution or ideal solution. He concluded that a dilute solution behaves like ideal gas.

(i) **Boyle-van't Hoff law of solution :** According to the law for dilute solution the product of osmotic pressure and volume is constant, provided the temperature is constant.

(Since $\pi \propto \frac{1}{V}$)

Mathematically, πV = Constant, at constant temperature.

(ii) **Charle-van't Hoff law for solution** : According to the law for a solution of fixed composition the osmotic pressure is directly proportional to absolute temperature.

Mathematically, $\pi \propto T$

(iii) **van't Hoff equation for dilute solution :** This equation is similar to the ideal gas equation ($PV = nRT$).

According to the laws stated above,

$\pi \propto \frac{1}{V}$ $\pi \rightarrow$ Osmotic pressure.

$\pi \propto T$

$\pi \propto \frac{T}{V}$ or, $\pi V = KT$

where K is a constant called van't Hoff constant for solution and it has the same value for all solutions. The value of K has been found to be the same as that of R i..e. gas constant.

$\pi V = RT$ (for 1 mole of the solute dissolved in V litres)

or, $\pi V = nRT$. .... (1) (for n moles of the solute dissolved in V litres)

$\pi V = \frac{W}{M} RT$ W → mass of the solute

M → molecular mass of the solute.

or, $\boxed{M = \frac{WRT}{\pi V}}$ .... (2)

Again from equ. (l) $\pi = \frac{n}{V} RT$ or, $\boxed{\pi = CRT}$ ....(3)

where C is molar concentration of solution.

For a solution, at a given temperature both R and T are constants.

Hence, $\pi \propto C$.

Since osmotic pressure depends upon the molar concentration of the solution, it is a colligative property.

2.11 ABNORMAL MOLECULAR MASS :

As we have seen, the colligative properties of solutions depend on the number of solute particles present in the solution. Various relations hold good in dilute solution only when there is no change in molecular state of the solute. If the total number of particles of the solute changes in solution, the colligative property will also change accordingly. For example, if a sugar solution is taken, the experimental value of the colligative property will be same as the theoretical value, because one mole of the non-electrolyte sugar gives one mole of particle. On the other hand, a solution containing one mole of an electrolyte like NaCl will contain 2 moles of particles (1 mole of Na^+ and 1 mole of Cl^- ions). Similarly one mole of $BaCl_2$ would produce 3 moles of ions in solution. When benzoic acid is taken in benzene, the number of benzoic acid particles is reduced because of the association of benzoic acid particles in benzene. Colligative properties of the solution depend upon the number of particles, the value observed will be higher or lower than the calculated values.

Since the molecular mass is inversely related to the colligative properties, in case of dissociation of the solute, the observed molecular mass will be less than the calculated value and in case of association, the observed molecular mass will be more than the calculated value.

Van't Hoff Factor '*i*' - In order to account for the abnormal colligative properties, van't Hoff introduced a factor '*i*', known as van't Hoff factor '*i*' is defined as the ratio between the observed value of the colligative property and the calculated value.

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property}}$$

$$= \frac{\text{No.of particles after dissociation or association}}{\text{No. of particles taken ideally}}$$

As we know, molecular mass is inversely proportional to colligative property. Therefore, van't Hoff factor '*i*' can be written as

$$i = \frac{\text{Theoretical molecular mass}}{\text{Experimental molecular mass}}$$

$$\text{Thus, } i = \left(\frac{\Delta P}{P_o}\right) \Big/ \left(\frac{\Delta P}{P_o}\right) = \frac{(\Delta T_b)_{obs}}{(\Delta T_b)_{Cal}} = \frac{(\Delta T_f)_{obs}}{(\Delta T_f)_{cal}} = \frac{\pi_{obs}}{\pi_{cal}} = \frac{M_{cal}}{M_{obs}}$$

In case of association , $i < 1$ and in case of dissociation $i > 1$

Application of van't Hoff factor

van't Hoff factor '*i*' can be used to calculate the degree of association and the degree of dissociation.

(a) Degree of Association

Suppose one mole of solute A is dissolved in a definite volume of the solvent where it has undergone association. 'n' molecules of solute A has formed the associated molecule $(A)_n$, according to the reaction

$$\underset{(1-\alpha)}{nA} \rightleftharpoons \underset{\alpha/n}{A_n}$$

Let 'α' be the degree of association, then the no. of associated moles = $\frac{\alpha}{n}$ and the number of unassociated moles = $1-\alpha$

Total no. of moles in soln = $\frac{\alpha}{n} + 1 - \alpha = 1 + \left(\frac{1}{n} - 1\right)\alpha$

Thus van't Hoff's factor '*i*' = $1+(1/n-1)\alpha/1 < 1$ if n = 2 or more.

$$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

As colligative property $\alpha = \frac{1}{\text{mol.mass}}$

$$\frac{\text{Observed colligative property}}{\text{Theoretical colligative property}} = \frac{\text{Actual mol. mass}}{\text{Observed mol. mass.}}$$

The degree of association α can be calculated by knowing the value of '*i*' and 'n'

(b) Degree of Dissociation

Suppose one mole of solute A has undergone dissociation to give 'n' particles according to the reaction

$$\underset{(1-\alpha)}{A} \rightarrow \underset{\alpha}{B} + \underset{\alpha}{C} + \ldots\ldots\ldots\ldots$$

No. of particles before dissociation = 1

No. of particles after dissociation = $(1-\alpha)+n\alpha = 1+\alpha(n-1)$

Thus, van't Hoff's factor '*i*' = $\frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}} = \frac{1+\alpha(n-1)}{1}$

or, $\alpha = \frac{i-1}{n-1}$

The degree of dissociation α can be calculated by knowing the value of '*i*' and 'n'

CHAPTER (2) 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 standard atmospheric pressure.
5. Greater the vapour pressure of a liquid, the lesser would be its boiling point.

6. Raoult's law : The relative lowering of vapour pressure is equal to molefraction of solute.
7. Relative lowering of vapour pressure, elevation of boiling point and depression of freezing point are the **colligative properties.**
8. Viscosity of a liquid is its property by virtue of which it tends to oppose the relative motion between its different layers. It decreases with increase in temperature and increases with increase in pressure.
9. The spontaneous flow of solvent into a solution or from a more dilute to a concentrated solution through semipermeable membrane is known as **osmosis.**
10. The extra pressure which must be applied to the solution to stop the flow of solvent molecules through the semipermeable membrane is known as **osmotic pressure.**
11. The solutions having the same osmotic pressure are known as **isotonic solutions**.
12. Surface tension is the force in dynes acting at right angles to an imaginary line of unit length on the surface of a liquid. It decreases with increase of temperature.
13. Standard solution : A solution whose strength is known.
14. Grams per litre : Grams of solute per litre of the solution.
15. Normality : Number of gram - equivalents of the solute present per litre of the solution.
16. (N). It is temperature independant $\mathbf{N} = \frac{\text{Mass of solute in grams per litre}}{\text{Equivalent mass of the solute}}$
17. Molarity **:** Number of moles of solute present per litre of the solution. **(M).** It is temperature dependant.

$$\mathbf{M} = \frac{\text{grams per litre}}{\text{molecular mass of the solute}}$$

$$\text{Hence } \frac{N}{M} = \frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}}.$$

18. Molality **:** Number of moles of the solute present per 1000 g of the solvent **(m).** It is independent of temperature.

$$\mathbf{m} = \frac{\text{Mass of the solute in grams per 1000 g of solvent}}{\text{Molecular mass of the solvent}}$$

19. Molefraction : Ratio of the number of moles of the component to the total number of moles of all the components (solute and solvent) in the solution.
20. Percent Solution :

    (a) *Mass to mass:* Number of grams of the solute in 100 g of solution (w/w).

    (b) *Mass to volume :* Number of grams of the solute in 100 ml of solution. (w/v)

    (c) *Volume to volume :*Number of ml of the solute in 100 ml of solution. (v/v)

    (d) *Volume to mass :* Number of ml of the solute in 100 g of solution. (v/w).

21. Formality : Number of formula mass of the solute per litre of the solution. **(F)**
22. Parts per million : Number of parts by mass of solute present in one million (10^6) parts by mass of the solution
23. A solution is a homogeneous mixture of two or more substances. It may be binary, ternary or quaternary depending upon the no. of components present.
24. The mass in grams of a substance which when dissolved in 100 gms of a solvent forming a staturated solution at a particular temperature is called solubility.
25. Solubility Rule **:** The polar solids are soluble in polar solvents whereas nonpolar solids are soluble in nonpolar solvents.
26. Solubility = $\frac{\text{mass of solute in gms}}{\text{mass of solvent in gms}} \times 100$
27. If ΔH is +ve, the solubility inscreases with increase in temperature. If ΔH – ve, the solubility decreases with increase in temperature.
28. Henry's law : The amount of gas dissolved in a given volume of liquid at constant temperature is directly proportional to the pressure of the gas.

PROBLEMS WITH SOLUTION

1. The vapour pressures of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60g of ethanol and 40g of methanol. Calculate the total vapour of the solution and the molefraction of methanol in the vapour phase.

Solution :

According to Raoult's law

Partial vapour pressure = Vapour pressure of pure liquid x mole fraction.

Now moles of ethanol = $\frac{60}{46} = 1.304$ (molar mass = 46)

Moles of methanol = $\frac{40}{32} = 1.250$ (molar mass = 32)

Mole fraction of ethanol = $\frac{1.304}{1.304 + 1.250} = 0.51$

Mole fraction of methanol = 1 – 0.51 = 0.49

Partial vapour pressure of ethanol in solution, P(ethanol) = 44.5 x 0.51 = 22.69 mm of Hg

Partial vapour pressure of methanol in solution, P(methanol) = 88.7 x 0.49 = 43.46 mm of Hg

Total vapour pressure = P(ethanol) + P(methanol) = 22.69 + 43.46 = 66.15 mm of Hg.

Mole fraction of methanol in vapour phase = $\dfrac{\text{P(methanol)}}{\text{Total vapour pressure}} = \dfrac{43.46}{66.15} = 0.657$

2. Vapour pressure of water at 20^0C is 17.5 mm of Hg and lowering of vapour pressure of a sugar solution is 0.061 mm of Hg. Calculate.

(i) relative lowering of vapour pressure

(ii) vapour pressure of the solution

(iii) mole fraction of sugar and water.

Solution :

(i) Calculation of relative lowering of vapour pressure :

Vapour pressure of water (P_A^0) = 17.5 mm of Hg.

Lowering of vapour pressure ($P_A^0 - P_A$) = 0.061.

Relative lowering of V.P = $\dfrac{P_A^0 - P_A}{P_A^0} = \dfrac{0.061}{17.5} = 0.00348$

(ii) Calculation of V.P. of solution

P = V.P of solvent – lowering in V.P

= 17.5 – .061

= 17.439 mm of Hg

(iii) Calcutation of mole fraction of sugar and water.

Mole fraction of sugar, X_B solute

$$\frac{P_A^0 - P_A}{P_A^0} = X_B$$

Here, $\dfrac{P_A^0 - P_A}{P_A^0} = 0.00348$

Mole fraction of sugar. $X_B = 0.00348$

Mole fraction of water ($=X_A$) = $1 - X_B = 1 - 0.00348 = 0.9965$

3. The boiling point of pure water is 100^0C. Calculate the boiling point of an aqueous solution containing 0.6 g of urea (molar mass = 60) in 100 g of water. (K_b for water = 0.52K/m)

Solution : We know that

$$mT_b = \frac{Kb \times W_B \times 1000}{M_B \times W_A}$$

K_b = 0.52 $K\,m^{-1}$, W_B = 0.6g, M_B = 60 and W_A = 100 g

$\therefore$ $mT_b = \frac{0.52 \times 0.6 \times 1000}{60 \times 100}$ = 0.052^0C.

Thus, b.p of the solution

= 100 + 0.052

= 100 . 052^0C.

4. 50 ml of benzene (density 0.879 g/ml) when added with 0.643 g of a compound lowers the freezing point from 5.51^0C. to 5.03^0C. If K for benzine is 5.12 K Kg mol–1, calculate the molar mass of the compound.

Solution : The molar mass M_B is calculated as

$$M_B = \frac{K_f \times W_B \times 1000}{W_A \times \Delta Tf}$$

Given W_B = 0.643g, W_A = (50ml) x (0.879 g/ml) (i.e. = 43.95 g)

K_f = 5.12 $K\,m^{-1}$, mT_f = 5.51 – 5.03 = 0.48^0

$$\therefore \quad M_B = \frac{5.12 \times 0.643 \times 1000}{43.95 \times 0.48} = 156.06$$

5. If 1.71 g of sugar (molar mass = 342) are dissolved in 500 ml of a solution at 300K, what will be its osmotic pressure ? (R = 0.082 Latm. K^{-1} mol^{-1})

Solution : According to van't Hoff equation

$$p = CRT = \frac{n}{V}RT = \frac{W_B RT}{M_B V}$$

W_B = 1.71 g, V = $\frac{500}{1000}$ L, T = 300 K

R = 0.082 L atm K^{-1} mol^{-1}.

Putting all the values, p = $\frac{1.71 \times 0.082 \times 300}{342 \times 500/1000}$ = 0.246 atm.

6. Osmotic pressure of a solution containing 7g of a protein per 100 ml of solution is 25 mm Hg at 37^0C. Calculate the molar mass of protein.

p = CRT

$$= \frac{n_B}{V} RT$$

$$= \frac{W_B RT}{M_B V}$$

$$\therefore \quad M_B = \frac{W_B RT}{\pi V}$$

Here, $W_B = 7g$, $T = 273+37 = 310K$,

$p = \frac{25}{760}$ atm., V = 100ml = 0.1 L

R = 0.082 litre. atm K^{-1} mol^{-1}

$$\therefore \qquad M_B = \frac{7 \times 0.082 \times 310}{\frac{25}{760} \times 0.1} = 54094$$

QUESTIONS

A. Very short answer type questions (One mark each) :

1. At 730 mm pressure, the boiling point of water is .... (more than 100^0C, less than 100^0C)
2. The boiling point of sea water at 760 mm pressure is .... (more than 100^0C, less than 100^0C).
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. Why is CCl_4 immiscible in water ?
12. Name one factor which influences the solubility of a solid in a solvent ?
13. How does boiling point of a liquid change with decrease in atmospheric pressure ?
14. What is the effect of pressure on the boiling point of a liquid ?
15. How does viscosity of a liquid vary with temperature ?
16. Between water and ether which has a higher vapour pressure ?
17. What is the order of increasing vapour pressure of the following at room temperature ?

    Water, Sugar solution in water, alcohol - water solution
18. What is the relationship between depression in freezing point of a solution and molecular mass of the solute ?

19. Why is vapour pressure of a solution lower than that of a pure solvent ?
20. What is the SI unit of viscosity ?
21. What is the SI unit of surface tension ?
22. Which of the following has higher vapour pressure at the same temperature ?

    CH_3OH (BP = 64.5^{0}C) C_2H_5OH (BP = 78.3^{0}C)

B. Short answer type questions (Two marks each) :

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 molality of a solution.
7. Define molarity of a solution.
8. What is the equivalent mass of sodium carbonate ?
9. Define and illustrate equivalent mass of an acid
10. Define 'Molality'.

    29.25 g of NaCl is present in 529.25 g of the solution. Find out the molality.
11. What is the molality of a solution containing 40 g of NaOH in 1000 ml of water ?
12. Write down the equation that will show the relationship between normality and molarity.
13. Define surface tension.
14. (a) Define the terms (i) viscosity (ii) coefficient of viscosity.
    (b) What do you understand by viscosity of a liquid ?
15. Distinguish between diffusion and osmosis.
16. Explain why ?
    (a) In summer, earthen pots are used to keep water cool.
    (b) Liquid drops are spherical.
    (c) Egg shrinks in size when placed in sodium chloride solution.
    (d) The boiling point of water is more than that of ether.
    (e) Ammonia is used as a refrigerant.
17. What do you mean by osmosis ?
18. What do you understand by "osmotic pressure".
19. What do you understand by viscosity of a liquid ?
20. Calculate the vapour pressure of the solution at 100^{0}C containing 3gms of cane sugar in 33 gms of water. [molecular weight of sugar = 342]
21. The relation of heat of vapourisation to the boiling point in absolute scale of liquids is approximately 21. The relation is known as........ .

22. Why surface tension of a liquid decreases with increase in temperature ?
23. Between sea water and pure water, which will boil at a higher temperature ? Give reason.
24. Why glycerol is more viscous than water ?
25. What is reverse osmosis and how is it helpful ?
26. What is the effect of temperature on the surface tension of a liquid ? Explain with reason.
27. Distinguish between diffusion and osmosis.
28. 0.265 gms of sodium carbonate is present in 100ml of the solution. What is its normality ?
29. Calculate the normality of the following
    (a) 0.585 g NaCl / 100 cc soln.
    (b) 0.49 g H_2SO_4 / 1000 cc soln.
30. What is van't Hoff's factor ? How is it related to the degree of association of a solute with solvent ?

C. Short answer type questions (Three marks each) :

1. Define the term solution. How many types of solutions can be formed?
2. A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% $^{W}/_{W}$. What would be the molality and mole fraction of each component of the solution?
3. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.
4. Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 ml. of 0.15 M solution is methanol.
5. Vapour pressure of water is 12.3 kPa at 300K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.
6. A solution of sucrose is prepared by dissolving 68.4 g in 1000 g of water. Calculate the vapour pressure of solution at 20°C. The vapour pressure of water of 293K is 0.023 atm. Assume that the solution behaves ideally. (Molar mass of sucrose = 342 g mol^{-1}).
7. A solution containing 18 g of non-volatile solute in 200 g of water freezes at 272.07K. Calculate the molecular mass of the solute (Water freezes at 273K and its K_f = 1.86 Kg mol^{-1}).
8. The boiling point of a solution containing 5.0 g of of non-volatile solute in 1 Kg of a solvent at 0.05° higher than that of pure solvent. Calculate the molecular mass of the solute (Molecular mass and K_b for a solvent are 78 and 2.53K Kg/mol^{-1} respectively).

9. A 5% solution of $CaCl_2$ at 0°C developed an osmotic pressure of 15 atmosphere. Calculate the degree of dissociation.
10. 5.85 g of NaCl is dissloved in 90 g water. What is the mole fraction of NaCl?
11. A solution of 2.4 g of a substance in 25g water boiled at 100.8°C at 1 atm. pressure . Calculate the molecular mass of the substance (Boiling elevation constant for water = 0.52°C per 1000g of it)
12. 19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in freezing point of water observed is 1.0°C. Calculate the Van't Hoff factor and dissociation constant of CH_2FCOOH.

D. Long answer type questions (7 marks each) :

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) Osmosis (c) Osmotic pressure.
6. Describe briefly about osmosis and osmotic pressure.
7. Write short notes on :
   (a) Osmotic pressure
   (b) Viscosity
   (c) Surface tension.
   (d) Osmosis.
   (e) Boiling point and freezing point.
8. 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.
9. Explain the effect on the boiling point and freezing point when a non-volatile solute is dissolved in a volatile solvent.
10. What is viscosity ? How does it vary with rise of temperature ? Mention some applications of viscosity in eveyday life.

11. Discuss briefly the effect of temperature on,

    (a) Surface tension and (b) Viscosity.

12. State Raoult's law. A solution of 2.4 g of a substance in 25g of water boiled at 100.8^0C at 1 atm. pressure. Calculate the molecular mass of the substance (Boiling elevation constant for water = 0.52^0C per 1000 g of it)

13. What is osmotic pressure ? How will you determine the molecular mass of a substance by this method ?

    The osmotic presure of 200ml of aqueous solution containing 1gm protein at 27^0C in 2.0×10^{-1} atm. Calculate the molecular mass of protein (R = 0.082 L atm. mol^{-1} K^{-1})

14. Define molality of a solution.

15. Define molarity of a solution.

16. Define 'Molality'.

    29.25 g of NaCl is present in 529.25 g of the solution. Find out the molality.

17. What is the molality of a solution containing 40 g of NaOH in 1000 ml of water ?

18. Write down the equation that will show the relationship between normality and molarity.

19. Four solutions A, B, C, and D contain 1g each of HCl, HNO_3, H_2SO_4 and H_3PO_4 respectively per 100 ml. Arrange the solutions in the increasing order of their molarity and normality.

20. (a) Calculate the molarity when 73g of HCl is dissolved in water to make 1500 ml solution.

    (b) Calculate the molarity of seminornal Na_2CO_3 solution. Na = 23, C = 12

    (c) 5.85 g of NaCl is dissolved in 90 g of water. What is the mole fraction of NaCl?

21. What is the molality of a solution containing 0.25 mole of the solute in 250 g of the solvent ?

22. Sp. gr of HCl solution is 1.17. 100 g of HCl solution contains 36.5 g of acid. Calculate the normality of the solution.

23. 200 ml of 0.2 M NaOH and 300 ml of 0.3 M NaOH are mixed. Find out the molarity of the resulting solution.

E. Multiple choice type (One marks each) :

1. When KCl is dissolved in water, the

   (a) Boiling point is raised.

   (b) Boiling point is lowered.

   (c) Boiling point remains unchanged.

2. An aqueous solution of methanol in water has vapour pressure,
   - (a) Equal to that of water.
   - (b) Equal to that of methanol.
   - (c) More than that of water.
   - (d) Less than that of water.
3. Compared to Jalandhar, the vapour pressure of water at Simla is,
   - (a) Lower
   - (b) More
   - (c) Equal.
4. Dissolution of a solid in a solvent.
   - (a) Increases its vapour pressure.
   - (b) Lowers the vapour pressure.
   - (c) Does not change its vapour pressure.
   - (d) Decreases boiling point
5. 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
6. With increase in temperature, the vapour pressure of a liquid.
   - (a) Decreases
   - (b) Does not change.
   - (c) Increases
7. 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.
8. When an egg is placed in concentrated sodium chloride solution, it shrinks due to
   - (a) Osmosis
   - (b) Diffusion
   - (c) Decomposition
9. The unit of viscosity is poise which means
   - (a) Dyne Cm^{-2}
   - (b) dyne
   - (c) dyne cm^{-2} sec^{-1}
   - (d) dyne cm

10. The internal resistance to flow possessed by liquid is called its
    - (a) Surface tension
    - (b) Fuidity
    - (c) (n)
    - (d) Viscosity
11. A liquid in capillary tube rises due to
    - (a) Surface tension
    - (b) Vapour pressure
    - (c) Osmosis
    - (d) Viscosity
12. When salt water is slowly frozen the first solid which separates is
    - (a) ice
    - (b) salt
    - (c) a compound formed from water and salt
    - (d) solid solution of salt and ice
13. 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.
14. 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.
15. 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
16. When a dry grape or raisin is placed in water, it swells due to
    - (a) Difflusion
    - (b) Osmosis
    - (c) Absorption
    - (d) Surface tension

17. Dissolution of solute in a solvent
    - (a) lowers its vapour pressure
    - (b) increases its vapour pressure
    - (c) increases its freezing point
    - (d) lowers its boiling point
18. Egg when placed in a concentrated solution of common salt gets shrinked due to
    - (a) diffusion
    - (b) surface tension
    - (c) decomposition
    - (d) osmosis
19. Which of the following solution shows highest osmotic pressure ?
    - (a) 0.1 M glucose
    - (b) 1 % urea
    - (c) 0.1 M common salt
    - (d) all show equal osmotic pressure
20. The boiling point of water in a pressure cooker is
    - (a) below 100^0C.
    - (b) above 100^0C.
    - (c) 100^0C.
    - (d) depends upon the size of pressure cooker.
21. The osmotic pressure of a dilute solution is directly proportional to the
    - (a) Diffusion rate of the solute.
    - (b) Concentration of the solute.
    - (c) Elevation of boiling point.
    - (d) Flow of solvent from a concentrated solution to a dilute solution.
22. Which of the following 0.1 M aqueous solutions will have the lowest freezing point ?
    - (a) Potassium sulphate
    - (b) Sodium chloride
    - (c) Urea
    - (d) Glucose
23. One of the following is not affected by the change in temperature
    - (a) Normality
    - (b) Molarity
    - (c) Molality
    - (d) none of these.

24. 10ml of conc. H_2SO_4 (18 molar) is diluted to 1 litre. The approximate strength of dilute acid would be

(a) 0.18 N (b) 0.09 N

(c) 0.36 N (d) 18.O N

25. 12g of H_2SO_4 is dissolved in water to make 1200 ml of the solution. The concentration in normality is

(a) 0.051 (b) 0.102

(c) 0.122 (d) 0.204

26. The molarity of pure water is

(a) 55.6 (b) 50

(c) 100 (d) 18

27. 5.85 g of NaCl is dissolved in 90 g of water. The molefraction of the solute is

(a) 0.01 (b) 0.1

(c) 0.2 (d) 0.0196.

28. The normality of 26.5 g of Na_2CO_3 present in one kilolitre solution is

(i) 0.25 N (ii) 0.05 N

(iii) 0.5 N (iv) none of these.

ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS

1. (a)
2. (c)
3. (b)
4. (b)
5. (b)
6. (c)
7. (b)
8. (a)
9. (c)
10. (d)
11. (a)
12. (a)
13. (c)
14. (b)
15. (b)
16. (b)
17. (a)
18. (d)
19. (c)
20. (a)
21. (b)
22. (a)
23. (iii)
24. (iii)
25. (iv)
26. (i)
27. (iv)
28. (iv)

* * *

UNIT - III

CHAPTER - 3

ELECTROCHEMISTRY

3.1 INTRODUCTION :

Electrochemistry deals with the interaction of electrical energy with chemical species. It is divided into two categories : (i) Electrical energy performing chemical change (electrolysis) and (ii) Conversion of chemical energy to electrical energy i.e. producing electricity by redox reactions. All electrochemical reactions involve transfer of electrons and therefore, they are **redox** reactions.

Substances are divided into two types on the basis of conduction of electricity through them. Substances which conduct electric current are called **conductors** and substances which do not conduct electricity are called **non-conductors or insulators.**

Conductors are again divided into two types i.e.

(i) Metallic or electronic conductors (ii) Electrolytes or electrolytic conductors.

Metallic Conductors - These are metals through which electric current can pass without any transfer or change in chemical properties of matter. Metals are best conductors, e.g., copper, aluminium etc. This property is not restricted to pure metals, it is also possessed by most of the alloys of metals, carbon, certain solid salts and oxides.

Electrolytic conductors or Electrolytes - Substances which allow the passage of electricity through their aqueous solution or fused state are called electrolytes. Passage of electric current results in transfer of matter and changes in concentration.

Examples : Fused salts, acids, bases and their aqueous solutions.

Non-electrolytes - Substances which do not conduct electric current through their aqueous solutions are called non-electrocytes. Examples are - cane sugar, urea, glycerol, benzene etc.

Distinction between metallic and electrolytic conduction

Metallic conduction	*Electrolytic conduction*
1. It occurs due to flow of electrons.	1. It occurs due to movement of ions in solution or a fused electrolyte
2. No change in chemical properties of conductor takes place.	2. It involves chemical reactions at the electrodes.
3. Does not involve transfer of matter.	3. It involves transfer of matter in form of ions.
4. It shows an increase in resistance as temperature increases.	4. It shows a decrease in resistance as temperature is increased.

Properties of electrolytes

1. Electrolytes conduct electricity in molten of fused state or in aqueous solutions.
2. Chemical reaction takes place at the electrodes and electrolytes are chemically decomposed.
3. Electrolytes on being dissolved, positive and negative ions are formed in solution.
4. All electrolytes do not conduct electricity to the same extent. Some electrolytes provide greater number of ions, these are called **strong electrolytes.** Examples are hydrochloric acid, sodium hydroxide etc. (strong acids and strong bases, also strongly ionic salts). Some other electrolytes conduct electricity to lesser extent, because these provide lesser number of ions. These are **weak electrolytes.** Examples are acetic acid, oxalic acid etc.

3.2 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION :

(1) When an electrolyte is dissolved in water, it splits up into ions. *The process of splitting up of an electrolyte into positive and negative ions (cations and anions respectively) is called ionisation or electrolytic dissociation.*

For examples :

$$\underset{\text{unionised molecule}}{NaCl} \rightleftharpoons \underset{\text{Cation}}{Na^+} + \underset{\text{Anion}}{Cl^-}$$

(2) Properties of the electrolytes in solution are due to the properties of the ions produced on dissociation.

(3) Electrical conductivity of an electrolyte is due to the movement of ions towards the oppositely charged electrodes. Conductivity depends upon the number of ions in the solution. Greater the number of ions, greater is the conductivity.

(4) Electrolytes in solution split up into ions. Ions reunite to form the original molecules. Thus, there is dynamic equilibrium between the ions and unionised molecules.

(5) *The extent to which an electrolyte undergoes dissociation into ions is called* **degree of dissociation or ionisation.**

$$\text{Degree of ionisation} = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number molecules dissolved.}}$$

Degree of ionisation is different for different electrolytes. *Electrolytes having high degree of inisation are called* **strong electrolytes** *and electrolytes having low degree of ionisation are called* **weak electrolytes.**

3.3 STRONG AND WEAK ELECTROLYTES :

All ionic compounds (such as KCl, NaCl, KNO_3 etc.), strong acids (such as HCl, H_2SO_4, HNO_3 etc.) and strong bases (such as KOH, NaOH, etc.) ionise almost completely in aqueous solution. A very small fraction of these substances remain as unionised molecules. Such substances are called **strong electrolytes**. Law of ionic equilibrium can not be applied to such substances.

Examples : $KCl \rightarrow K^+ + Cl^-$ (almost completely ionised)

$NaOH \rightarrow Na^+ + OH^-$ (almost completely ionised)

$KNO_3 \rightarrow K^+ + NO_3^-$ (almost completely ionised)

Certain other acids like acetic acid, carbonic acid (H_2CO_3) and bases likeNH_4OH, $Ca(OH)_2$ etc. ionise slightly in solution. Large fraction of these substances remian as unionised molecules in solution. These are called **weak electrolytes.**

Examples :- $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ (very slightly ionised)

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (very slightly ionised)

A faction of the total number of molecules which exist as ions in solution is called its **degree of dissociation.**

$$\textbf{Degree of dissociation} = \frac{\text{Number of molecules dissociated into ions.}}{\text{Total number molecules dissolved}}$$

Ostwald's dilution law

When a weak electrolyte is dissolved in water, a very small fraction of it dissociates into ions in solution. An equilibrium exists between the ions and unionised molecules. Let us take the case of a weak acid. HA, of which 1 mole is dissolved in 'V' litres of water. Let 'x' moles of HA dissociate into ions at equilibrium.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial Conc.	0		0		0
Conc. at equilibrium	(1–x)		x		x

At equilibrium $[HA] = \frac{1-x}{V}$, $[H^+] = \frac{x}{V}$ and $[A^-] = \frac{x}{V}$

Applying law of equilibrium, $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{\frac{x}{V} \times \frac{x}{V}}{\frac{(1-x)}{V}} = \dfrac{x^2}{V(1-x)}$

where K_a is the dissociation constant of acid. Greater the value of K_a, stronger is the acid.

$$\left[\frac{1}{V \text{ litres}} = C \text{ moles per litre}\right]$$

For a very weak electrolyte, 'x' is extremely small and can be neglected in the denominator.

Thus, $K_a = \dfrac{x^2}{V} = Cx^2$ or, $x = \sqrt{\dfrac{Ka}{C}}$

Similarly, for a weak base, $x = \sqrt{\dfrac{K_b}{C}}$, where K_b is the dissociation constant of base.

Problems :

1. *Calculate the amount of acetic acid present in one litre of its solution, having* α = *1% and* $K_a = 1.8 \times 10^{-5}$

	$CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
Initially	1	0	0
After dissociation,	$1-\alpha$	α	α

where 'α ' is the degree dissociation, if concentration of acetic acid is C mol. litre^{-1}

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} = \frac{\alpha C.\ \alpha C}{C\,(1-\alpha)} = \frac{\alpha^2 C^2}{C(1-\alpha)}$$

If 'α' is very small, $1 - \alpha = 1$, $K_a = \dfrac{\alpha^2 C^2}{C} = \alpha^2 C$

Then $1.8 \times 10^{-5} = C \times \left(\dfrac{1}{100}\right)^2$ or C = 0.18 mol. litre^{-1}.

Therefore, 1 litre solution contains 0.18 moles = 0.18 × 60g = 10.8g.

(Mol. mass of CH_3COOH = 60)

2. *Calculate the concentration of H+ and degree of dissociation of 0.2M acetic acid solution, having* $K_a = 1.8 \times 10^{-5}$

	$CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
Initially,	1	0	0
After dissociation,	$1-\alpha$	α	α

Let initial concentration of acid be C moles. litre^{-1} and α be the degree of dissociation.

So, $[H^+] = \alpha C = C\sqrt{\dfrac{K_a}{C}} = \sqrt{K_a C} = \sqrt{(1.8 \times 10^{-5} \times 0.2)} = 1.9 \times 10^{-3}$ mol. litre^{-1}

$$\text{Also, } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.2}} = 0.0095 \text{ or } 0.95\%$$

3.4 ELECTROLYSIS :

The process of decomposition of an electrolyte in solution or in the fused state by passing electric current is known as electrolysis.

Aqueous solution of an electrolyte is taken in a glass vessel. Two metal plates are dipped in the solution and upper end of the plates are connected to the two poles of a battery. These metal plates are called electrodes. The electrode connected to the positive pole of the battery is called **anode** and that connected to the negative pole of the battery is called cathode. Electric current enters the electrolyte through the anode and leave the electrolyte through the cathode. Electrolyte is dissociated into positive and negative ions and move to the oppositely charged electrodes on passing the current. *Cations* (Positive ions) are liberated at cathode and anions (negative ions) are liberated at anode.

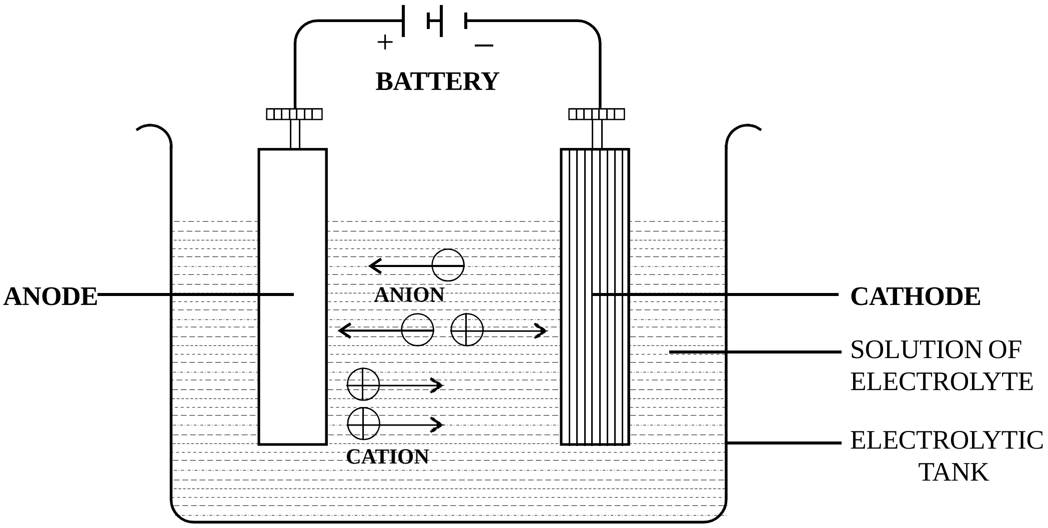


Fig. 3.1 Electrolysis

The process of electrolysis can be described in the following manner.

(i) Electrolyte dissociates into positive and negative ions.

(ii) *At anode* - Anions being liberated at anode lose electrons and get converted to neutral atom (primary process). Neutral atom may combine with another atom to form molecule or may react with water. (secondary process).

(iii) *At cathode* - Cations being liberated at cathode, gain electrons and form neutral atoms which get deposited on cathode (Primary process) or may react with water (secondary process)

Examples -

electrolysis of fused NaCl

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

At cathode $Na^+ + e \longrightarrow Na$ liberated at cathode

At anode $Cl^- - e \longrightarrow Cl$ (primary process)

$Cl + Cl \longrightarrow Cl_2(g)$ (secondary process) – liberated at anode.

Electrolysis of aqueous solution of NaCI

$NaCl \longrightarrow Na+ + Cl^-$

At cathode $Na^+ + e \longrightarrow Na$ (primary process)

$2Na + 2H_2O \longrightarrow 2NaOH + H_2$ (g) (secondary process)

Hydrogen is liberated at cathode.

At anode $Cl^- - e \longrightarrow Cl$ (primary process)

$Cl + Cl \longrightarrow Cl_2(g)$ (secondary process) – liberated at anode.

Electrolysis of aqueous solution copper sulphate

Using copper electrodes -

$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$H_2O \longrightarrow H^+ + OH^-$

At cathode $Cu^{2+} + 2e^- \longrightarrow$ Cu, deposited on cathode.

At anode Cu – anode goes into solution forming Cu^{2+} ions

$Cu \longrightarrow Cu^{2+} + 2e$, equivalent amount of copper goes into the solution.

Using platinum electrodes -

$CuSO_4 \longrightarrow Cu^{2+} + SO_4{}^{2-}$

$H_2O \rightleftarrows H^+ + OH^-$

At cathode $Cu^{2+} + 2e \longrightarrow$ Cu, deposited on cathode.

At anode $OH^- - e \longrightarrow OH$

$2OH \longrightarrow H_2O + O$

$O + O \longrightarrow O_2$, liberated at anode.

3.5 FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday studied the quantitative relationship between the amount of chemical change observed at the electrodes and the quantity of electricity passed through the solution. The result of his investigation is expressed in the form of two laws.

1. **First law -** *The mass of the substance liberated at the electrode during the process of electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.*

If 'W' is the mass of substance liberated at the electrode and 'Q' is the quanitity of electricity (in Coulombs) passed through the electrolyte, then

$W \propto Q$ But, $Q = C.\,t$

where C = current in amperes and t = time in seconds.

then, $W \propto C.t$ or $W = Z.C.t.$ or $Z = \frac{W}{C.t}$

where 'Z' is a constant known as ***Electrochemical equivalent***.

If C = 1 ampere and t = 1 second, then W = Z.

Therefore, ***electrochemical equivalent*** *of a substance is defined as the the mass of the substance liberated when one ampere of current is passed through the electrolyte for one second.*

It can also be defined as *the mass of substance liberated by the passage of one coulomb of electricity.*

1 coulomb = 1 ampere × 1 second
(unit of electricity)

Faraday (F) is a bigger unit of electricity.

1 Faraday = 96500 coulombs.

It has been found that by passing one Faraday (96500 coulombs) of electricity through the electrolyte, 1 gm equivalent of the substance is liberated.

For example, on passing 1 Faraday or 96500 coulombs of electricity through silver nitrate solution, 108 gm (1gm. equiv. of silver) of silver is deposited at the cathode.

Mass of substance liberated by passing 96500 coulombs of electricity = 1 gm. equiv.

When one coulomb of electricity is passed,

$\frac{\text{1 gm. equivalent}}{96500}$ = *Electrochemical equivalent of substance is deposited.*

Therefore, electrochemical equivalent (E.C.E.) = $\frac{\text{Chemical equivalent}}{96500}$

Hence, E.C.E. or Z for silver = $\frac{108}{96500} = 0.0011181$

2. **Second law -** *When the same quantity of electricity is passed through different electrolytes connected in series, the masses of different substances liberated at the electrodes are proportional to their equivalent masses.*

Let there be three voltameters containing solutions of copper sulphate, silver nitrate and acidulated water and these are connected in series, so that same amount of electricity is passed through the electrolytes for a given time. It is found that the masses of copper, silver and hydrogen liberated at the respective electrodes are in the ratio of their equivalent masses or chemical equivalents.

Thus, $$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

This law becomes useful in determining equivalent mass of substances.

$$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\frac{\text{Mass of copper deposited}}{96500}}{\frac{\text{Mass of silver deposited}}{96500}} = \frac{\text{E.C.E. of copper}}{\text{E.C.E of silver}}$$

$$= \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

Problems based on Faraday's Laws

1. What current strength in amperes will be required to liberate 10gm. of iodine from KI solution in one hour (Eq. mass of KI = 127)

$W = 10$ gm. $Z = \frac{127}{96500}$, $t = 3600$ seconds

$W = Z.C.t.$

or, $$C = \frac{W}{Z.t} = \frac{10 \times 96500}{127 \times 3600} = 2.11 \text{ ampere.}$$

2. A *current of 3 amp. passing through $AgNO_3$ solution for 20 minutes deposited 4g. of silver. What is the E.C.E. of silver ?*

Here, $C = 3$ amp. $t = 20 \times 60$ seconds

$W = 4$g.

$W = Z.C.t.$

or, $$Z = \frac{W}{C.t.} = \frac{4}{3 \times 20 \times 60} = 0.00111$$

3. *0.2964 g. of copper was deposited on passage of a current of 0.5 amp. for 30 minutes through a solution of copper sulphate. Calculate atomic mass of copper.*

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

For the deposit of at.mass or 1 mole of Cu-atoms 2 Faraday of electricity are required.

Here, $W = 0.2964$g. $Q = C.t = 0.5 \times 30 \times 60 = 900$ coulombs.

900 coulombs deposit 0.2964g of Cu.

$$\therefore \text{193,000 will deposit} = \frac{0.2964 \times 193000}{900} = 63.56\text{g of Cu}$$

Hence, at. mass. of copper = 63.56

4. *Calculate the E.C.E. of Cu. and Ag when that of H_2 is 0.0000104 (At. mass of Ag = 107.88 and that of Cu. = 63.54)*

$$\frac{\text{E.C.E of } H_2}{\text{E.C.E. of Ag}} = \frac{\text{Eq. mass. of } H_2}{\text{Eq. mass. of Ag.}}$$

$$\text{Thus, E.C.E. of Ag} = \frac{0.0000104 \times 107.88}{1} = 0.01112$$

$$\text{E.C.E. of Cu} = \frac{0.0000104 \times 31.77}{1} = 0.00033$$

$$(\because \text{Eq. mass. of copper} = \frac{\text{At. mass}}{2} = \frac{63.54}{2} = 31.77)$$

5. (a) *What is the charge in coulomb on a CO_3^{2-} ion ?*

(b) *Calculate approximately, how much current is necessary to produce oxygen gas at the rate of 1 ml. per socond ?*

(a) 6.02×10^{23} electrons correspond to 96,500 coulombs (1 Faraday)

2 electrons present on CO_3^{2-} ion correspond to $\frac{96{,}500 \times 2}{6.02 \times 10^{23}} = 3.2 \times 10^{-19}$ Coulombs

(b) 1 Faraday = 96,500 coulombs.

1g. equiv (8g) of oxygen = $\frac{22.4}{4}$ litres = 5,600 ml at N.T.P.

Hence, for the production 1 ml. of oxygen,

coulombs required = $\frac{96{,}500}{5{,}600} = 17.23.$

Current in amp/sec. = $\frac{17.23}{1} = 17.23$

3.6 APPLICATIONS OF ELECTROLYSIS :

(a) **Electroplating :** This is done for decoration by depositing gold, silver etc. on baser metals and protection of metals by depositing nickel, chromium etc. on baser metals. Also broken parts of metals are repaired by depositing the metals electrolytically.

The article to be electroplated is cleaned mechanically by sand paper, washed with NaOH and excess of water. This article is made the **cathode.** The metal to be deposited is made the anode. The electrodes are suspended in a tank made of glass, wood or cement. Electrolyte taken in the tank is a soluble salt of the metal which is to be deposited. Electrolyte used should be highly soluble, a good conductor and should not undergo oxidation, reduction or hydrolysis. For best electroplating, low current density, low temperature and high metal concentration in the electrolyte is essential. Anode and cathode are connected to the positive and negative pole of battery respectively.

Examples of some common electrolytes used :

(i) Copper sulphate solution with dilute sulphuric acid – Copper plating.

(ii) Potassium argentocyanide $K[Ag(CN)_2]$ –Silver plating.

(iii) Nickel ammonium sulphate – Nickel plating.

(b) **Electrorefining :** Metals obtained in the extraction process contain impurities. To purify the metals like copper, silver, lead etc electrorefining process is used. In this process a sheet of impure metal is made **anode.** If copper metal is to be refined, a sheet of pure copper is made the cathode. Electrolyte used is a solution of copper sulphate mixed with dilute sulphuric acid. Anode and cathode are connected to the positive and negative pole of battery respectively. On passing the current copper from the impure anode goes into the solution as Cu^{++} ions and from the electrolytic solution pure copper is deposited on the cathode.

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

At cathode $Cu^{2+} + 2e \longrightarrow Cu$ (deposited on cathode)

(c) **Electrotyping :** Reproduction of objects of art on wood carvings are concerted to printing plates by the electrodeposit method. Impression of the object of art is taken on the block of wax. The impression of wax is coated with graphite (a good conductor). This plate is made the cathode. Anode is made of copper and both are suspended in a tank of copper sulphate. On passing electric current copper metal is deposited on the impression on wax. After depositing the metal, wax is melted and the metal plate so obtained is used in printing.

(d) **Electrolytic extraction of metals :** Certain active metals like sodium, potassium, magnesium, calcium etc. are extracted by the electrolysis of their fused salts. For example, when fused sodium chloride is electrolysed sodium metal is liberated at the cathode.

3.7 ELECTROLYTIC CONDUCTANCE :

Ohm's law which is valid for metallic conductors is also applicable to electrolytic conductors. It states that :

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

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

where 'I' is in amperes, 'E' in volts and 'R' is measured in ohms.

Resistance (R) *of any conductor varies (i) directly as the length of the conductor (l) and (ii) inversely as the area of cross section of the conductor (a).*

Thus, $R \propto l$ .... (i)

and $R \propto \frac{1}{a}$ .... (ii)

Combining (i) and (ii), we have $R \propto \frac{l}{a}$

or, $R = \rho \frac{l}{a}$ where 'ρ' (rho) is a constant which depends upon the nature of material and is called **specific resistance.**

When $l = 1$ cm, a = 1sq.cm, then R = specific resistance (ρ)

Therefore, *specific resistance is equal to the resistance in ohms of a material which is 1 cm in length and 1 sq. cm in area of cross-section. Thus, specific resistance is the resistance of one cm cube of the material.*

Conductance (C) — In electrochemistry the term **conductance** is used instead of resistance. **Conductance is the reciprocal of resistance.** $C = \frac{1}{R}$

As the unit of resistance is **ohm,** the unit of conductance is **ohm^{-1}** or **mho.**

Specific Conductance k (Kappa) :- It is the reciprocal of specific resistance i.e.

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{1}{a} = \frac{1}{a} \times \text{conductance (C)}$$

If $l = 1$ cm and a = 1 sq. cm., then, k = C

Thus, **specific conductance is defined as the conductance of a solution in a cell in which the electrodes are 1 cm apart and have unit (1 sq. cm) area.**

The term $\frac{l}{a}$ is called **cell constant.**

Therefore, specific conductance (k) = cell constant × conductance.

or **cell constant** = $\frac{\text{specific conductance}}{\text{conductance}}$

The unit of specific conductance is ohm^{-1} cm^{-1}

Equivalent conductance (Λ) : Specific conductance is a property of the conducting medium. But while dealing with electrolytic solutions a quantity of greater significance known as **equivalent conductance** is more commonly used. In these cases, conductance also depends upon the concentration of electrolyte or the number of ions present in the solution.

Equivalent conductance is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by ' Λ ' (lambda)

Equivalent conductance is related to specific conductance by the following relation.

Equivalent conductance = specific conductance × V

where V is the volume in c.c. containing one gram equivalent of the electrolyte.

Therefore, $$\Lambda = k \times V = \frac{1000 \times k}{C}$$

where C is the concentration of the electrolyte in gram. equivalent per litre.

Unit of equivalent conductance is **ohm^{-1} . cm^2 / gm. equiv.**

Molar conductance (μ) : Molar conductance of a solution is the conducting power of all the ions provided by one gram mole of electrolytic solution. It is denoted by "μ" (Mu)

Molar conductance is related to specific conductance by the relation :

$$\mu = k \times V = \frac{k \times 1000}{C}$$

where 'k' is the specific conductance 'V' is the volume of the electrolytic solution containing one mole of the electrolyte and 'C' is the molar concentration (number of moles of electrolyte per litre of the solution)

The unit of molar conductance is **ohm^{-1} . cm^2 mole^{-1}.**

3.8 MEASUREMENT OF CONDUCTANCE :

The Wheatstone bridge method is generally employed for this purpose. This method measures the resistance of solution, the reciprocal of which gives the conductance. A schematic diagram of the apparatus is shown in fig 3.2.

Unknown solution of electrolyte is taken in a suitable conductivity cell placed in a thermostat. Resistance of the electrolyte can not be measured by applying direct current because of the following reasons.

(i) Electrode reactions change the concentration of electrolyte about the electrode.

(ii) The products of electrolysis produce an opposing potential. In order to avoid these

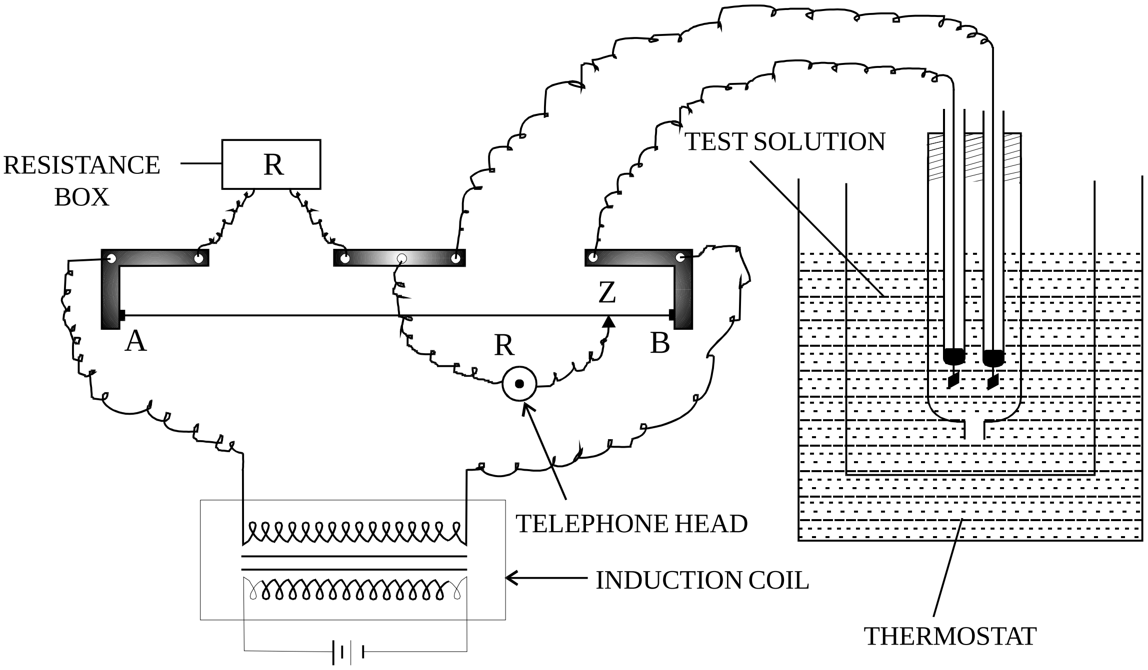


Fig. 3.2 Conductivity determination

difficulties, the resistance of electrolyte is measured by applying an alternating current with a frequency of the order of kilo Hertz from an induction coil. 'R' is the resistance box and a telephone head is used to detect the current. AB is a uniform wire and sliding contact point 'Z' moves over it

When current flows, a known resistance R is introduced through the resistance box. The resistance should be about the same order as that of the solution. The sliding contact Z is moved along the wire AB until no sound (or minimum sound) is heard in the detector. At this null point,

$$\frac{\text{Resistance of the solution}}{\text{Resistance R}} = \frac{\text{length ZB}}{\text{length ZA}}$$

Since 'R' is known and length ZB and ZA can be read from the scale fixed below the wire AB, the resistance of the solution can be calculated. Reciprocal of resistance gives the conductance.

Problems on Conductance

1. *A decinormal solution of sodium acetate when placed between two electrodes each 1.5 cm square and placed at a distance of 0.72cm has a resistance of 52.4 ohms. Calculate its specific conductance and equivalent conductance.*

$$R = \rho \frac{l}{a}$$ Here, l = 0.72 cm, a = 1.5 sq. cm, R = 52.4 ohm.

$$\rho = \frac{R.a}{l} = \frac{52.4 \times 1.5}{0.72} = 163.8 \text{ ohm cm}$$

Specific conductance (k) $= \frac{1}{\rho} = \frac{1}{163.8} = 0.0061$ mhos.cm^{-1}

Equivalent conductance = k × V = 0.0061 × 10, 000 = 61 mhos.cm^{2} /g.eq.

2. *In a conductivity cell, 0.01 N KCl solution gave a resistance of 225.0 ohms while a 0.01N solution of HCl gave a resistance of 77.1 ohms. Specific conductance of KCl solution is 0.00141 mhos.cm^{-1}. Calculate the specific and equivalent conductance of HCl solution.*

Specific resistance (ρ) = R $\times \frac{a}{l}$, where $\frac{l}{a}$ = cell constant

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance of KCl solution}}$$

$$= \frac{0.00141}{1/225} = 0.00141 \times 225 = 0.317 \text{ cm}^{-1}$$

specific conductance of HCl solution = conductance × cell constant.

$$= \frac{1}{77.1} \times 0.317 = 4.11 \times 10^{-3} \text{ mhos.cm}^{-1}$$

Equivalent conductance (Λ) = k x V

$= 4.11 \times 10^{-3} \times 100{,}000 = 4.11 \times 10^{-3} \times 10^{5} = 4.11 \times 10^{2}$ mhos.cm^{2}/g.equiv.

3. *Electrolytic conductance of 0.20 mol. l^{-1} solution of KCl at 298K is 2.48×10^{-2} ohm^{-1}. cm^{-1}. Calculate its molar conductance.*

specific conductance (k) = 2.48×10^{-2} ohm^{-1} cm^{-1}

∴ 0.2 mol KCl will be present in

$\frac{1000}{0.2}$ cm^{3} = 5000 cm^{3} solution.

Thus, V = 5000 cm^{3} mol^{-1} solution

Molar conductivity = μ = k × V

$= 2.48 \times 10^{-2} \times 5000 = 124$ ohm^{-1} cm^{2} mol^{-1}

4. N/10 *solution of NaCl has specific conductance of 0.001119 ohm^{-1} cm^{-1}. Find out equivalent conductivity.*

Equivalent conductance (Λ) $= \frac{1000k}{C}$

Here, $\frac{N}{10}$ solution means C = 0.1

$$\therefore \Lambda = \frac{0.001119 \times 1000}{0.1} = 11.19 \text{ ohm}^{-1} \text{ cm}^{2} \text{ g.equiv.}^{-1}$$

Factors affecting equivalent conductance

(1) It increases with increase in temperature of solution.

(2) Increase in ionic interaction decreases equivalent conductance.

(3) It is more or less inversely proportional to viscosity of the solvent.

(4) Association of ions leads to decrease in equivalent conductance.

(5) Strong ion-solvent interaction can increase the size of the ions leading to decrease in equivalent conductance.

But the most important factor is the concentration of the electrolyte or its dilution, which is discussed below.

3.9 EFFECT OF DILUTION ON EQUIVALENT CONDUCTANCE :

Conductance of the solution depends upon -
(i) Nature of electrolyte (ii) Dilution (iii) Temperature
Electrolytes are divided into two types :- (a) **strong electrolytes.**
(b) **weak electrolytes.**

Strong electrolytes : Acids such as HCl, H_2SO_4 etc, alkalies such as NaOH, KOH etc. and most of the salts ionise completely in solution and thus have high values of conductance even at high concentrations, are known as **strong electrolytes.**

Weak electrolytes : Some acids like acetic acid and bases like ammonium hydroxide do not ionise completely in solution and have low values of conductance are known as **weak electrolytes.**

Effect of dilution : Equivalent conductance of any electrolyte increases with increasing dilution i.e., decreasing concentration of the solution. Results of conductance measurement of many electrolytes shows that variation of equivalent conductance with concentration depends upon the type of electrolyte (fig 4.3). A solution which contains larger number of ions compared to another solution of same concentration at the same temperature, is said to be **strong electrolyte** and the other having low degree of ionisation is called **weak electrolyte.** Increase in equivalent conductance with dilution is not so large in case of strong electrolytes, as in the case of weak electrolytes.

On plotting equivalent conductance of some electrolytes against concentration the curves obtained are shown in fig 3.3 below.

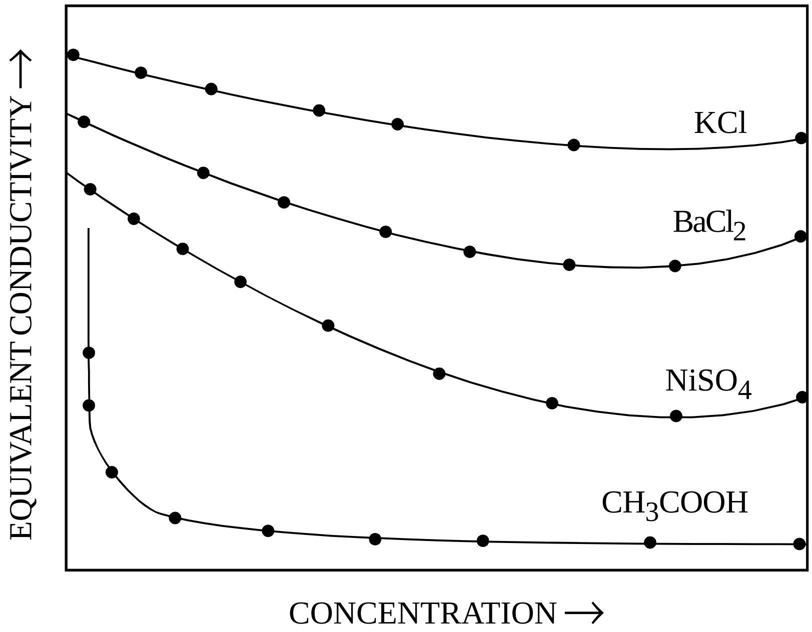


Fig. 3.3 Change in equivalent conductivity with dilution

It is observed that for strong electrolytes, there is a tendency for equivalent conductance to approach a certain limiting value when concentration approaches zero. This limiting value is called *equivalent conductance at infinite dilution* or zero concentration denoted by Λ_0. In case of strong electrolytes it is found by extrapolating the equivalent conductance graph to zero concentration.

In case of weak electrolytes, it is observed that at the higher concentrations the equivalent conductance is very low but in the more dilute solutions the values rise rapidly. In such cases (like acetic acid) the limiting value can not be attained by extrapolating the graph to zero concentration. However, for weak electrolytes the value may be obtained indirectly by using **Kohlrausch's law.**

With increase in degree of dissociation due to dilution more number of ions are furnished and equivalent conductance increases. When limiting value of equivalent conductance is approached, the degree of dissociation is unity. At any other concentration degree of dissociation is calculated from the conductance ratio. i.e. the ratio opf equivalent conductance at any concentration (Λ_c) to that at infinite dilution (Λ_0)

$$\alpha = \frac{\Lambda c}{\Lambda_0}$$

$$\text{Degree of dissociation} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution.}}$$

3.10 KOHLRAUSCH'S LAW :

It has already been observed that equivalent conductance of solution increases with dilution until it becomes constant. This limiting value, Λ_0 is known as *equivalent conductance at infinite dilution.*

Kohlrausch (1875) studied the equivalent conductances at infinite dilution (Λ_0) for a number of pairs of strong electrolytes having the same cation or anion. The values are recorded in Table - 4.1 below.

Table - 3.1

Λ_0 values of some pairs of electrolytes at 298K.

Electrolyte	Λ_0	Difference	Electrolyte	Λ_0	Difference
KCl	149.86	23.41	KBr	151.92	2.06
NaCl	126.92		KCl	149.86	
KBr	151.92	23.41	LiBr	117.09	2.06
NaBr	128.51		LiCl	115.03	

From the table it is found that replacement of potassium ion in any of electrolytes having a common anion produces the same difference (23.41 ohm^{-1}cm^{-2} g. equiv^{-1}) in Λ_0, irrespective of the chloride ion in any of the electrolytes, having a common cation produces the same difference (2.06 ohm^{-1} cm^{2} g.equiv^{-1}) in Λ_0.

Thus he concluded that the difference in conductances of any two cations or anions appears to be the same, irrespective of the nature of the other ions with which they are associated. Kohlrausch concluded that at infinite dilution, where dissociation of all electrolytes is complete, each ion migrates independently and contributes to the total equivalent conductance of an electrolyte a definite share, which depends only on its nature and not at all on that of the ion with which it is associated. He put forward the *law of independent migration of ions* which states that :

At infinite dilution, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and that the value of equivalent conductance at inifinite dilution for any electrolyte is given by the sum of the contributions of the two ions.

So, $\Lambda_0 = \lambda^0{}_a + \lambda^0{}_c$

where λ^0_a and λ^0_c are called the ionic conductances at infinite dilution of the anion and cation respectively.

Application: Equivalent conductance at infinite dilution can be obtained graphically by extrapolation for strong electrolytes. But this method can not be applied for weak electrolytes. However, conductance of weak electrolytes can be evaluated by the application of Kohlrausch law. For example, equivalent conductance of acetic acid at infinite dilution can be evaluated from the equivalent conductance at infinite dilution of hydrochloric acid, sodium chloride and sodium acetate by the following procedure.

$$\lambda^0 CH_3COO^- + \lambda^0 H^+ = (\lambda^0 H^+ + \lambda^0 Cl^-) + (\lambda^0 CH_3COO^- + \lambda^0 Na^+) - (\lambda^0 Na^+ \ \lambda^0 Cl^-)$$

$$\text{or, } \Lambda_0 CH_3COOH = \Lambda_0 HCl + \Lambda_0 CH_3COONa - \Lambda_0 NaCl$$

Putting the conductance value of Λ_0HCl, $\Lambda_0 CH_3COONa$ and Λ_0NaCl in the above equation $\Lambda_0 CH_3COOH$ can be calculated.

Problem

(1) *Equivalent conductance of sodium propionate, hydrochloric acid and sodium chloride at infinite dilution are 85.9, 426.1, 126.4 mhos.cm²eq⁻¹ respectively at 298 K. Calculate equivalent conductance at infinite diulation for propionic acid.*

(i) $\Lambda_0 C_2H_5COONa = \lambda^0 C_2H_5COO^- + Na^+$

(ii) $\Lambda_0 HCl = \lambda^0 H^+ + \lambda^0 Cl^-$

(iii) $\Lambda_0 NaCl = \lambda^0 Na^+ + \lambda^0 Cl^-$

Adding (i) and (ii) and subtracting (iii) from it, $\Lambda_0 C_2H_5COOH$ can be obtained.

$$\Lambda_0 C_2H_5COOH = \Lambda_0 C_2H_5COONa + \Lambda_0 HCl - \Lambda_0 NaCl$$
$$= 85.9 + 426.1 - 126.4 = 385.6 \text{ mhos cm}^2\text{eq}-1$$

(2) *Calculate the degree of dissociation of sodium chloride in 0.1N solution. The equivlaent conductance at this dilution is 98.4 mhos cm^2 eq^{-1} and ionic of sodium and chloride ions are 43.4 and 65.5 mhos. cm^2 respectively.*

$\Lambda_c NaCl = 98.4 \text{ mhos.cm}^2\text{eq}^{-1}$

$\Lambda_0 NaCl = \lambda^0 Na^+ + \lambda^0 Cl^- = 43.4 + 65.5 = 108.9$

$$\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{98.4}{108.9} = 0.9036$$

Hence degree of dissociation is 0.9036

3.11 ELECTROCHEMICAL CELLS :

Electrochemical cells can be grouped into two categories :

(i) **Electrolytic cells** (ii) **Galvanic cells**

An **electrolytic cell** *is a device in which the external supply of electrical energy is necessary in order to bring about a physical or chemical change in the cell.*

On the other hand in a **galvanic cell** *the energy released by a physical or chemical change is transformed into electrical energy.* Examples are Daniell cell, Laclanche cell, dry cell, storage battery etc.

Chemical reactions often result in energy changes. In an electrochemical cell, the energy change appears in form of electricity as a result of chemical reactions called **redox reactions** (reduction and oxidation). Electrical energy is produced in the cell due to oxidation at one electrode and reduction at the other electrode of the cell.

Oxidation involves loss of electrons.

For example : $Zn \longrightarrow Zn^{2+} + 2e$

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

$Fe^{2+} \longrightarrow Fe^{3+} + e$ etc.

Reduction involves the gain of electrons.

For example : $Fe^{3+} + e \longrightarrow Fe^{2+}$

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

A reaction in which oxidation and reduction take place simultaneously is called **redox reaction.**

For example : $Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$

$Zn \longrightarrow Zn^{2+} + 2e$ (oxidation half reaction)

$Cu^{2+} + 2e \longrightarrow Cu$ (reduction half reaction)

Galvanic cell

Materials : Let us consider an electrochemical cell of the type Zn-$CuSO_4$. In this case two beakers are used. Zinc and copper rods are used as electrodes and a salt bridge is used to have continuity between the two solutions in beakers.

In one of the beakers 0.1 M $ZnSO_4$ solution is taken in which a zinc rod is dipped. It is called **zinc-half cell.** In another beaker 0.1M $CuSO_4$ solution is taken in which a copper rod is dipped. It is called **copper-half cell.** Solutions in the two beakers are connected by an inverted U-tube containing an electrolyte. Two ends of the U-tube have porous plugs. Zinc rod which serves as **anode** is connected to the copper rod which serves as **cathode** by copper wires having a galvanometer in the circuit.

The arrangement is shown in Fig. 3.4 below:

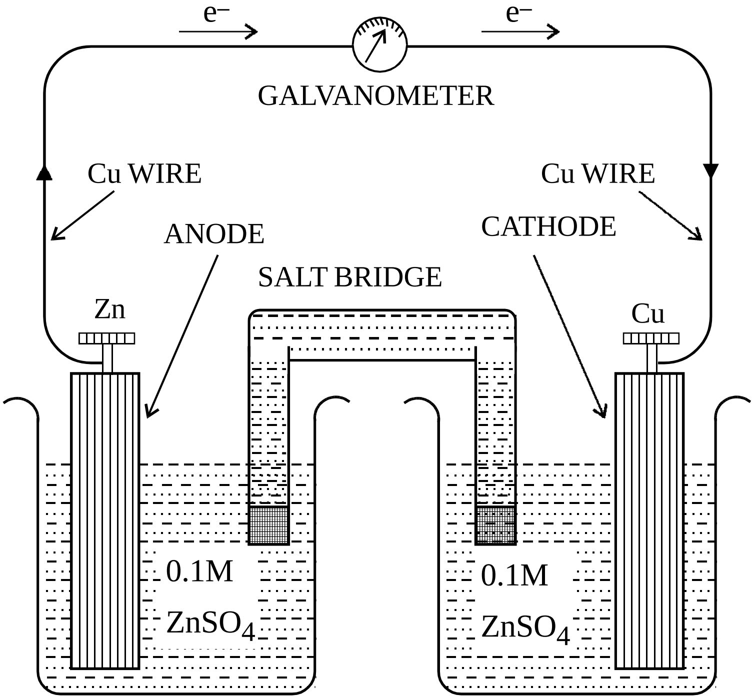


Fig. 3.4 Electrochemical cell

Working

(i) On connecting the two rods, zinc rod dissolves to from Zn^{2+} ion which goes into solution.

Thus, oxidation takes place at the Zn-anode (loss of electron)

$$Zn.\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e$$

This constitutes the Zn-$ZnSO_4$ half cell (oxidation half cell)

(ii) Electrons produced at the zinc-electrode flow through the copper wire and the Cu-electrode into $CuSO_4$ solution. Copper ions in the solution are reduced and copper is deposited on the cathode. Thus, reduction takes place at the copper electrode. (gain of electron).

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s).$$

This constitutes the Cu-$CuSO_4$ half cell (reduction half cell)

In the outer circuit electron flows from Zn-rod (anode) to Cu-rod (cathode). The conventional current flow is in opposite direction to that of flow of electrons.

(iii) **Salt bridge** is the device containing an electrolyte like KCl, KNO_3 etc. (in *agar* gel) in the U-tube which maintains continuity between the two half cells.

To sum up the functions in an electrochemical cell the following points are to be remembered.

(a) Electrochemical cell converts the energy produced in a chemical reaction to electrical energy.

(b) Anode is the electrode at which oxidation half reaction takes place.

(c) Cathode is the electrode at which reducation half reaction takes place.

(d) Electrons flow in the external circuit from anode to cathode.

(e) Current flows in opposite direction to the flow of electrons.

(f) Salt bridge maintains continuity between the solution in two half cells.

(g) The cell is represented by writing the oxidation half cell in the left hand side and reducation half cell in the right hand side with salt bridge in the middle indicated by two vertical lines.

$$\text{Zn} \mid \text{Zn}^{2+} \text{ (0.1 M)} \mid \text{Salt bridge} \mid \text{Cu}^{2+}, \mid \text{Cu. (0.1M)}$$

$$\text{or, simply, Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu.}$$

Daniell cell

The **galvanic cell** *in which* Zn - $CuSO_4$ *reaction occurs is known as* **Daniell cell.** Working principle of the cell has been described under galvanic cell. In the Daniell cell the salt bridge is replaced by porous pot, so that the two electrolytes remain separated but the ions diffuse through the pot. The arrangement is shown in Fig. 3.5.

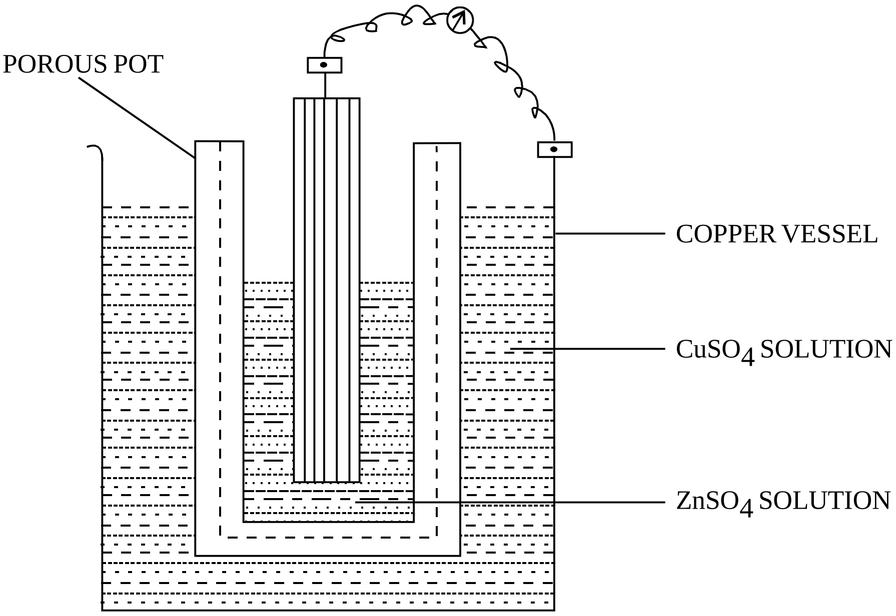


Fig. 3.5 Daniell cell

In this case copper sulphate solution is taken in a copper vessel which serves as **cathode.** Zinc sulphate solution is taken inside the porous pot in which zinc rod is dipped which serves as **anode.** Porous pot is placed in the copper sulphate solution. Working of the cell is similar to that described under galvanic cell.

3.12 CELL REACTIONS :

(i) Zn, | $ZnSO_4$ | KCl | Hg_2Cl_2 (s), | Hg.

Zinc rod dipped in $ZnSO_4$ solution. Salt bridge consists of KCl and the calomel electrode consitsts of Hg_2Cl_2 (s), Hg (*l*)

At anode $Zn (s) \longrightarrow Zn^{2+} + 2e$

At cathode $Hg_2Cl_2(s) + 2e \longrightarrow 2Hg(l) + 2Cl^-$

electron flows from znic-anode to mercury-cathode.

(ii) Zn, | $ZnSO_4$ | K_2SO_4 | HCl, | H_2, Pt

Here zinc rod is dipped in zinc sulphate solution Salt bridge consists of potassium sulphate. Hydrogen gas at one atomospheric pressure is passed through platinum electrode dipped in hydrochloric acid. Zinc rod serves as the anode and platinum electrode serves as cathode.

At anode $Zn (s) \longrightarrow Zn^{2+} (aq) + 2e$

At cathode $2H^+(aq)+2e \longrightarrow H_2(g)$

Electron flows from zinc electrode to hydrogen electrode.

(iii) Cu, | $Cu(NO_3)_2$ || $AgNO_3$ |Ag with KNO_3 solution as salt bridge.

At anode, $Cu(s) \longrightarrow Cu^{2+} (aq) + 2e$

At cathode, $Ag^+(aq) + e \longrightarrow Ag(s)$

Copper rod dipped in $Cu(NO_3)_2$ solution serves as anode and silver rod dipped in $AgNO_3$ solution serves as cathode. Election flows from copper to silver electrode.

(iv) Zn, $Zn(NO_3)_2$ || KNO_3 || $AgNO_3$, Ag with KNO_3, salt bridge

Similarly, at anode, $Zn \longrightarrow Zn^{2+} + 2e$

At cathode $Cu^{2+} (aq) + 2e \longrightarrow Cu(s)$

Electrons flow from zinc to silver electrode.

(v) Pt, H_2, HCl | K_2SO_4 || $CuSO_4$, Cu

Platinum electrode is dipped in hydrochloric acid. Hydrogen gas under one atmospheric pressure is bubbled through it. Copper electrode is dipped in $CuSO_4$ solution. K_2SO_4 solution serves as the salt bridge.

At anode, $H_2(g) \longrightarrow 2H^+(aq) + 2e$

At cathode $Cu^{2+} (aq) + 2e \longrightarrow Cu(s)$

Electrons flow from hydrogen to copper electrode.

3.13 ELECTRODE POTENTIAL :

In the electrochemical cell one electrode loses electrons (oxidation) and the other electrode gains electron (reduction). The **tendency of an electrode to lose or gain electrons is called**

electrode potential. It is called **oxidation potential,** where oxidation takes place at the electrode and **reduction potential** where reduction takes place at the electrode.

In the half cell, if the metal rod is suspended in a solution of one molar concentration and temperature is 298K, the electrode potential is called **standrad electrode potential (E^0).** If a gas is involved, instead of solution the standard conditions are 298K and one atmospheric pressure.

(i) Absolute electrode potential can not be determined (as no half cell works independently). Therefore , electrode potential is measured with respect to a standard electrode, **(Electrode potential of standard hydrogen electrode is zero).**

(ii) Electrode potential of an electrode changes with change in the concentration of ions in solution in contact with the electrode.

$$\text{Reduction potential of an electode} \propto \text{Concentration of ions}$$

$$\text{Oxidation potential of an electrode} \propto \frac{1}{\text{Concentration of ions}}$$

(iii) Electrode potential is expressed in volts.

Standard hydrogen electrode is used as reference electrode to determine electrode potentials of other electrodes.

3.14 SINGLE ELECTRODE POTENTIAL :

When the two half cells constituting an electrochemical cell is connected through a voltmeter to measure the potential difference between the two electrodes, this is called the e.m.f. of the cell. The contribution of each electrode to the cell potential is called **single electrode potential.** But the potential of a single electrode cannot be measured. Therefore, one electrode is chosen arbitrarily as a standard electrode (whose potential is known) to measure the potential difference between the standard electrode and any other electrode. A standard (normal) hydrogen electrode is taken as the standard reference electrode and its standard electrode potentail is taken to be zero volt.

Standard hydrogen electrode : It consists of a platinum foil coated with finely divided platinum black and dipped in an acid solution of one molar concentration. Hydrogen gas at a pressure of one atmosphere is continuously bubbled into the solution and temperature is maintained at 298 K. The reaction taking place at the electrode is

$$H_2(g) \longrightarrow 2H^+(aq) + 2e$$

$$2H^+(aq) + 2e \longrightarrow H_2(g)$$

Depending upon the type of reaction, hydrogen electrode can act as an anode or cathode in the electrochemical cell. Potential of all other electrodes are found by coupling it with a standard hydrogen electrode.

Thus, single electrode potential of an electrode is measured by joining it with standard hydrogen electrode (using salt bridge) and measuring the e.m.f. of the galvanic cell.

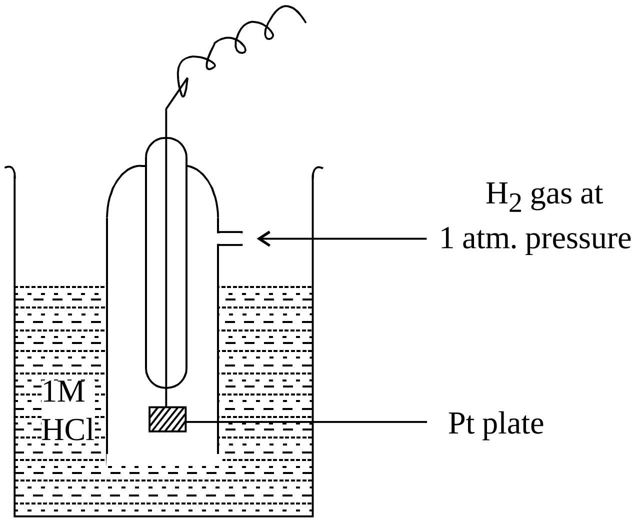


Fig. 3.6 Standard Hydrogen electrode

3.15 NERNST EQUATION :

Nernst gave a relationship between reduction of an electrode and concentration of ions in the electrode reaction.

$$M^{n+}(aq) + ne \longrightarrow M(s)$$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{M}{[M^{n+}]}$$

As the concentrations of pure solids and liquids are taken as unity, the equation can be written as–

$$E = E^0 + \frac{2.303RT}{nF} \log (M^{n+})$$

where, $R = 8.31\ JK^{-1}\ mol^{-1}$

T = Temperature in Kelvin, usually 298 K

n = Number of moles of electrons

F = Faraday = 96,500 coulombs.

Equilibrium constant from Nernst Equation

Consider the redox reaction in a cell at equilibrium

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

Equilibrium constant, $K_c = \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$. From Nernst equation, we have

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = E^0 - \frac{0.0591}{2} \log K_c$$

or, $E^0_{cell} = \frac{0.0591}{2} \log K_c$ at 298 K.

or, $\mathbf{E^0_{cell} = \frac{2.303RT}{nF} \log K_c}$ **(General equation)**

Free Energy Change in Electrochemical cell

In electrochemical cell, chemical energy is converted into electrical energy. Electrical energy is produced due to the work done in the cell and electrical work done is equal to the decrease in free energy. Change in free energy of the system (ΔG) is negative which indicates that electrical work is done in the system on the surroundings.

Electrical work done = Quantity of electricity flowing × E.m.f. of the cell.

In a cell reaction, if 'n' moles of electrons are transferred, the quantity of electricity following = nF Faradays

Suppose E_{cell} = E.m.f. of the cell.

$\therefore$ Electrical work done = nF × E.m.f. of cell = $nF.E_{cell}$

For a spontaneous reaction, ΔG is negative.

Under standard condition, i.e. molar Conc. = 1M, T = 298 K,

$\Delta G^0 = -nF\, E^0$ cell where ΔG^0 is the standard free energy change.

Then, $\Delta G^0 = -$ RT ln K_c where 'K_c' is the equlibrium constant of cell reaction.

Therefore, $\Delta G^0 = - 2.303$ RT log K_c

Using this equation either ΔG^0 or K_c can be calculated.

3.16 ELECTROMOTIVE FORCE (E.M.F.) OF A CELL :

Electrochemical cell is made of two half cells containing two electrodes. One of the electrodes must have a higher electode potential than the other electode. Due to this potential difference between the two electodes electrons flow from electrode of higher potential to the electrode at lower potential. The difference between the electrode potentials of two half cells is called as **electromotive force** (e.m.f.) of the cell or **cell potential** or **voltage**.

E.m.f. of a cell is measured by connecting the voltmeter between the two electrodes of a cell. Magnitude of e.m.f. depends upon the nature of the electrodes and concentration of solutions of the two half cells.

Example - Daniell cell Zn, $ZnSO_4$ (1M) | $CuSO_4$ (1M), Cu.

Concentration of the solutions is 1M and temperature 298 K

E.m.f. of the cell = 1.10 volts.

Therefore, $E_{cell} = E_{anode} - E_{cathode}$ (in terms of oxidation potential)

and $E_{cell} = E_{cathode} - E_{anode}$ (in terms of reduction potential)

An electrode with higher oxidation potential (lower reduction potential) is called anode and an electrode with lower oxidation potential (higher reduction potential) is called cathode.

3.17 ELECTROCHEMICAL CELLS :

Types of Electrochemical cells

As discussed earlier, electrochemical cells are those in which the chemical energy is converted to electrical energy. Mainly, there are two types of electrochemical cells which produce electricity from a chemical reaction. They are

(i) Primary cells or Dry cells or Primary batteries

(ii) Secondary voltaic cells or Reversible cells.

(i) Primary cells (Dry cells)

Any battery or dry cell used for production of electrical energy is a voltaic cell or galvanic cell where chemical energy of the redox reaction is converted to electrical energy. In this type of cell, once the chemicals are consumed, further reaction is not possible and the cell stops producing electricity. Any attempt to regenerate by reversing the current flow through the cell from an external source of electrical energy fails. The household batteries like Eveready, Panasonic, Nippo etc are all primary batteries. They are named as ‘‘dry cells’’ or ‘‘dry batteries’’ because they do not use any solution. Dry cells are light, compact and their voltage do not vary appreciably during use. A single cell has a potential of nearly 1.5V.

Other such cells include ‘‘Mercury cells’’ also called ‘‘botton cells’’ suitable for low current devices like watches, hearing aids etc and the cell potential of each units is around 1.3 volts. Alkaline dry cells are similar to ordinary dry cells, but use concentrated KOH instead of NH_4Cl as in dry cells. The cell potential is around 1.5 volts.

(ii) Secondary voltaic cells or Reversible cells :

Secondary voltaic cells or Reversible cells are those in which the original reactants of the cell are regenerated by passing direct current from an external source in the opposite direction i.e. they can be recharged. A good secondary cell can be discharged (while supplying electric current) and recharged several times for reuse.

Lead accumulator or Lead storage battery :

Lead accumulator or Lead storage battery is the most important secondary cell commonly used in automobiles and inverters.

It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. The electrolyte is a 38% solution of sulphuric acid ($\approx$ 4M). The whole container is made of either glass or a polymeric material like bakelite (Fig. 3.7). The oxidation half cell is Pb/H_2SO_4 and the reduction half cell is PbO_2 / H_2SO_4. Since H_2SO_4 is common to both the electrodes, the cell can be represented as $Pb \mid H_2SO_4 \mid PbO_2$

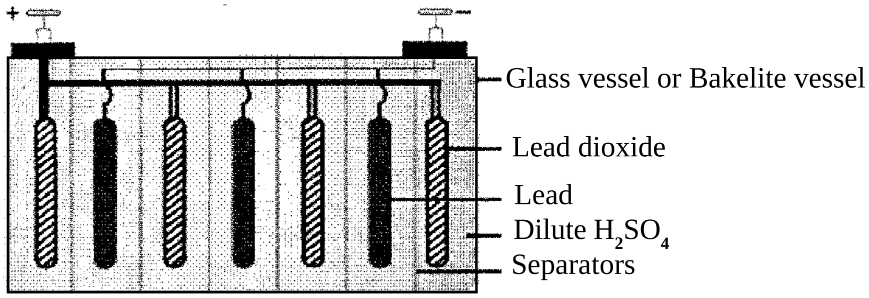


Fig. 3.7 Lead accumulator

When the battery is in use, it is said to be in **discharging mode**. While in discharging mode, the half cell reaction is as follows.

Oxidation half cell (at anode) : $Pb_{(s)} + SO_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^{-}$

Reduction half cell (at cathode) : $PbO_{2(s)} + SO_{4}{}^{2-}{}_{(aq)} + 4H^{+} + 2e^{-} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

The overall cell reaction is $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4\ (aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

When the battery is **re-charged** i.e. while in recharging mode, the opposite reaction takes place. At the oxidation half cell, reduction takes place

$PbSO_4(s) + 2e_{4}^{2-} \longrightarrow Pb(s) + SO_{\mathbf{4(aq)}}$ and at the reduction half cell, oxidation takes place.

$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + SO_{4}{}^{2-}{}_{(aq)} + 4H^{+} + 2e^{-}$

Thus, the over all reaction in recharging mode is

$2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

Water is consumed and H_2SO_4 is formed thus raising the specific gravity of the electrolyte. In the recharging process the positive electrode is coated with dark brown lead dioxide and the negative electrode with grey spongy lead. The emf of the cell rise and the electrical energy supplied is converted into chemical energy which is stored in the cell.

The charging process is monitored by measuring the specific gravity of the electrolyte. It varies from 1.28 when fully charged (H_2SO_4 and H_2O) to 1.2 when discharged (mostly water). The potential of a fully charged cell is 2.1 volts. It should not be discharged below 1.8V. This secondary cell has a low internal resistance i.e. it can deliver a high current. It can be recharged a very large number of times without deterioration.

Since each cell has a potential of about 2.1V, six such cells connected in series make up a 12 volt car battery.

Nickel -Cadmium Rechargeable cells (NiCad)

Now a days electronic gadgets like telephone, mobile phone, portable CD players, calculators, pagers, digital cameras etc use these type of secondary rechargeable cells. Though these are dry cells, they are **rechargeable**. The cell can be represented as

$Cd \mid OH^{-} \parallel NiO_2$

At the anode, $Cd + 2OH^{-} \longrightarrow Cd(OH)_2 + 2e^{-}$

At the cathode, $NiO_2 + 2H_2O + 2e^{-} \longrightarrow Ni(OH)_2 + 2OH^{-}$

The over all cell reaction is $Cd + NiO_2 + 2H_2O \longrightarrow Cd(OH)_2 + Ni(OH)_2$ during discharging mode i.e. while in use.

The potential of such a battery is around 1.2 volt.

Fuel Cells

Fuel cells are galvanic cells which convert the energy produced during combustion of fuels like hydrogen, methane, carbon monoxide, methanol etc. directly into electrical energy Electricity produced by thermal plants create a lot of pollution. Again, the primary cells can produce electricity for a short period since the quantity of the oxidising and reducing agent is limited. But in fuel cells, electrical energy can be obtained indefinitely as long as fuel supply is maintained for outside source. The most successful fuel cell is the hydrogen-oxygen fuel cell and was used in Apollo space programme to generate power and the water produced as byproduct was used as drinking water for the astronauts.

A hydrogen-oxygen fuel cell consists of three compartments separated by porous graphite electrodes (anode and cathode) impregnated with finely divided platinum or palladium as catalyst. The electrolyte in the central compartment is a resin containing concentrated aqueous sodium hydroxide solution. A schematic diagram of a H_2–O_2 fuel cell is given in Fig.3.8. Hydrogen as is fed into one compartment and oxygen gas, into another. The gases diffuse slowly through porous electrodes and so does the electrosyte. Chemical reactions take place. Hydrogen is oxidised at the anode and oxygen is reduced at the cathode in presence of electrolyte.

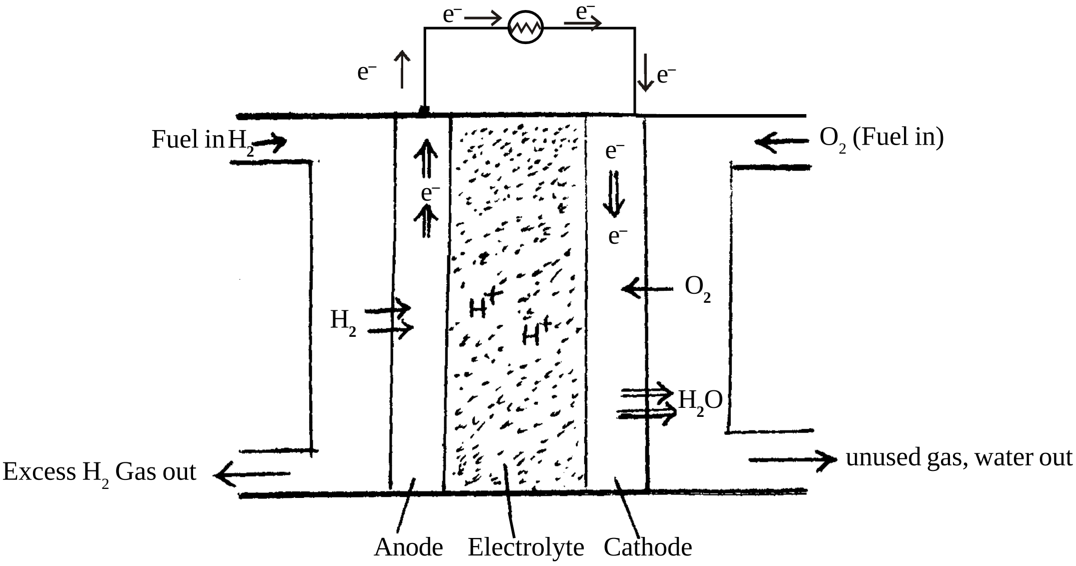


Fig. 3.8 Schematic diagram of H_2– O_2 Fuel cell

At the anode, hydrogen is oxidised to H^+ ions, which are neutralised by OH^- ions of the electrolyte.

$2H_2 \rightleftharpoons 4H^+ + 4e^-$

$4H^+ + 4OH^- \rightleftharpoons 4H_2O$

Thus, at the anode, $2H_{2(g)} + 4OH^-_{(aq)} \rightleftharpoons 4H_2O_{(l)} + 4e^-$

At the cathode, oxygen is reduced to OH^- ions

$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-_{(aq)}$

The net cell reaction is $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(l)}$

The water produced vapourises off as the cell is operated at a temperature above 100^0C. This is then condensed and used. The electrolyte allows only charged particles to move through it from anode to cathode and not electrons which move through the external circuit producing current.

An individual fuel cell produces a very small amount of direct current (DC) of about 1 volt. So several such fuel cells are stacked or placed in series to increase the current output. The main advantages of the fuel cells are

(a) they are non-polluting.

(b) like secondary cells, they do not need to recharge.

(c) the efficiency of fuel cells is about 70% compared to thermal plants where efficiency is about 40%

Recently, fuel cell technology has advanced a lot. Modified electrodes, catalysts and electrolytes have increased the efficiency of such cells considerably. They are used in automobiles, buses, air planes, boats, motor cycles and submarines.

3.18 ELECTROCHEMICAL SERIES :

When the potential of the electrode is measured by dipping the electrode in normal solution of one of its salts with normal hydrogen electrode, it is known as the **normal** electrode potential or standard electrode potential (E^0). for example, the standard electrode potential of Zn/Zn $^{2+}$ electrode can be determined by setting up a cell of the type.

$$Zn \mid Zn^{2+} \parallel H+ (a= 1) \mid H_2\ (1atm) \mid Pt$$

$$E_{cell} = E_{Zn,\ Zn^{2+}} - E_{H_2,\ H^+} = E_{Zn,\ Zn^{2+}} - 0)\ (\text{since } E_{H_2,\ H_+} = 0)$$

$$= E_{Zn,\ Zn^{2+}}$$

The e.m.f. of the cell was found to be 0.763 volt, hence $E_{Zn,\ Zn^{2+}}$ is 0.763 volt. Similarly, standard electrode potential of several other elements can be determined. *When the metals are arranged in the order of their standard electrode potentials on hydrogen scale, a series is obtained which is known as* **electrochemical series** or **electromotive potential series.**

Table 3.2 below gives the standard electrode potential E^0 of a number of electrodes at 298K. In this series, a negetive potential indicates the tendency greater than hydrogen to go into the solution in the ionic from. *Therefore* **the metal having more negative potential displaces those with more positive potentials from their solutions.**

Table 3.2 Standard electrode potentials (Reduction) at 298K

Electrode	Electrode reaction	E^0 (volts)
Li^+, Li	$Li^+ + e \rightleftharpoons Li\ (s)$	– 3.04
K^+, K	$K^+ + e \rightleftharpoons K\ (s)$	– 2.92
Ba^{2+}, Ba	$Ba^{2+} + 2e \rightleftharpoons Ba$	– 2.906
Ca^{2+}, Ca	$Ca^{2+}\ 2e \rightleftharpoons Ca\ (s)$	– 2.87
Na^+, Na	$Na^+ + e \rightleftharpoons Na(s)$	– 2.71
Mg^{+2}, Mg	$Mg^{2+} + 2e \rightleftharpoons Mg\ (s)$	– 2.370
Al^{3+}, Al	$Al^{3+} + 3e \rightleftharpoons Al(s)$	–1.660
Zn^{2+}, Zn	$Zn^{2+} + 2e \rightleftharpoons Zn\ (s)$	– 0.76
Fe^{2+}, Fe	$Fe^{2+} + 2e \rightleftharpoons Fe\ (s)$	–0.44
Cd^{2+}, Cd	$Cd^{2+} + 2e \rightleftharpoons Cd\ (s)$	– 0.40
Co^{2+}, Co	$Co^{2+} + 2e \rightleftharpoons Co\ (s)$	– 0.28
Ni^{2+}, Ni	$Ni^{2+} + 2e \rightleftharpoons Ni\ (s)$	–0.24
Sn^{2+}, Sn	$Sn^{2+} + 2e \rightleftharpoons Sn\ (s)$	–0.14
Pb^{2+}, Pb	$Pb^{2+} + 2e \rightleftharpoons Pb\ (s)$	–0.13
$2H^+$, H_2 (g), Pt	$2H^+ + 2e \rightleftharpoons H_2(g,\ 1\ atm)$	+ 0.00
Cu^{2+}, Cu	$Cu^+ + 2e \rightleftharpoons Cu$	+ 0.337
Ag^+, Ag	$Ag^+ + e \rightleftharpoons Ag$	+ 0.791

Application of Electrochemical series

(1) **To Calculate e.m.f. of a cell:** Standard e.m.f. (E^0) of a cell can be calculated by the following procedure.

- (i) Write the half cell reactions with their electrode potentials.
- (ii) Balance each half cell reaction to equate number of atoms and change.
- (iii) Balance the electrons in both the half cell reactions.
- (iv) Subtract equation with lower value of E^0 from the equation with higher value of E^0

E^0_{cell} = Redn. potential of Redn. half cell - Redn. potential of oxdn. half cell.

Example - To calculate e.m.f. of the cell Zn, Zn^{2+} | | Ag^+, Ag.

$$Zn(s) - 2e \longrightarrow Zn^{2+}, \quad E^0 = -0.76v \quad (i)$$

(Redn. potential)

$$Ag^+ + e \longrightarrow Ag, \quad E^0 = 0.79v. \quad (ii)$$

(Redn. potential)

Multiply eqn (ii) with 2 and subtract eqn (i) from it

Then, we have $Zn(s) + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

Thus, Zn– electrode acts as anode and Ag – electrode as cathode.

$E^0cell = E^0_{cathode} - E^0_{anode} = 0.79 - (-0.76) = 1.55$ volt.

(2) **To predict the anode or cathode in a cell.**

An electrode with higher oxidation potential (lower reduction potential) is taken as *anode.* The electrode with lower oxidation potential (higher reduction potential) is taken as *cathode.*

For example, in the cell, Zn l Zn^{2+} || Cu^{2+} | Cu.

E^0 for zinc = –0.763 volt, E^0 for copper = +0.337volts

(Redn. potential) (Redn. potential)

Therefore, Cu-electrode is the cathode and Zn-electrode is anode.

(3) **To predict whether a particular redox reaction can occur or not.**

For example, reaction $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$

Reducation potential of Cu = + 0.337volt and that of Zn = – 0.763volt

Thererfore, the above reaction can not occur. Cu-can not displace zinc as zinc has a higher position in the E.C. series.

But the reaction, $Cu^{2+} + Zn \longrightarrow Zn^{2+}$ Cu.

can occur and znic can displace copper from its salt solution.

(4) **To predict reactivity of elements.**

On the basis of electrode potentials, a given set of elements can be arranged in the order of their reactivity. An element whose oxidation potential is more (or reduction potential is less) is said to be more active. A more reactive metal can displace a less reactive metal from its solution, but not the vice-versa. For example, zinc can displace copper from its salt solution. In order of reduction potential the series can be arranged as follows.

Increasing order of Reactivity $\longleftarrow$

$$\text{Li} < \text{K} < \text{Ba} < \text{Ca} < \text{Na} < \text{Mg} < \text{Al} < \text{Zn} < \text{Co} < \text{Fe} < \text{Cd} < \text{Ni} < \text{Sn} < \text{Pb} < \text{H}_2 < \text{Cu} < \text{Ag}$$

$\longleftarrow$ Decreasing order of Reduction potential

The metals which are above hydrogen in electrochemical series can displace hydrogen from mineral acids, but the metals which are below hydrogen (Cu, Ag etc.) can not liberate hydrogen from mineral acids.

Problems on E.m.f. (1) Calculate the e.m.f. of the galvanic cells having following reactions.

(i) $2Cr\ (s) + 3Cd^{2+}\ (aq) \longrightarrow 2Cr^{3+}(aq) + 3\ Cd\ (s)$

(ii) $Fe^{2+}(aq) + Ag^{+}\ (aq) \longrightarrow Fe^{3+}\ (aq) + Ag\ (s)$

$E^0_{Cr^{3+}/Cr} = -0.73v$, $E^0_{Cd^{2+}/Cd} = -0.40v$, $E^0_{Fe^{2+}/Fe^{3+}} = 0.77v$

$E^0_{Ag^{+}/Ag} = +0.80v$

Solution

(i) Cell is represented as $Cr/Cr^{3+}(aq) \,||\, Cd^{2+}\ (aq) \,|\, Cd$.

$E^0_{cell} = E^0_{\ cathode} - E^0_{anode} = -0.40 - (-0.73) = -0.40 + 0.73 = 0.33$ volt

(ii) Cell is represented by $Fe^{2+} \,|\, Fe^{3+}(aq) \,||\, Ag+ \,|\, Ag$

$E^0_{cell} = 0.80 - (0.77) = 0.03$ volt.

3.19 CORROSION :

The slow coating of surfaces of metallic objects with oxides or other salt of the metal is called **corrosion**. In corrosion, a metal is oxidised by loss of electrons to oxygen by which the metal is positively charged and oxygen is negatively charged. Thus the metal oxide is formed. Corrosion of metal iron takes place in presence of water and air. Though the chemistry of corrosion is quite complex, it may be considered essentially as an electrochemical phenomenon. At the place of corrosion oxidation takes place and that spot behaves as anode. The anodic reaction can be written as:

Anode : $2Fe(s) \longrightarrow 2Fe^{2+} + 4e-$ .... (1)

$E^0_{Fe^{2+}/Fe} = -0.44\ V$

Electrons released at the anode move through the metal and go to another spot on the metal and reduce oxygen in presence H^+ ion. The H^+ ion is supposed to be generated from carbonic acid (H_2CO_3) formed due to dissolution of carbon dioxide in air with water ($CO_2 + H_2O \longrightarrow H_2CO_3$). At this cathodic spot the following reaction takes place

Cathode : $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O\,(l)$ .... (2)

$E^0_{H^+ | O_2 | H_2O} = 1.23\ V$

By adding equation (1) and (2), the overall reaction is obtained.

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O\,(l)$$

$$E^0_{cell} = 1.23\ V - (-0.44V) = 1.67\ V \text{ .... } (3)$$

The Fe^{2+} ions are further oxidised by the atomspheric oxygen to Fe^{3+} ions which come out as a rust in the form of hydrated ferric oxide ($Fe_2O_3 \cdot x\ H_2O$) and with further production of hydrogen ions. Like iron, silver, copper, bronze articles also get corroded by developing oxides or other salts on their surfaces. Prevention of corrosion is of great importance because of damage of structures, buildings, bridges etc. by it. Corrosion can be prevented by coating the surface with paints, by some other chemicals or by covering the sufaces of corrosion prone metals with inert metals like Zn, Sn, Pt etc. An electrochemical method is to provide a sacrificial electrode of another metal (like Zn, Mg, Sn etc.) which corrodes itself but keep the object intact.

CHAPTER (3) AT A GLANCE

1. **Electrolytic dissociation** The process of splitting up of an electrolyte into positively and negatively charged ions is called electrolytic dissociation.

2. **Degree of dissociation (α)** The fraction of the total substance which exists as ions in solution is called its degree of dissociation.

3. **Electrolysis** The process of chemical decomposition of an electrolyte in solution or in fused state by the passage of electric current is known as electrolysis.

4. **Faraday's laws of electrolysis:** *1st law* **–** The mass of substance liberated at the electrode as a result of electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. (W = z.c.t)

   2nd law: When the same quantity of electricity is passed through different electrolytes connected in series, then the mass of different substances liberated at the electrodes are proportional to their chemical equivalents.

5. **Electrochemical equivalent** It is defined as the mass of substance liberated when one ampere of current is passed through the electrolyte for one second (or one coulomb of electricity passed)

$$1\text{Faraday} = 96,500 \text{ coulombs. E.C.E. (z)} = \frac{\text{Chemical equivalent}}{96,500}$$

6. **Specific conductance (k)** Specific resistance is defined as equal to the resistance in ohms of a material of 1 cm length and the 1 sq. cm in area of the cross section. Reciprocal of specific resistance is specific conductance. Unit = $\text{ohm}^{-1}\text{cm}^{-1}$.

7. **Equivalent conductance (Λ)** is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

   Unit = $\text{ohm}^{-1}\text{cm}^{2}$/g.equiv

8. **Molar conductance(μ)** is defined as the conducting power of all the ions furnished by one gram mole of electrolyte in a given solution.

   Unit = ohm^{-1}. $\text{cm}^{2}\text{mole}^{-1}$

9. **Kohlrausch law** Equivalent conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions. $\Lambda_0 = \lambda^0{}_c + \lambda^0{}_a$

10. **Electrochemical cell** It is a device in which redox reaction takes place indirectly and the chemical energy is converted to electrical energy. Lead accumulator is a secondary reversible voltaic cell used in automobiles, inverters etc.

11. **Electrode potential** Tendency of an electrode to lose or gain electrons is called its electrode potential. Electrode potential at 298K and in one molar concentration is called *standard electrode potential.*

12. **E.m.f. of cell** $E_{cell} = E_{cathode} - E_{anode}$ (in terms of reduction potential).

13. **Electrochemical series** Arrangements of elements in the increasing order of their standard electrode potentials (reduction potentials)

QUESTIONS

A. Very Short answer type questions (One mark each) :

1. Give the correct answer

(i) What happens to equivalent conductance when solution is diluted ?

(ii) What is the amount of substance liberated by the passage of 1 Faraday of electricity ?

(iii) Define specific conductance.

(iv) Define equivalent conductance.

(v) Define molar conductance.

(vi) State Kohlrausch law.

(vii) What is electrode potential ?

(viii) What is the unit of equivalent conductance ?

(ix) Define electrochemical equivalent.

(x) What is the unit of molar conductance ?

(xi) What is cell constant ?

(xii) What is electromotive force ?

(xiii) In the outside circuit of a cell electron flows from which electrode ?

(xiv) Which gas is liberated at anode due to electrolysis of molten sodium hydride ?

(xv) Which gas is liberated at cathode due to the electrolysis of aqueous solution of sodium chloride ?

(xvi) What is the unit of e.m.f. ?

(xvii) What is an electrochemical cell ?

(xviii) Define degree of dissociation of an electrolyte ?

(xix) What is the unit of specific conductance ?

(xx) What is the basis on which anode or cathode is identified in a cell ?

(xxi) What is the relationship between chemical equivalent and electrochemical equivalent ?

(xxii) What is the function of a salt bridge ?

(xxiii) What happens to the conductance of a solution when temperature is increased ?

(xxiv) Oxidation and reduction take place at which of the electrodes in a cell ?

(xxv) What is the e.m.f. of a standard hydrogen electrode ?

(xxvi) What do you mean by strong electrolyte ?

(xxvii) During electrolysis of aqueous solution of NaCl at which electrode chlorine is liberated.

(xxviii) What is the charge in coulombs on CO_3^{2-} ion ?

(xxix) How many coulombs of electricity are required to produce 20 gram of calcium form molten $CaCl_2$?

(xxx) Write the cell representation when Zn electrode is connected to standard hydrogen electrode :

(xxxi) What is the charge in coulombs on Cu^{+2} ion?

(xxxii) In an electrochemical cell, reduction taken place at ______.

(xxxiii) What is the relation between standard e.m.f. of a cell and equilibrium constant?

(xxxiv) One faraday of electricity will deposit __________ weight of a metal.

(xxxv) What is the unit of equivalent conductance? How does the equivalent conductance vary with dilution?

(xxxvi) What is the basis on which anode or cathode is identified in a chemical cell?

(xxxvii) What do you understand by strong and weak electrolytes?

(xxxviii) How many coulombs of electricity are required to produce 20g of calcium from molten $CaCl_2$?

(xxxix) Represent the cell and the standard emf of the cell having the following reaction.

$$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightleftharpoons 2Cr^{3+}_{(aq)} + 3Cd(s)$$

$$E^\circ_{Cr^{3+}/Cr} = 0.73V \text{ and } E^\circ_{Cd^{2+}/Cd} = -0.40V$$

(xl) State and explain Kohlrausch's law.

(xli) How many moles of aluminium can be prepared by the electrolysis of molten alumina with a current of six Faradays.

(xlii) Explain why copper sulphate solution cannot be stored in zinc vessel?

2. Fill in the blanks :

(a) Conductance of a solution ___________ with dillution.

(b) Amount of substance liberated by the passage of one coulomb of electricity through an electrolyte is called ____________

(c) The more __________ the standard reduction potential, the _____________ is the ability to displace hydrogen from acids.

(d) Conduction of electricity in solution is due to _____________

(e) At ___________ electrode in a cell oxidation takes place.

(f) At ______ electrode in a cell reduction takes place.

(g) In electrochemical cell _________ energy is concerted to _________ energy.

(h) E.m.f. of a standard hydrogen electrode is ___________.

(i) Zinc has a _____________ tendency to lose electrons than copper.

(j) In a galvanic cell electron flows from __________ to __________ through the connecting wires.

(k) In a galvanic cell the difference between reducation potential of cathode and anode is called ____________

(l) An aqueous solution of silver nitrate ____________ be stored in a copper vessel.

(m) According to electrochemical series zinc is ___________ active than iron.

(n) Electrolysis of molten sodium hydride liberates _________ gas at the ________.

(o) Electrochemical equivalents of two metals are in the ratio of their __________

(p) E.C.E. × ____________ = Chemical equivalent.

(q) Mass of substance liberated at the electrode is directly proportional to _________

(r) On electrolysis of aqueous solution of sodium chloride __________ is liberated at cathode.

(s) The unit of cell constant is ____________

(t) The unit of equivalent conductance is _______________ .

(u) The unit of specific conductance is ____________

(v) In a Daniell cell copper vessel serves as ____________

(w) In electrochemical series the elements are arranged in order of ________reduction potentials.

(x) Standard electrode potential of hydrogen electrode is _______________

(y) Specific conductance × ____________ = Equivalent conductance.

(z) Conductance of a solution __________ with increase in temperature.

(z1) In an electrochemical cell reduction takes place at _________

(z2) One Faraday of electricitys will deposit _________ weight of a metal.

(z3) A current of 0.5 ampere flowing for 30 minutes deposits 0.2964g of a metal at the cathode. Calculate the equivalent mass of the metal.

3. **Give reasons :**

(a) Sodium can not be extracted by the electrolysis of aqueous solution of sodium chloride.

(b) Silver nitrate solution can not be stored in a copper vessel.

(c) Copper sulphate solution can be stored in a zinc vessel.

(d) Blue colour of copper sulphate solution is dishcharged by dipping an iron rod in it.

4. **Answar the following :**

(a) What is the difference between a galvanic cell and electrolytic cell ?

(b) What is the difference between electrode potential and cell potential ?

(c) How electrochemical series predicts the feasibility of a reaction ?

(d) What is the function of a salt bridge ?

(e) What is the relation between standard e.m.f. of a cell and equilibrium constant ?

5. The molar conductance of a solution of $AlCl_3$ in found to be 130 mho cm^2 mol^{-1} at 298K. What would be its equivalent conductance at the same temperature ?

B. Short answer type questions (Two marks each) :

1. Distinguish between strong electrolytes and weak electrolytes.
2. Define conductance, specific conductance and equivalent conductance.
3. What are the electrolytic products of fused NaCl? Write equations.
4. What is the difference between electrochemical equivalent and chemical equivalent?
5. What is electroplating?
6. What are the main difference between electromotive force of cells and cell potential?
7. Write down the notations of representing cathode, anode, and galvanic cell.

8. What are reference electrodes? What is the electrode potential?
9. What are fuel cells? What are its advantages?
10. Write the reasons of corrosion.
11. How metal corrosion is prevented?
12. Calculate the time required for a current of 2 amp. to decompose one gram mole of water.
13. When a current strength of 965 amp. can deposit 0.9g of Al metal in 20 sec. What is the efficiency of electrolysis?
14. Standard oxidation potential of iron electrode is + 0.44V. Calculate the potential of Fe, $FeSO_4$ (1M) at 25°C.
15. What is lead storage battery?
16. Write down Nerst equation. How is it useful in calculating the potential of a cell?
17. 1N salt solution surrounding two platinum electrodes, 2.1 cm apart and 6.3 cm^2 in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductance of the solution.
18. $Ag^+ + e^- \rightarrow Ag$; $E^0 = +0.8$ V and $Zn^{2+} + 2e \rightarrow Zn$; $E^0 = -0.76$ V.
    Calculate the cell potential for the reaction, $2Ag + Zn^{2+} \rightarrow Zn + 2Ag^+(aq)$
19. Write down the working of mercury dry cell.
20. Write down the working of nickel-cadmium cell.

C. Short answer type questions (Three marks each) :

1. What happens to the pH of NaCl solution after electrolysis and why ?
2. Specific conductance of a 0.12 N solution of electrolyte is 2.4×10^{-2} ohm^{-1} cm^{-1}. Calculate its equivalent conductance.
3. What is electrochemical series ? What is its significance ?
4. The equivalent coductance of 0.001N KCl solution is 147 ohm^{-1} cm^2 gm eq^{-1} at 25°C. Find the specific conductance.
5. The specific conductance of 0.12N solution of an electrolyte is 0.024 ohm^{-1} cm^{-1}. Find its equivalent conductance.
6. Explain why rusting of iron is faster in saline water than in ordinary water. Write equations.
7. An electronic current is passed through two solutions (a) $AgNO_3$ and (b) a solution of 10g of blue vitriol in 500 ml of water using platinum electrodes separately. After 30 min. it was found that 1.307g Ag was deposited. What is the concentration of Cu^{2+} after electrolysis?
8. A current of 1.7 amp is passed through 300 mL of 0.16 M $ZnSO_4$ solution for 230 seconds with a current efficiency of 90%. Find the concentration of divalent zinc in solution.
9. The standard potential of Ni^{2+}/Ni is – 0.236 V. If this electrode is coupled with a hydrogen electrode, the emf of the cell becomes zero. Calculate the pH of the acid used in electrode.
10. E^0 values for $Fe^{3+} + 3e \rightarrow Fe$ and $Fe^{2+} + 2e \rightarrow Fe$ are – 0.036 V and –0.44 V respectively. Calculate E^0 nnd ΔG^0 for the cell reaction $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$.

11. When salt spread on road to melt ice and snow during winter, corrosion of motor cars is a major problem, justify.

12. E° of Ag electrode is 0.8V and solubility product of AgI is 1×10^{-16}. Calculate the potential of Ag electrode at 25°C in a saturated AgI solution in water.

D. Long answer type questions (7 marks each) :

1. State and explain Faraday's laws of electrolysis. How many grams of Aluminium can be produced by the elctrolysis of molten alumina with a current of 3 amperes for 10 minutes.

2. Define and explain equivalent conductance and specific conductance. A 0.1N solution of NaCl has a specific conductance of 0.00119 mhos cm^{-1}. Find its equivalent conductance.

3. **Explain the terms :**

   (a) Conductance (b) Specific conductance.

   (c) Equivalent conductance (d) Molar conductance

4. State and explain Kohlrausch law. How can this law be used to find equivalent conductance of acetic acid at infinite dilution ?

5. State and explain Faraday's second law of electrolysis. How does this help in determining equivalent mass of the metal ?

6. **Write notes on :**

   (a) Electroplating (b) Electrorefining (c) Galvanic cell

   (d) Electrotyping (e) Electrochemical series

7. What is meant by electrode potential ? Explain in the half cell reactions of

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

8. Discuss the applications of electrochemical series.

9. A current of 0.5 amperes was passed through a solution of silver nitrate for six minutes. Find the mass of silver deposited (At. mass of Ag = 108)

10. The resistance of N/5 solution of an electrolyte in a cell was found to be 45 ohm. Calculate the equivalent conductance of the solution if the electroldes in a cell are 2.2 cm apart and have an area of 3.8 sq.cm.

11. State and explain Faraday's laws of electrolysis. 0.2015gm of copper were deposited by a current of 0.25 ampere in 45 minutes. What is the E.C.E. of the copper ?

12. Describe the construction and working of Daniell cell.

13. The following reaction occurs in a cell $Zn(s) + Co^{2+} \rightleftharpoons Co(s) + Zn^{2+}$.

    Write the elctrode reaction and findout the e.m.f. cell, given

    $Zn \longrightarrow Zn^{2+}, E^0 = 0.76v$ $Co \longrightarrow Co^{2+}, E^0 = 0.28v.$

14. What are the difference between ionisation and electrolysis ? What are strong and weak electrolytes, discuss with examples.

15. What is the difference between e.m.f. and potential difference ?

16. Give two applications of electrolysis.

17. Define equivalent and molar conductance. Give their relationship with specific conductance. How does equivalent conductance vary with increase in temperature ?

    How many atoms of calcium will be deposited from fused $CaCl_2$ by a current of 25 milliamperes passes for 60 seconds ?

18. State and explain equivalent conductance and specific conductance. Calculate the mass of silver deposited when a current of one ampere is passed through $AgNO_3$ solution for 1 hour. The electrolchemical equivalent of silver is 1.21×10^{-3}

19. Define and explain specific conductance and equivalent conductance. Why on dilution the specific conductance decreases and equivalent conductance increases ?

    A 0.1 N solution of sodium acetate has a specific conductance 0.0061 ohm^{-1} cm^{-1}. Calculate the equivalent conductance of the solution.

20. What is a galvanic cell ? Explain with an example. Calculate the half cell potential at 298K for the reaction Cu^{2+} (aq) + 2e $\longrightarrow$ Cu (s), where $[Cu^{2+}]$ is 5.0 M and E^0 is + 0.34 volt.

21. State and explain Faraday's laws of electrolysis. 0.2015g of copper was deposited by a current of 0.25 amp in 45 min. Find out the electrochemical equivalent of copper.

22. Define equivalent and molar conductnce. Give their relationship with specific conductance. How does equivalent conductance vary with increase in temperature? How many atoms of calcium will be deposited from fused $CaCl_2$ by a current of 25 milliamperes passed for 60 secs?

23. State and explain equivalent conductance. Calculate the mass of silver deposited when a current of one ampere is passed through $AgNO_3$ solution for 1 hour. The electrochemical equivalent of silver is 1.21×10^{-3}.

24. State and explain Faraday's laws of electrolysis.

    When a current of 1.5 amp. strength is passed through a solution of salt of a metal (at mass = 112) for 15 min, 0.783g of the metal is deposited. Find out the valency of the metal.

25. Describe specific and equivalent conductance. How are they related? What is the effect of dilution on them?

    The specific conductivity of an N / 20 solution of KCl at 25°C is 0.002765 mhos. If the resistance of the same solution placed in the cell is 2000 ohms, what is the cell constant?

26. Define and explain specific conductance and equivalent conductance.

    A 0.01 N solution of NaCl has a specific conductance of 0.001112 ohm^{-1} cm^{-1}. Find its equivalent conductance.

27. State and explain Faraday's laws of electrolysis.

    How many grams of chlorine will be produced by the electrolysis of molten sodium chloride with a current of 5.5 amperes for 25 minutes?

E. Multiple choice questions (One mark each) :

(i) The electric charge for electrode deposition of the gram equivalent of a substance is–

(a) one ampere for one second (b) 96500 coulombs
(b) charge on one mole of electrons (d) one ampere for one hour

(ii) Which is the strongest reducing agent ?

(a) Zn(s) (b) Cr (s)
(c) $H_2(g)$ (d) $Fe^{2+}(aq)$

(iii) Faraday's law of electrolysis are retated to

(a) atomic number of cation (b) atomic number of anion
(c) equivalent mass of electrolyte (d) speed of the cation

(iv) Molten sodium chloride conducts electricity due to the presence of ______

(a) free electrons (b) free ions
(c) free molecules (d) atoms of sodium and chlorine

(v) The unit of specific conductance is ________

(a) Ohm (b) $Ohm^{-1}cm^{-1}$
(c) Coulomb (d) Faraday

(vi) The electrode at which the electrons flow into an electrolyte is ___________

(a) anode (b) metal
(c) cathode (d) solid

(vii) The charge (in coulomb) on the Na+ ion (oxide) is __________

(a) 96500 (b) 4.8 × 10+19
(c) 4.8×10^{-19} (d) 1.6×10^{-19}

(viii) 96500 Coulomb will deposit __________ of metal.

(a) one electrochemical equivalent (b) one gm
(c) one gm. equivalent (d) One gm. molecular mass.

(ix) Which one of the following is a weak electrolyte ?

(a) sodium chloride (b) copper sulphate
(c) acetic acid (d) Sodium chloride.

(x) ____________ is an example of strong electrolyte.

(a) Ammonium hydroxide (b) Acetic acid
(c) Sodium acetate (d) Sodium chloride

(xi) Which is the strongest reducing agent ?

(a) Zn(s) (b) Cu(s)
(c) $H_2(g)$ (d) $Fe^{2+}(aq)$

(xii) The unit of cell constant is ___________

(a) $ohm^{-1}cm^{2}$ (b) cm^{-1}
(c) $ohm^{-1}cm^{-1}$ (d) $ohm^{-1}cm^{2}/gm.equiv.$

(xiii) For a redox reaction to proceed in a cell, the e.m.f must be

(a) positive (b) negative

(c) zero (d) fixed

(xiv) Moles of aluminium produced by passing six Faraday of electricity is __________

(a) 2 moles (b) 6 moles

(c) 3 moles (d) 1 moles.

(xv) __________ grams of chlorine can be prepared by the electrolysis of molten sodium chloride with 10 amperes current passed for 10 minutes.

(a) 2.2 (b) 4.4

(c) 3.8 (d) 5

(xvi) Which of the following type of reactions occur at the anode during electrolysis ?

(a) Dissociation (b) Substitution

(c) Reduction (d) Oxidation

ANSWERS

A.1. (i) increases (ii) 1 gm equivalent (viii) ohm^{-1}cm^{2} equiv^{-1} (x) ohm^{-1}cm^{2}mol^{-1} (xiv) hydrogen (xv) hydrogen (xvi) volt (xix) ohm^{-1}cm^{-1} (xxiii) increases (xxiv) anode-oxdn, cathode-redn (xxv) zero (xxvii) anode (xxviii) 3.2×10^{-19} coulombs

2. (a) increases (b) Electrochemical equivalent (c) negative, greater (d) ions (e) anode (f) cathode (g) chemical, electrical (h) zero (i) greater (j) anode, cathode (k) cell potential (l) can not (m) less (n) hydrogen, anode (o) chemical equivalent (p) 96500 (q) chemical equivalents (r) hydrogen (s) cm^{-1} (t) ohm^{-1}cm^{2} gm. equiv^{-1} (u) ohm^{-1} cm^{-1} (v) cathode (w) decreasing (x) zero (y) V (z) increases.

E. Multiple Choice Type :

(i)	b	(v)	b	(ix)	c	(xiii)	a
(ii)	a	(vi)	c	(x)	d	(xiv)	a
(iii)	c	(vii)	d	(xi)	a	(xv)	a
(iv)	b	(viii)	c	(xii)	b	(xvi)	d

* * *

UNIT - IV

CHAPTER - 4

CHEMICAL KINETICS

Chemical kinetics is that branch of physical chemistry, which deals with the study of the rate of chemical reactions and the mechanism by which they occur. In other words, it deals with how fast or slow the reaction is and through what mechanism a particular chemical reaction occurs. The rate of a chemical reaction depends upon the experimental conditions such as nature of reactants temperature, catalysts, the concentration of the reactants and certain energy radiations.

4.1 TYPES OF CHEMICAL REACTIONS :

On the basis of the speed, the chemical reactions can be classified into the following categories.

(a) **Fast or Instantaneous reactions :** These are reactions which are completed immediately. These reactions occur so fast that, it is practically impossible to measure the exact speed of such reactions.

For example, (i) the precipitation of silver chloride, and (ii) the decolourisation of acidified potassium permanganate with ferrous sulphate solutions are instantaneous reactions.

$$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)}\downarrow + NaNO_{3(aq)}$$

$$2KMnO_4 + 8H_2SO_4 + 10\,FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(b) **Moderate reactions :** There are many reactions which proceed at measurable speed. The rates of such reactions can be conveniently measured. Some common examples of such reactions are,

(i) Hydrolysis of ethyl acetate in presence of sodium hydroxide (Saponification of ester)

$$\underset{\text{(ethyl acetate)}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{(sodium acetate)}}{CH_3COONa} + C_2H_5OH$$

(ii) Hydrolysis of the aqueous solution of sucrose in presence of HCI. (Inversion of cane sugar)

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

(c) **Extremely slow reactions :** These are reactions which take a long time to complete. These reactions proceed with very slow speed and it is not possible to measure the exact speed of such reactions.

Rusting of iron is an example of extremely slow reaction.

$$Fe + H_2O + CO_2 \longrightarrow \underset{\text{(Rust)}}{Fe(OH)\ (HCO_3)}$$

4.2 THE RATE OF A REACTION :

The quantity of a reactant species consumed or the quantity of a product species formed in unit time in a chemical reaction is termed the rate of that reaction. As the reaction proceeds the concentration of the reactants gradually decrease, while that of products gradually increase, with time. This can be illustrated in the following figure. But the concentration does not increase or decrease uniformly.

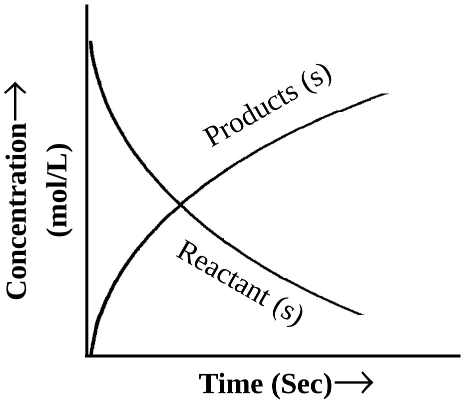


Fig. 4.1 Plot of concentration Versus time

Consider a reaction, A ⟶ B

$$\therefore \quad \text{Rate of the reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

Here, the –ve sign is due to that fact that the molar concentration of reactant A decreases with time and the +ve sign is due to that fact that concentration of B increases with time. Since rate of reaction is never uniform, it changes with time. Since rate of reaction is directly propertional to the concentration of the reactants, it can be concluded that the rate of the reaction gradually falls with time. Thus we can not measure the velocity or rate of the reaction simply by dividing the amount of reactant transformed by the time taken for such a transformation.

It is essential, therefore, to consider an infinitesimally small interval of time dt, an interval so small that it may be assumed that the velocity is constant throughout the interval and if dx is the amount of substance transformed in this interval, then the velocity of reaction at that instant is given by $\frac{dx}{dt}$

Thus rate of the reaction $\frac{dx}{dt} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$

The rate of the reaction is also represented by $-\frac{dc}{dt}$, where dc is the concentration of reactant left behind after a short interval of time dt.

$$\therefore \quad \text{Rate of the reaction} = -\frac{dc}{dt} = +\frac{dx}{dt}$$

Determination of rate of a reaction :

We know that the rate of a reaction is directly proportional to the molar concentration of the reacting species. The molar concentration decreases progressively but not uniformly. Hence, the change in concentration with time does not indicate the rate of a reaction.

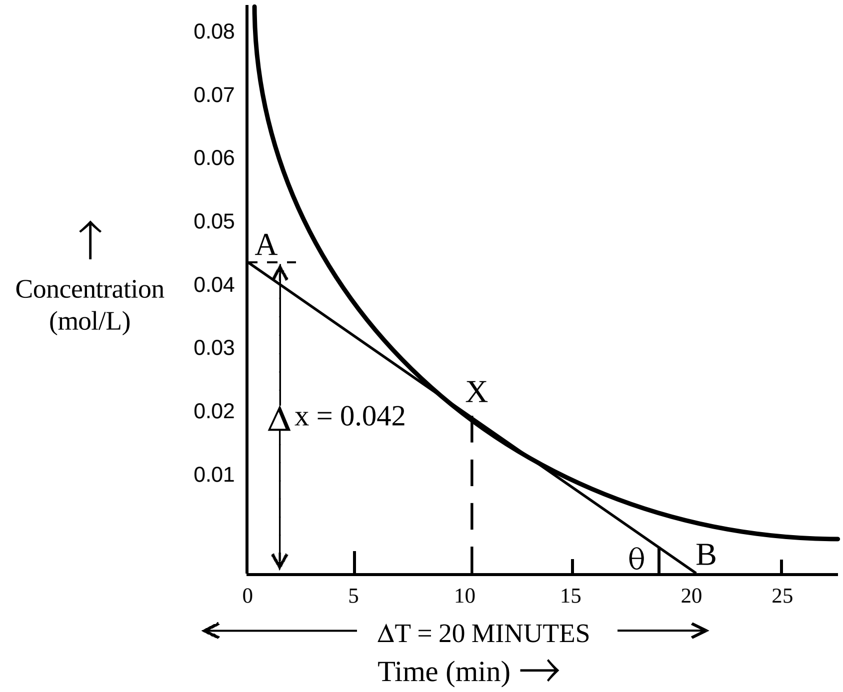


Fig. 4.2 Determination of rate of reaction

Suppose we are to determine the rate of the reaction after ten minutes. Draw a perpendicular at the point on X-axis corresponding to 10min. Locate the point 'x' where it touches the curve. Draw a tangent at point 'x' and extend it on both sides. Let it cut this X and Y axis at points B and A respectively.

The slope of the tangent = tanθ = Rate of the reaction at 10 min.

$$\therefore \quad \text{Rate of the reaction} = \tan\theta = \frac{OA}{OB} = -\frac{dc}{dt} = \frac{dx}{dt}$$

$$\therefore \quad \text{Rate of the reaction} = \frac{dx}{dt} = \frac{0.042}{1200\ \text{sec}} = 3.50 \times 10^{-5}\ \text{moles/litre/sec.}$$

The unit of rate of the reaction = moles/litre/sec

Instantaneous and Average Rate of reaction

As stated earlier, the **rate of a reaction** is defined as the change in concentration of a reactant or product per unit time. It is expressed as (a) Rate of decrease of concentration of any of the reactants or (b) Rate of increase of concentration of any of the products.

Consider a hypothetical reaction.

$$A \longrightarrow B$$

where A is the reactant and B is the product.

Let us suppose that $[A_1]$ and $[B_1]$ be the concentrations of A and B respectively at time t_1 and $[A_2]$ and $[B_2]$ be the concentration of A and B respectively at time t_2.

So, $\Delta t = t_2 - t_1$

$\Delta[A] = [A_2] - [A_1]$

$\Delta[B] = [B_2] - [B_1]$

(the square brackets are used to express molar concentration)

$$\text{Rate} = \text{Rate of disappearance of A} = \frac{\text{Decrease in Conc}^{n}\text{of A}}{\text{Time taken}} = \frac{\Delta[A]}{\Delta t} \quad \text{...............} (1)$$

$$\text{Also, Rate} = \text{Rate of appearance of B} = \frac{\text{Increase in Conc}^{n}\text{of B}}{\text{Time taken}} = \frac{+\Delta[B]}{\Delta t} \quad \text{...............} (2)$$

Equation (1) and (2) represent the **average rate** of the reaction, r_{av}.

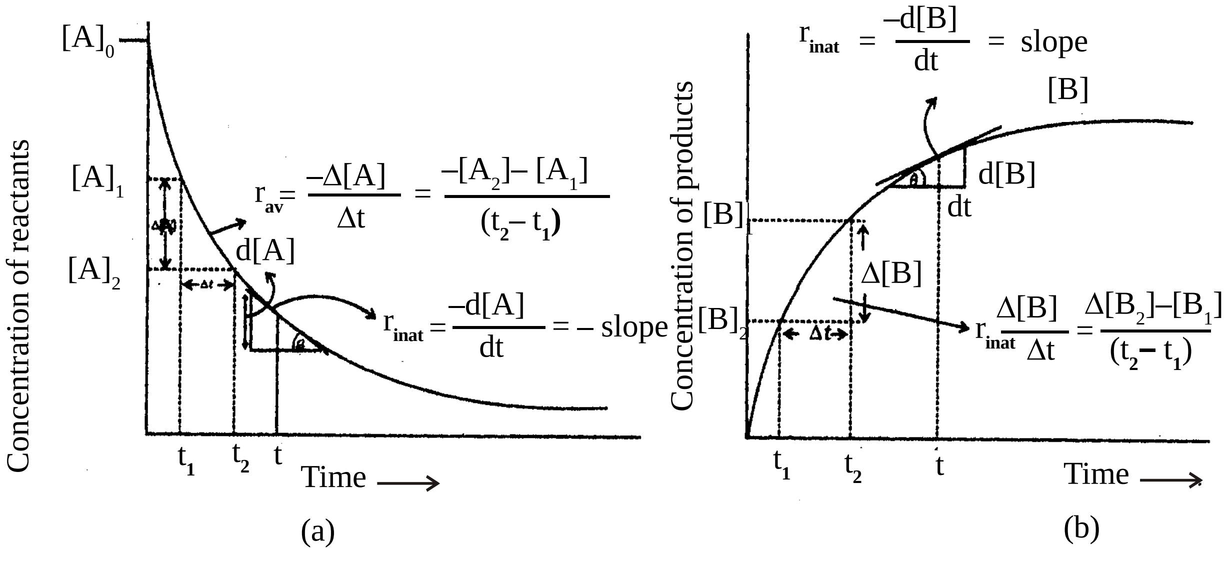


Fig. 4.3 Instantaneous and average rate of a reaction

To predict the rate of reaction at a particular instant of time average rate can not be used. This is because the average rate would be constant for the time interval for which it is calculated. So to express the rate at a particular moment of time we have to determine the instantaneous rate. For this we have to consider the average rate at the smallest time interval 'dt' (i.e. when $\Delta t \rightarrow 0$)

$$\text{So, } r_{av} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

$$\text{As } \Delta t \rightarrow 0, \text{ or } R_{inst} = \frac{d[A]}{dt} = \frac{d[B]}{dt}$$

Graphically $r_{\textbf{inst}}$ can be determined by drawing a tangent at time 't' on either of the curves for concentration of A and B versus time 't' and calculating its slope (Fig.3.3)

Rate constant : Consider a simple reaction,

$$A \longrightarrow B$$

According to law of mass action,

$$\frac{dx}{dt} \propto [A]$$

$$\text{or,} \quad \frac{dx}{dt} = k\,[A] \text{ .... (1)}$$

where, k = proportionality constant known as **rate constant** or **velocity constant** or **specific reaction rate**. It is a constant only at constant temperature.

Units of rate constant : The unit of rate constant for a given reaction is $\text{Mol}^{1-n}\ \text{lit.}^{n-1}$ time–1 where n is the order of reaction. ($M^{1-n}\ L^{n-1}\ T^{-1}$)

(i) For a **first order reaction**,

$$A \longrightarrow \text{Product (s)}$$

$$\text{Rate of the reaction,} \quad \frac{dx}{dx} = k\,[A]$$

$$\text{or, } k = \frac{dx/dt}{[A]} = \frac{\text{moles/L/sec}}{\text{mol/L}} = \frac{\text{moles lit.}^{-1}\ \text{sec}^{-1}}{\text{mol.lit.}^{-1}} = \text{sec}^{-1}$$

Unit of Rate constant in first order reaction is time^{-1} or sec^{-1}.

(ii) For a **second order reaction**,

$$A + B \longrightarrow \text{Product (s)}$$

$$\frac{dx}{dt} = k\,[A]\,[B]$$

$$\text{or, } k = \frac{dx/dt}{[A]\,[B]} = \frac{\text{moles lit.}^{-1}\ \text{sec}^{-1}}{\text{moles lit.}^{-1}.\ \text{moles lit.}^{-1}} = \text{lit.mol.sec}^{-1}$$

(iii) For a **third order reaction**,

$$3\,A \longrightarrow \text{Product(s)}$$

$$\therefore\ \frac{dx}{dt} = k\,[A]^3$$

$$\text{or, } k = \frac{dx/dt}{[A]^3} = \frac{\text{moles. lit}^{-1}\ \text{sec}^{-1}}{(\text{moles.lit}^{-1})^3} = \text{lit}^2\ \text{mol}^{-2}\ \text{sec}^{-1}$$

(iv) For a zero order reaction, A ⟶ Product, $\frac{dx}{dt} = k[A]^0$

$$\text{or, } k = \frac{\text{rate}}{[A]^0} = \text{mol. lit.}^{-1}\ \text{sec}^{-1}$$

Rate of the reaction and Rate constant :

Consider a general reaction

$$aA + bB + \cdots\cdots\cdots \longrightarrow lL + mM + \ldots\ldots\ldots$$

where ***a,b,I,m*** be the number of moles of A,B,L,M respectively. Rate of such reaction decrease in concentration of a reactant per mole or increase in concentration of a product per mole.

$$\text{Rate of reaction (r)} = \frac{-d\,[A]}{dt} \times \frac{1}{a} = k\,[A]^a\,[B]^b$$

where k = Rate constant or velocity constant

$$\text{or, } r = \frac{-d[B]}{dt} \times \frac{1}{b} = \frac{d[L]}{dt} \times \frac{1}{l} = \frac{d[M]}{dt} \times \frac{1}{m}$$

If concentration of the reactants are taken as unit i.e. if [A] = [B] = 1 then

$$r = k\,[A]^a\,[B]^b = k.1.1. = k$$

i.e **rate of the reaction = rate constant**

So, when the reactants involved in a reaction are at their unit concentrations,the rate of the reaction is equal to rate constant.

Difference between rate of reaction and rate constant :

Rate of reaction	**Rate constant**
1. It is the rate of change of concentration of any of the reactants or products at a particular instant.	1. It is the proportionality constant in the rate law.
2. Rate of the reaction depends upon temperature and also on concentration of reactants.	2. Rate constant depends upon temperature but is independent of the concentration of reactants.

Factors influencing the rate of a reaction :

Rate of a reaction is greatly influenced by the following factors:

(a) Nature of the reactants.

(b) Effect of concentration.

(c) Presence of catalyst.

(d) Temperature.

(e) Surface area of the reactants.

and (f) Radiations.

(a) Nature of the reactants : A chemical reaction involves the rearrangement of atoms between the reacting molecules to form the product. If such arrangement involves lesser number of bond, the reaction proceeds faster. If the reactant is a single element, then the rate of a reaction depends upon its electronic structure. The rate of a reaction is fast, if it involves ionic species. On the other hand, rates of moleculars reactions and oxidation - reduction reactions are quite slow.

Examples : (i) Sodium and calcium both react with water. But the former reacts very rapidly and the latter, moderately. This is because, sodium is an active metal because of the electronic configuration of its atom i.e, $1s^2\ 2s^2 2p^6 3s^1$

$$2Na + 2H_2O \xrightarrow{\text{Rapid}} 2NaOH + H_2$$
$$Ca + 2H_2O \xrightarrow{\text{Moderate}} Ca(OH)_2 + H_2$$

(ii) The reaction between sodium sulphate and barium chloride is instantaneous

$$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl \text{ (ionic reaction)}$$

(iii) The hydrolysis of cane sugar proceeds at a slower rate.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6} \text{ (molecular reaction)}$$

(iv) It has been observed that even if the concentration and temperature of the reactants are constant, the reaction rate is widely influenced by the internal structure of the molecule.

Thus, $NO + \frac{1}{2}O_2 \xrightarrow{25^0} NO_2$ (very fast)

$$CO + \frac{1}{2}O_2 \xrightarrow{25^0} CO_2 \text{ (very slow)}$$

(b) Effect of concentration : The effect of concentration on reaction velocity can be explained on the basis of kinetic theory. According to this theory, the rate of chemical reaction is determined by the number of collisions per second between the reacting molecules. If the number of molecules of a reactant is increased, the number of collisions will also increase. Therefore, the rate of reaction will become higher with the rise of concentration. Also according to law of mass action,the rate of a chemical reaction is proportional to the product of molar concentration of reactants.

(c) **Presence of catalyst :** The presence of catalyst influences the rate of chemical reaction. The catalyst itself does not undergo any change in the chemical composition at the end of the reaction.

For example, the rate of decomposition of $KClO_3$ is considerably increased by the addition of MnO_2. In this reaction MnO_2 acts as a catalyst.

$$2KClO_3 \xrightarrow{MnO2} 2KCl + 3O_2$$

The role of catalyst is most specific. It may be consumed in one step, but finally it is regenerated after the end of the reaction. A substance whose presence slows down the rate of the chemical reaction is called an **inhibitor**.

(d) **Effect of temperature :** Temperature plays a vital role in influencing the rate of a reaction. A reaction which does not start at ordinary temperature, proceeds at a faster rate, if the reactants are slightly warmed. On warming, heat energy is supplied which increases the kinetic energy of the reacting species. With this, the number of collisions between the reacting molecules increases. At this stage, the kinetic energy possessed by the molecules exceeds the energy barrier and thus the products are formed.

The effect of temperature is generally represented in terms of temperature coefficients. The **temperature coefficient** is defined as the ratio of the rate constants of a reaction at two temperatures separated by 10 degree centigrade, usually 25^0C and 35^0 C. For most of the reactions, the value of temperature coefficient is 2 to 3.

$$\text{Temperature coefficient} = \xrightarrow[K_t]{K_{t+10}} \approx 2 \text{ or } 3$$

where, k_t = rate constant at t^0C and $k_{(t+10)}$, at 10^o higher.

This shows that, the rate of a reaction is increased considerably with the increase of temperature.

For example, when copper turnings are added to conc. H_2SO_4, no reaction takes place between them. But on heating the reaction proceeds at a faster rate.

$$Cu + 2H_2SO_4 \xrightarrow{heat} CuSO_4 + 2H_2O + SO_2$$

(e) **Surface area of the reactants :** With increase in surface area, the rate of reaction increases

Examples are :

(i) Coal dust burns brilliantly in air than a lump of it.

(ii) Wood chips burn rapidly than a log of wood.

(iii) Rate of dissolution of powdered sugar is more than that of sugar crystals.

Thus, decrease in particle size increases the surface area. Consider a cube of size (5cm × 5cm × 5cm).

Total surface area = $6a^2 = 6 \times 5 \times 5 = 150$ cm^2 (where 'a' is side of the cube = 5cm)

Total volume = $a^3 = 5 \times 5 \times 5 = 125\ cm^3$

If the same cube is divided into 125 small cubes each having dimension (1cm × 1cm × 1cm) then total surface area = $125 \times 6 = 750\ cm^2$

Total volume = $1cm^3 \times 125 = 125\ cm^3$

(f) **Effect of radiations :** The rate of certain reactions increases when light radiations fall on the reacting species. Generally, ultraviolet rays, X–rays and γ–rays are characterised by shorter wavelength and greater frequency. When they fall on the reacting molecules, hυ amount of energy is transferred to the reacting species. Consequently, the reacting molecules acquire sufficient energy to cross the energy barrier and the products are easily formed.

For example, $H_{2(g)} + Cl_{2(g)} \xrightarrow{slow} 2HCl$ (dark)

$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl$ (fast)

4.3 MOLECULARITY OF A REACTION :

Molecularity of a reaction may be defined as the number of reacting species(molecules,atoms or ions) which take part in rate determining step of a chemical reaction.**The rate determining step in the slowest of all the steps involved in a chemical reaction.** If a reaction involves the decomposition of a single species, it is called **unimolecular.** Similarly, if the reaction involves the collision of two species, it is **bimolecular** and if three species take part in a collision leading to the formation of a product, it is called **termolecular**.

For example :

(i) Decomposition of nitrogen pentoxide

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2 \text{ (\textit{unimolecular})}$$

(ii) Decomposition of ammonium nitrite in aqueous solution

$$NH_4NO_2 \rightarrow N_2 + 2H_2O \text{ (\textit{unimolecular})}$$

(iii) Hydrolysis of ester in acid medium

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH \text{ (\textit{bimolecular})}$$

(iv) Dissociation of HI

$$2HI \rightarrow H_2 + l_2 \text{ (\textit{bimolecular})}$$

(v) Oxidation of sulphur dioxide to sulphur trioxide

$$2SO_2 + O_2 \rightarrow 2SO_3 \text{(\textit{termolecular})}$$

Consider a reaction which takes place in more than one step. Formation of nitrosyl fluoride takes place in two steps

$$2NO + F_2 \rightarrow 2ONF$$

Rate of such reaction = k[NO] $[F_2]$

Step I : $NO + F_2 \xrightarrow{slow} ONF + F$ (rate = k_1[No] $[F_2]$)

Step II : $NO + F \xrightarrow{fast} ONF$ (rate = k_2 [NO] [F])

Step I is slower than step II, therefore rate determining. Hence rate of equation for step I is the rate equation for the overall change. This is a bimolecular reaction since only two molecules participate in the rate determining step. Moleculartiy of a reaction is always a whole number. Reactions having molecularity more than three are rare.

4.4 ORDER OF A REACTION :

Order of a reaction may be defined in a number of ways; (i) "The total number of molecules or atoms whose concentration actually change as a result of chemical change", (ii) "The total number of molecules or atoms whose concentration determine the rate of reaction" and (iii) The sum of the power or powers of concentration terms that occur in rate equation. Order of reaction is an experimentally determined quantity and can not be written from a balanced chemical equation.

Consider a general reaction,

$$nA + mB \longrightarrow \text{Product (s)}$$

where, A and B are the reactants having *n* and *m* as the number of moles, respectively.

Thus, $\frac{dx}{dt} = k\,[A]^n\,[B]^m$

The sum (n+m) represents the *order of the reaction.*

A few examples are given below.

(a) Reaction of first order : In these reactions, only one reactant molecule undergoes chemical change.

Thus, $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$

or, $\frac{dx}{dt} = k[N_2O_5]^1$

Also, in case of first order reaction, the concentration of one reacting substance changes during a chemical change.

But hydrolysis of ester in acid medium, although a bimoecular reaction, is of first order. Since water is present in large excess, the change in concentration of water does not influence the rate of reaction. The rate of reaction is determined by the help of change in concentration of ester only.

So, $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

$$\frac{dx}{dt} = k\,[CH_3COOC_2H_5]$$

This type of reaction is known as **pseudounimolecular reaction**.

(b) Reaction of second order : A reaction is said to be of the second order, if its rate is determined by the variation of two concentration terms or the rate of the reaction is proportional to the second power of the concentration of a single reacting substance.

In general, the second order reaction may be of two types.

(i) When the concentration of both the reactants are same.

$$2A \longrightarrow \text{Products.}$$

For example, dissociation of HI.

$$2HI \longrightarrow H_2 + I_2$$

$$\frac{dx}{dt} = k\,[HI]^2$$

(ii) When the concentration of both the reactants are different.

$$A + B \longrightarrow \text{Products}$$

For example, $H_2 + I_2 \longrightarrow 2HI$

$$\frac{dx}{dt} = k\,[H_2]\,[I_2]$$

(c) Reaction of third order : In these reactions, the sum of the exponents of the concentrations of the reactant species is 3. Generally, they are represented as follows:

$$2A + B \longrightarrow \text{Products}$$

$$\text{or,}\quad A + 2B \longrightarrow \text{Products}$$

For example, $2NO + O_2 \longrightarrow 2NO_2$

Since, $\frac{dx}{dt} = k\,[NO]^2\,[O_2]^1$

$\therefore$ Order of the reaction will be = 2 + 1 = 3

(d) Reaction of zero order : Besides the reactions of first, second, and third order, there are certain reaction styled as zero order reaction.

In these reactions, the concentration of any of the reactants does not influence the rate of the reaction. The rate of the reaction is thus proportional to the zeroth power of the concentration of the reactants, that is, the reaction speed is constant.

For example, the reaction between hydrogen and chlorine in presence of sunlight to give hydrogen chloride.

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl_{(g)}$$

Since, $\frac{dx}{dt} = k[H_2]^0$ or $k[Cl_2]^0$, the order of reaction will be zero.

(e) Reactions of fractional order : Besides there are a few reactions of fractional order. e.g. $CH_3\,CHO \longrightarrow CH_4 + CO$. Here, rate = $k[CH_3CHO]^{3/2}$ and order = 3/2.

Comparision of molecularity and order of reaction :

The distinction between molecularity and order of a reaction are given below :

Molecularity	Order of reaction
Common points.	
1. The molecularity is dependent upon conditions of a reaction.	1. The order of a reaction also depends on the on the conditions of a reaction.
2. Reactions of higher molecularity (more than three) are rare.	2. Reactions of higher order (higher than third order) are also rare.

Molecularity	Order of reaction
Differences :	
3. Molecularity is given by the total number of molecules of the reacting species which take part in the rate determining step of the reaction.	3. Order of a reaction is given by the number of molecules whose concentrations change as a result of the reaction.
4. The molecularity of each step of a reaction is separately determined.	4. Order of a reaction, as determined by the slowest step of a reaction refers to the order of the whole reaction.
5. Molecularity of a reaction is always a whole number.	5. Order of reaction can be a whole number, a fraction or zero.
6. Molecularity of a reaction can be theoretically predicted by studing the balanced equation for the reaction.	6. Order of a reaction is always determined by experimental methods.
7. Molecularity refers to mechanism of the reaction.	7. It does not refer to mechanism through which the reaction proceeds.

4.5 RATE EQUATIONS :

4.5.1 Rate Equation of the First order Reaction

A first order reaction is that, in which the concentration of only one reactant changes or in which the rate of reaction is proportional to the first power of the concentration of the reactant.

In general, such a reaction is represented as,

A	$\longrightarrow$	Product (s)	
'a'		0	(Initially, t = 0)
(a – x)		x	(after time 't' sec.)

Let the initial concentration of A = 'a' mol/L

After time 't', let x mol/L of A have decomposed.

So concentration of A after time 't' becomes (a – x) mol/L

∴ According to law of mass action,

rate of the reaction, $\frac{dx}{dt} \propto (a - x)$

$$\text{or,} \quad \frac{dx}{dt} = k(a - x) \quad \text{.................................. (1)}$$

k = Proportionality constant, called **rate constant** or **velocity constant** or **specific reaction** rate. It has definite value at a definite temperature.

Eqn. (1) can be written as,

$$\frac{dx}{a-x} = k.dt. \quad \text{...................... (2)}$$

on integrating eqn (2) we get,

$$\int \frac{dx}{a-x} = \int k.dt$$

or, – ln (a–x) = k.t + I .... (3)

where I = Integration constant.

When t = 0, x = 0.

Substituting these values in eqn. (3) we get,

– ln a = I .... (4)

From eqn. (3) and (4), we get,

– ln (a–x) = k.t – ln a

or, ln a – ln (a – x) = k.t

or, k.t = ln a/a–x

or, $k.t = 2.303. \log \frac{a}{a-x}$

$$\text{or, } k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{......................} (5)$$

Eqn. (5) is known as the **rate equation for first order reaction.**

Characteristics of 1st order reaction :

1. The unit of constant in first order reaction is time^{-1} or sec^{-1} .
2. The time taken for the completion of same fraction of change or any fraction of change is independent of the initial concentration of the reactant.

Let $t_{1/2}$= the time taken for the completion of half of the reaction. (Initial concentration 'a' becomes half i.e. 'a' becomes a/2)

$t_{1/2}$ is also known as half-life time.

At $t_{1/2}$, $x = \frac{a}{2}$

Putting these values in eqn (5), we get, $k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$

$$\text{or, } k = \frac{2.303}{t_{1/2}} \log 2 \text{ or, } k = \frac{2.303}{t_{1/2}} \times 0.301 \text{ or, } t_{1/2} = \frac{0.693}{k}$$

or, $t_{1/2}$ = Constant. Similarly, we can find $t_{1/3}$ = Constant and $t_{1/4}$ = Constant.

3. A change in concentration unit does not affect the rate constant. Let the new concentration be 'm' times the first one. That is, when 'a' is made ma, (a – x) changes to m(a–x).

and $k = \frac{2.303}{t} \log \frac{ma}{m(a-x)}$

or, $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Thus, expression for k remains unaltered.
If a graph plotted between log (a –x) and 't' from the experimental values is found to be linear, the reaction is of the first order.

4. **Evaluation of k :** k can be evaluated by using the rate equation (5). By determining the concentration of reactants at different time intervals and knowing the initial concentration, 'k' can be calculated.
Alternately, k can be evaluated by graphical method. Rearranging eqn. (5)

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$= \frac{2.303}{k} \log a - \frac{2.303}{k} \log (a-x)$$

$$\text{or, } \log (a-x) = \frac{-k}{2.303}\, t + \log a$$

Thus, by plotting log(a–x) at different time intervals aginst the corresponding time intervals we get a straight line having a –ve slope, the intercept being log a.

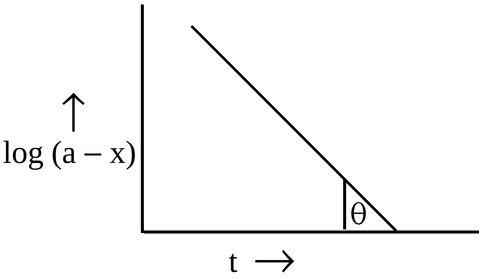


Fig. 4.4 Plot of log (a – x) against time 't' in 1st order reaction

$$\text{Slope} = \tan\theta = -\frac{k}{2.303}$$

$$\text{or, } k = -2.303 \times \text{slope}$$

Examples of 1st order reaction.

(i) *Dissociation of PCl_5*

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

(ii) *Decomposition of nitrogen pentoxide :*

Nitrogen pentoxide is a volalite crystalline solid, which decomposes in gaseous state or when dissolved in some organic solvents like CCl_4. The reaction is represented by the equation,

$$N_2O_5 \longrightarrow \underset{\substack{\rightleftharpoons \\ 2NO_2}}{N_2O_4} + 1/2\ O_2$$

(iii) *Decomposition of hydrogen peroxide :*

The decomposition of hydrogen peroxide in aqueous solution is catalysed by the presence of finely divided platinum and the reaction is represented by the equation.

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

(iv) *Decomposition of ammonium nitrite in aqueous solution :*

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iv) *Hydrolysis of ester in presence of acid.*

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

The reaction can be studied by titrating a known volume of reaction mixture with standard alkali at regular intervals.

If $V_0 \rightarrow$ Volume of alkali used initially equivalent to mineral acid alone.

$V_t \rightarrow$ Volume of alkali used after interval 't'

$V_\infty \rightarrow$ Volume of alkali used when the reaction is complete (i.e. after 24 hours)

Then, $a = (V_\infty - V_0)$

$x = (V_t - V_0)$

So, $a - x = V_\infty - V_0 - V_t + V_0 = (V_\infty - V_t)$

and $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

$$= \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Example : 5 ml of methyl acetate was added to a flask containing 100 ml of 0.1 NHCl maintained at temperature of 25^0C . 5 ml of reaction mixture was drawn at different intervals of time and titrated against standard alkali. The following data were obtained.

Time (min) -	0	75	119	183	∞
ml. alkali used -	4.81	6.05	6.55	7.37	10.52

From the above data show that the reaction is of first order.

Solution :

$(V_\infty - V_0) = 10.52 - 4.81 = 5.71$

Time min.	$(V_\infty - V_t)$	$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$
75	4.47	$k = \frac{2.303}{75} \log \frac{5.71}{4.47} = 3.263 \text{ min}^{-1}$
119	3.97	$k = \frac{2.303}{119} \log \frac{5.71}{3.97} = 3.047 \text{ min}^{-1}$
183	3.15	$k = \frac{2.303}{183} \log \frac{5.71}{3.15} = 3.228 \text{ min}^{-1}$

The velocity constant k in all the cases are almost constant. Hence, the reaction is of first order.

4.5.2 Rate Equation of the Zero order Reaction

Reactions in which the concentrations of the reactants do not change with time and therefore, the rate of the reactions remains constant throughout, are termed as **zero order reactions**.

The rate of the reaction for zero order can be expressed as,

$$\frac{dx}{dt} = k \text{ .... (1)}$$

or, $dx = k.dt$ .... (2)

On integration with proper limits, it gives,

$$\int_{x=x^0}^{x=x} dx = k\int_0^t dt$$

or, $x - x^0 = k.t$

or, $k = \frac{x - x^0}{t}$

Since at the start of a reaction when t = 0, no product is formed i.e. $x^0 = 0$, Hence

$$k = \frac{x}{t} \text{ .... (3)}$$

This is the **rate equation for a zero order reaction**. It suggests that *the rate of zero order reactions are independent of the amount or concentration of reactant present*.

Characteristics of Zero order reaction :

1. The unit of rate constant in zero order reaction is mol. L^{-1} s^{-1}
2. A graph of concentration of product (x) against time (t) for such a reaction gives a straight line passing through the origin.
3. Half life is defined as the time required to reduce the concentration to half of its original value. For a zero order reaction, half life is proportional to the initial concentration of the reactant.

$t = t_{1/2}$ when $x = a/2$, where 'a' is the initial concentration of the reactant.

we get, $a = k\, t_{1/2}$

or, $t_{1/2} \propto a$

Examples : (i) A well known photochemical reaction between hydrogen and chlorine is a zero order reaction.

$$H_2(g) + Cl_2(g) \xrightarrow{h\upsilon} 2HCl(g)$$

If the gases are confined in a long tube, dipping in water, the HCl will be dissolve as soon as it is formed. Since here pressure remains constant, the volumes of the two gases H_2 and Cl_2 are reduced. This keeps the concentrations of $[H_2]$ and $[Cl_2]$ unaltered. That is, the change in the concentrations is zero and the rate of reaction is independent of the concentration of the reactants.

Hence the order of reaction is zero.

(ii) Some heterogeneous reactions of zero order taking place on the surfaces are given below :

$$2N_2O \xrightarrow[\text{catalyst}]{\text{hot Pt wire}} 2N_2 + O_2$$

$$2NH_3 \xrightarrow[\text{catalyst}]{\text{Tungsten}} N_2 + 3H_2$$

$$2HI \xrightarrow[\text{catalyst}]{\text{Gold}} H_2 + I_2$$

In the above cases, the reactions occur on the surface of the catalyst. When the surface becomes saturated, the amount of absorbed gas is constant. Further increase in pressure can not change the surface concentration. Therefore, the rate of reaction is independent of the concentration of the reactant in gas phase.

4.5.3 Fractional Life Period

It is the time required to complete a particular fraction of a reaction. For example,

Half life period - It is the time required by the reaction to undergo 50% conversion into products. It is represented by T_{50} or $t_{½}$

(1) For a **zero order** reaction, the rate of reaction is

$k_o = \frac{x}{t}$ where x = amount of product formed after time interval 't'

k_o = rate constant

At T_{50}, $x = \frac{a}{2}$ where a = initial concentration of the reactant.

Hence, $T_{50} = \frac{x}{k_o} = \frac{a}{2k_o}$

At $t = T_{75}$, $x = \frac{3a}{4}$ (T_{75} is the time required by the reactant to decompose 75%)

Hence, $T_{75} = \frac{x}{k_0} = \frac{3a}{4k_0} = \frac{3}{2}.\frac{a}{2k_0} = 1.5\ T_{50}$

Thus, $T_{50} \alpha\ a$

(ii) For a **1st order** reaction, the rate equation is

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

If $t = T_{50}$, $x = \frac{a}{2}$

$$k_1 = \frac{2.303}{T_{50}} \log \frac{a}{a-\frac{a}{2}}$$

$$\text{or, } T_{50} = \frac{2.303}{k_1}\log\frac{a}{a-\frac{a}{2}} = \frac{2.303}{k_1}\log 2 = \frac{0.693}{k_1}$$

$$\text{If } t = T_{75},\ x = \frac{3a}{4} \text{ and } k_1 = \frac{2.303}{T_{75}}\log\frac{a}{a-\frac{3a}{4}} = \frac{2.303}{T_{75}}\log 2^2$$

$$T_{75} = \frac{2.303}{k_1}\log 2^2 = 2.\frac{2.303}{k_1}\log 2 = 2\times T_{50}$$

Similarly, $T_{87.5} = 3 \times T_{50}$
and $T_{99.9} = 10 \times T_{50}$

So, **the time for undergoing a definite fraction of reactant in 1st order rection is independent of concentration.**

4.6 ACTIVATION ENERGY :

The concept of activation energy is important to understand why a mixture of oxygen and hydrogen (1:2 by volume) remains unreacted at room temperature but undergoes a vigorous change if an electric spark is passed through it.

$$2H_2 + O_2 \xrightarrow{\text{at } 20^0\text{ C}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Electric spark}} 2H_2O$$

From this we can conclude that, the molecules undergoing a chemical reaction must possess a minmum amount of energy, so that the collisions between themselves result in a reaction. This minimum amount of energy is called **threshold energy (E_{th})**. Prior to their collision, molecules of the reactants in their normal state do possess their respective internal energy. Let the average energy of the reactants be E_r, which is less than the threshold energy. Now the excess energy that the reactant molecules (having energy less than the threshold energy) must acquire in order to yield products is called **activation energy**. Thus,

Activation energy (E_a) = Threshold energy(E_{th}) – Average energy possessed by the molecules of the reactants (E_r)

$$\text{or,}\quad E_a = E_{th} - E_r$$

Definition of Activation energy : The extra energy supplied to the reactant molecules to attain threshold energy for undergoing chemical reaction is called **activation energy.**

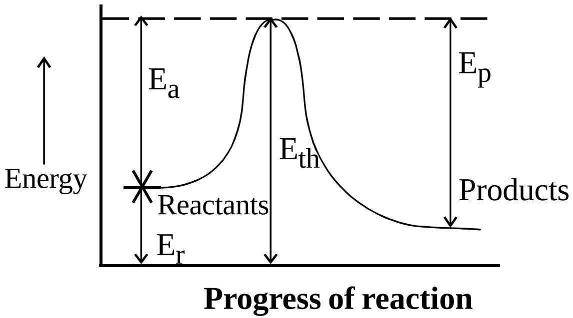


Fig. 4.5 Plot of energy versus progress of reaction

E_a = Energy of activation of reactants

E_p = Energy of activation of products.

When $E_p > E_a$, the reaction is exothermic. When $E_p < E_a$, the reaction is endothermic.

The reactant molecules must acquire a certain amount of energy before they can react upon collisions to yield the products. That is to say, they must overcome the energy barrier in order to yield the products. The barrier determines the magnitude of the threshold energy that they require to yield the products. As a matter of fact, reactions proceeding at a faster rate have low value of activation energy and those which proceed slowly possess comparatively high value of the activation energy.

Determination of Activation energy :

Arrhenius pointed out that a reasonable equation for the variation of rate constant with temperature can be derived on the basis of the van't Hoff's equation. According to an equation suggested by van't Hoff,

$$\frac{d\ln K_c}{dT} = \frac{\Delta E}{RT^2} \quad \text{.......................... (1)}$$

where, K_c = Equilibrium constant = k_1/k_2 (k_1 and k_2 are rate constant for forward and backward reaction respectively.)

$$\frac{d\ln k_1}{dT} - \frac{d\ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} \quad (\text{ where, } \Delta E = E_1 - E_2)$$

This may split into,

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d\ln k_2}{dT} = \frac{E_2}{RT^2}$$

or, In general,

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \quad \text{............................... (2)}$$

On integrating equation (2), we get,

$$\int \frac{d\text{lin}k}{dT} = \int \frac{E}{RT^2} \text{ or, } \int d\text{lin}k = \int \frac{E}{RT^2} . dT$$

$$\text{or, } \ln k = -\frac{E}{RT} + \text{constant .... (3)}$$

$$\text{or, } \log k = \frac{-E}{2.303RT} + \text{constant .... (4)}$$

Plot of log k vs 1/T gives a straight line with slope = $-E/2.303R$

where, E = Activation energy.

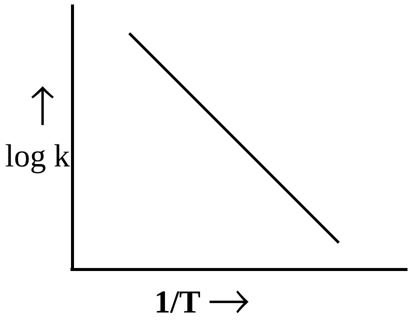


Fig. 4.6 Plot of log k versus 1/T

From equation (3), we can get,

$$\mathbf{k = Ae^{-E/RT}} \quad \text{................................ (5)}$$

This equation is known as **Arrhenius equation.** Here A is a constant known as **frequency factor** or **collision number.**

4.7 COLLISION THEORY FOR UNIMOLECULAR REACTION :

This theory was developed by **Arrhenius** and **van't Hoff**. According to this theory, a chemical reaction occurs by the collision between the reacting molecules. So, for a chemical reaction to occur

(a) the reactant molecules are brought closer to each other and collide amongst themselves.

(b) the reactant molecules must possess certain amount of minimum energy before they react upon collision.

(c) the reactant molecules must be properly oriented.

Collision between the molecules

The molecules are always in a state of motion. During their motion they collide with each other. As a result of these collisions the chemical reaction takes place. But all the collisions do not lead to chemical reaction. Only some effective collisions are taken into account.

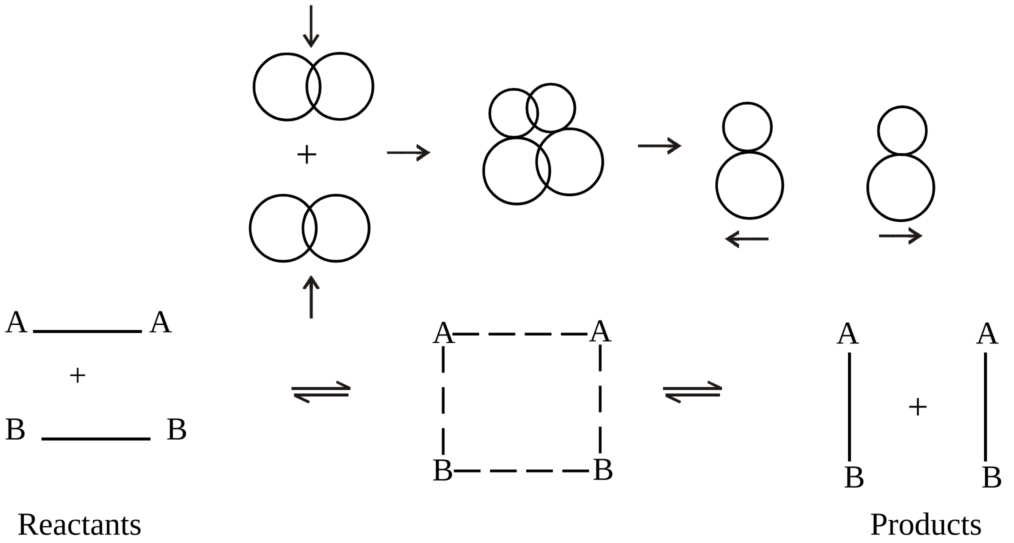
The **collision theory** postulates that only the reactants which possess certain minimum amount of energy known as **threshold energy** collide amongst themselves giving some effective collisions leading to a chemical reaction.

As a result of collisions there is redistribution of energy among the molecules. Consequently the number of molecules having energys more than the threshlod energy is low and the number of molecules having lower energy is very high. Hence a small fraction of total moleules acquire energy which is equal to or greater than the threshold energy. These molecules are said to be **activated** molecules. The difference between the threshold energy and the average energy possessed by the molecules is known as **Energy of activation or Activation energy**. Thus,

Activation energy (A.E) = Threshold energy (E_{Th}) - Average energy of reactants (E_R).

Orientation of colliding molecules

For a chemical reaction to occur the colliding molecules should be properly oriented. The following figure clearly depicts the proper orientation of colliding molecules.



The energy required for effective collisions between the reactant molecules that are poorly oriented is much higher than that required for properly oriented ones.

4.8 SOLVED NUMERICAL PROBLEMS :

Example 1 What is the rate of reaction and the order of reaction if the mechanism of the reaction as,

$2\,NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow reaction)

$H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast reaction)

Solution : We know, the slowest step is the rate determining step.

Hence, the rate of the reaction = $k\,[NO]^2\,[H_2]^1$

$\therefore$ Order of the reaction = 2 + 1 = 3

Example 2. For the following reactions, state the order with respect to each reactant and the overall order.

(a) $3\,NO(g) \longrightarrow N_2O(g) + NO_2(g)$

Rate = $k\,[NO]^2$

(b) $H_2O_2 + 3I^- + 2H^+ \longrightarrow 2H_2O + I_{3(aq)}$

Rate = $k\,[H_2O_2]\,[I^-]$

(c) $CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$

Rate = $k\,[CH_2\,CHO]^{3/2}$

(d) $CHCl_{3(g)} + Cl_{2(g)} \longrightarrow CCl_{4(g)} + HCl_{(g)}$

Rate = $k\,[CHCl_3]\,[Cl_2]^{1/2}$

(e) $C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl(g)$

Rate = k $[C_2H_5Cl]$

What are the dimensions of rate constant in each case.

Solution :

(a) Rate = k $[NO]^2$

Since, here only one reactant is present, the order with respect to NO or overall order is same. It is equal to 2.

Dimension or unit of k, $k = \dfrac{\text{Rate}}{[NO]^2} = \dfrac{mol.L^{-1}s^{-1}}{(mol.L^{-1})^2} = mol^{-1}L.\ s^{-1}$

(b) Rate = k $[H_2O_2][I^-]$

Here, the order of the reaction with respect to H_2O_2 is one and also with respect to I^- is one.

∴ The overall order of the reaction = 1 + 1 = 2

Unit of k, $k = \dfrac{\text{Rate}}{[H_2O_2][I^-]} = \dfrac{mol.L^{-1}\,s^{-1}}{(mol.L^{-1})(mol.L^{-1})} = mol^{-1}\ L.s^{-1}$

(c) Rate = k $[CH_3CHO]^{3/2}$

Since only one reactart involves, the order of the reaction is some always.

The order of the reaction = 3/2 = 1.5

Unit of k, $k = \dfrac{\text{Rate}}{[CH_3CHO]^{3/2}} = \dfrac{mol.L^{-1}s^{-1}}{(mol.L^{-1})\ (mol.L^{-1})^{3/2}} = mol^{-1/2}\ L^{1/2}\ s^{-1}$

(d) Rate = k $[CHCl_3]\ [Cl_2]^{1/2}$

Order of the reaction with respect to $CHCl_3$ = 1

and order of the reaction with respect to Cl_2 = 1/2

∴ Overall order of the reaction = 1 + 1/2 = 3/2 = 1.5

Unit of k = $mol^{-1/2}\ L^{1/2}\ s^{-1}$

(e) Rate = k $[C_2H_5Cl]$

∴ The order of the reaction = 1

Unit of k , $k = \dfrac{\text{Rate}}{[C_2H_5Cl]} = \dfrac{mol.L^{-1}s^{-1}}{(mol.L^{-1})} = Sec^{-1}$

Example 3. For the decomposition of N_2O_5 given as,

$$N_2O_{5(g)} \longrightarrow N_2O_{4(g)} + 1/2O_2\ (g)$$

If the rate law = k $[N_2O_5]$ and k = $1.68 \times 10^{-2}\ sec^{-1}$, starting with 2.5 moles of $N_2O_{5(g)}$ in a 5.0 litre container at 298 K, how many moles of N_2O_5 would remain after 1.0 minutes ?

Solution : Initial concertation of $N_2O_5 = [N]_0$ = 2.5 = 0.5 mol/litre

Let [N] = final concentration

t = 1 minutes = 60 seconds.

The first order rate equation can be represented as,

$$k.t = 2.303 \log \frac{[N]_o}{[N]}$$

or, $$1.68 \times 10^{-2} \times 60 = 2.303 \log \frac{0.5}{N}$$

or, $$\log 0.5 - \log [N] = \frac{1.68 \times 10^{-2} \times 60}{2.303} = 43.76 \times 10^{-2}$$

or, $$\log [N] = \log 0.5 - 43.76 \times 10^{-2}$$

$$= -0.301 - 0.4376 = -0.738$$

$$= \bar{1}.262$$

$[N]$ = antilog $\bar{1}.262$ = 0.182 mol/lit.

Example 4. The rate constant for a first order reaction involving a compound A was found to be 0.082 min^{-1}. When the initial concentration of A is 0.15 mol/litre, how long will it take for the concentration of A to drop to 0.03 mol/litre.

Solution : $k = 0.082\ \text{min}^{-1}$ $\qquad k = \frac{2.303}{t} \log \frac{a}{a-x}$

or, $$t = \frac{2.303}{0.082} \log \frac{0.15}{0.03} = \frac{2.303}{0.082} \log 5$$

$$= \frac{2.303}{0.082} \times 0.6990 = 19.6 \text{ min.}$$

Example 5 : What percentage of the initial concentration of reactant is left in 2.0 hours for a reaction whose rate constant is $4.25 \times 10^{-5}\ \text{sec}^{-1}$?

Solution : Let the initial concentration of the reactant, a = 100 mol/L

Let, the concentration of the product after 2 hours be 'x' mol/L.

∴ The concentration of the reactant left after 2 hours = (100 – x) mol/L

we know, $k = 4.25 \times 10^{-5}\ \text{sec}^{-1}$

and t = 2 hour = 60 × 60 × 2 = 7200 sec.

According to first order rate expression

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

or, $$4.25 \times 10^{-5} = \frac{2.303}{7200} \log \frac{100}{100-x}$$

or, $$\log \frac{100}{100-x} = 0.1328$$

or, $\frac{100}{100-x}$ = antilog 0.1328 = 1.358

or, $\frac{100}{100-x}$ = 1.358

or, $100 - x = \frac{100}{1\text{-}358} = 73.64$

or, x = 100 – 73.64 = 26.36%

Example 6 : A first order reaction is 20% completed in 10 minutes. Calculate (i) k for the reaction and (ii) time taken for the reaction to go 75% completion.

Solution : (i) Let, initial concentration of the reactant, a = 100 mol/L

∴ Concentration of the product formed in 10 minutes, x = 20 mol/L

Hence, concentration of the reactant left after 10 minutes, (a –x) = 80 mol/L

We know, the rate eqn. for first order reaction is,

$$k = \frac{2303}{t} \log \frac{a}{a-x} = \frac{2303}{10} \log \frac{100}{100\text{-}20}$$

$$= \frac{2303}{10} [\log 10 - \log 8]$$

$$= 0.2303 \times (1-0.9031)$$

$$= 0.2303\ 0.0969 = 0.0223\ \text{min}^{-1}$$

(ii) Let, t = time taken for 75% completion.

so, in time t, x = 75 mol/L

and a – x = 25 mol/L

$$\therefore\ t = \frac{2303}{k} \log \frac{a}{a-x}$$

or, $$t = \frac{2.303}{0.0223} \log \frac{100}{25}$$

$$= \frac{2.303}{0.0223} \log 4 = \frac{2.303}{0.0223} \times 0.6021$$

= 62.15 min

Example 7 The half life period ($t_{1/2}$) of a first order reaction is 100 sec. Calculate the time required for 80% completion.

Solution : We know, for a first order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100\ \text{sec}} = 0.00693\ \text{sec}^{-1}$$

Now time required for 80% completion is given by,

$$t = \frac{2.303}{k} \cdot \log \frac{a}{a-x}$$

$$= \frac{2.303}{0.00693\ \text{sec}^{-1}} \cdot \log \frac{100}{(100-80)}$$

= 332.32 [log 100 – log 20] sec.

= 332.32 [2 –1.3010] sec.

= 332.32×0.6990 sec. = 232 sec.

Example 8. Concentration of a reactant A changed from 0.044M to 0.032M in 25 minutes. What was the average rate of the reaction during this interval ?

Solution : $$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{0.044-0.032}{25} = -\frac{0.012}{25}$$

= 1.00048 mole/litre/min

= 4.8×10^{-4} mole litre^{-1} min^{-1}

Example 9 : Calculate the half-life of a first order reaction, where the specific rate constant is (a) 200 sec^{-1}, (b) 2 min^{-1}, (c) 5 year^{-1}

Solution : The half-life of a first order reaction is represented by,

$$t_{1/2} = \frac{0.693}{k}$$

(a), When k = 200 sec^{-1},

$$t_{1/2} = \frac{0.693}{200\ \text{sec}^{-1}} = 0.0035\ \text{sec} = 3.5 \times 10^{-3}\ \text{sec.}$$

(b) When, k = 2 min^{-1},

$$t_{1/2} = \frac{0.693}{2\ \text{min}^{-1}} = 0.3465\ \text{min}$$

(c) When, k = 5 year

$$t_{1/2} = \frac{0.693}{5\ \text{year}^{-1}} = 0.1386\ \text{year.}$$

Example 10. The half life period of a reaction of first order is 100 sec. Calculate its rate constant.

Solution : We know, for a first order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

or, $$k = \frac{0.693}{t_{1/2}}$$

Now, $t_{1/2}$ = 100 sec.

$$\therefore\ k = \frac{0.693}{100\ \text{sec}} = 6.93 \times 10^{-3}\ \text{sec}^{-1}$$

Example 11. A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion ?

Solution : The rate equation for first order is,

$$k = \frac{2.303}{t} \times \log \frac{a}{a-x}$$

or, $$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\therefore\ t_{50\%} = \frac{2.303}{k} \log \frac{100}{100-50}$$

$$= \frac{2.303}{t} . \log 2 \text{ .... (i)}$$

and $$t_{80\%} = \frac{2.303}{k} . \log \frac{100}{100\text{-}80} = \frac{2.303}{k} \log 5 \text{ .... (ii)}$$

Dividing eqn (ii) by (i) we get,

$$\frac{t_{80\%}}{t_{50\%}} = \frac{\log 5}{\log 2}$$

We know, the time for 50% change = 693 minutes.

∴ Time for 80% change,

$$t_{80\%} = 69.3 \times \frac{\log 5}{\log 2} = \frac{69.3 \times 0.699}{0.301}$$

= 160.9 min

Example 12. If the half life of a first order reaction, 'A → product' is 2 minutes, how long will it take [A] to reach 25% of its initial concentration ?

Solution : $t_{1/2} = 2$ minutes

$$\therefore\ k = \frac{0.693}{t_{1/2}} = 0.346\ \text{min}^{-1}$$

If initial concentration of A = $[N_0]$

and final concentration of A will be, $\frac{[N_0]}{4}$

Hence, for a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[N_0]}{[N_0]/4}$$

$$= \frac{2.303}{0.346\ \text{min}^{-1}} \log 4$$

$$= \frac{2.303}{0.346\ \text{min}^{-1}} \times 0.6021 = 4 \text{ minutes.}$$

Hence, it will take 4 minutes.

Example 13. Show that the time required for the completion of 3/4th of reaction of first order is twice the time required for the completion of half of the reaction. [CHSE, 1991]

Solution : The rate requation for first order reaction is,

$$k = \frac{2.303}{t} . \log \frac{a}{a - x}$$

$$\text{or, } t = \frac{2.303}{k} . \log \frac{a}{a - x}$$

Let $t_{1/2}$ = half–life time

Hence, at $t_{1/2}$, $x = a/2$

When, $t_{3/4}$ = time required for the completion of 3/4th of the reaction.

at $t_{3/4}$, $x = 3a/4$

$$\therefore t_{1/2} = \frac{2.303}{k} . \log \frac{a}{a - \frac{a}{2}}$$

$$= \frac{2.303}{k} \log 2 \text{ .... (i)}$$

$$\text{Since, } t_{3/4} = \frac{2.303}{k} .\log \frac{a}{a - \frac{3a}{4}}$$

$$\text{or, } t_{3/4} = \frac{2.303}{k} . \log 4 \text{ .... (ii)}$$

Dividing eqn (ii) by (i), we get, $\frac{t_{3/4}}{t_{1/2}} = 2$

or, $t_{3/4} = 2 \times t_{1/2}$

Example 14. A first order gas reaction has $k = 1.5 \times 10^{-6}$ per second at 200^0c. If the reaction is allowed to run for 10 hours, what percentage of the intial concentration would have changed into the product ? What is the half life of the reaction ?

Solution : We know, $k = 1.5 \times 10^{-6}\ \text{sec}^{-1}$.

t = 10 hours = 36000 sec

Let the percentage of initial concentration changed into product = x.

If N_0 = initial concentration = 100

N = final concentration = (100 – x)

$$\therefore\ k = \frac{2.303}{t} . \log \frac{N_0}{N}$$

$$\text{or, } 1.5 \times 10^{-6}\ \text{sec}^{-1} = \frac{2.303}{36000\ \text{sec}} \log \frac{100}{100-x}$$

$$\text{or, } \log \frac{100}{100-x} = \frac{1.5 \times 10^{-6} \times 36000}{2.303} = 0.0234$$

Taking antilog, we get,

$$\frac{100}{100-x} = 1.055$$

or, $105.5 - 1.055\ x = 100$

or, $x = 5.2$

∴ The percentage of initial concentration which is changed into product = 5.2%.

Then, the half life of the reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}\ \text{sec}^{-1}} = 4.62 \times 10^{-5}\ \text{sec.}$$

Example 15. The value of rate constant for the decomposition of nitrogen pentoxide ($N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2} O_2$) is 3.46×10^{-5}at 25^0C and 4.87×10^{-3} at 65^0C. Calculate the energy of activation for the reaction. (R = 1.987 calories)

Solution : Here, $k_1 = 3.46 \times 10^5$ $T_1 = 273 + 25 = 298$ K

$k_2 = 4.87 \times 10^{-3}$ $T_2 = 273 + 65 = 338$ K

$$\therefore \log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \left[\frac{T_2 - T_1}{T_2 .\ T_1}\right]$$

Putting the values in the above equation,

We get, Ea = 24,800 calories = 24.8 kcals.

Example 16. The specific rate constant for a reaction increases by a factor of 4 if the temperature is changed from 27^0C to 47^0C. Find the activation energy for the reaction. (R = 1.98 calories)

Solution : We know, the activation energy at two different temperature, can be calculated by taking the help of the following equation.

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303\ R} \left[\frac{T_2 - T_1}{T_2 .\ T_1}\right]$$

$$\text{Hence, } \log \frac{4k_1}{k_1} = \frac{Ea}{2.303 \times 1.98} \left[\frac{320 - 300}{320 \times 300}\right]$$

$$\text{or, } \quad 0.6021 = \frac{Ea}{2.303 \times 1.98} \times \frac{20}{320 \times 300}$$

$$\therefore\ Ea = 0.6021 \times 2.303 \times 1.98\ 4800$$

$$= 13180 \text{ calories}$$

$$= 13.18 \text{ kcals.}$$

CHAPTER (4) AT A GLANCE

1. **Activation energy :** The extra energy supplied to the reactant molecules to attain threshold energy to undergo chemical reaction is called activation energy.
   Activation energy, $E_a = E_{th} - E_r$

2. **Half-life period :** It is the time during which the concentration of reactants falls down to half of its initial value.
   $t_{1/2} = 0.693/k$

3. **Molecularity :** Total number of molecules or atoms or ions taking part in the rate determining step of chemical reaction.

4. **Order of a reaction :** Total number of molecules or atoms whose concentration actually changes as a result of chemical reaction.

5. **Rate of reaction :** Rate of reaction at a particular instant is the instantaneous rate of change of concentration of any one of the reactant or product at a particular instant.

6. (a) **First order rate equation** is $k = \frac{2 \cdot 303}{t} \log \frac{a}{(a - x)}$

(b) **Zero order rate equation is k** $= \frac{x}{t}$

7. **The unit of rate constant** for a given reaction is $M^{1-n} L^{n-1} t^{-1}$ where n is the order of reaction.

8. **The rate of the reaction** is equal to rate constants when the reactants are at their unit concentration.

9. Amount of reactants left after 'n' number of half life periods $a_n = \left(\frac{1}{2}\right)^n a_0$ (a_0 being the initial concentration of reactants.

10. Hydrolysis of ester in presence of mineral acid is a first order and pseudo unimolecular reaction whereas that in presence of alkali is a second order and bimolecular reaction.

11. The rate of a reaction is affected by nature of reactants, temperature, concentration of reactants presence of catalyst, certain energy radiation and surface area of the reacting species.

12. Upon raising the temperature by 10^0C, it is found that the reactant becomes two or three times the original value.

QUESTIONS

A. Very short type questions : (1 mark each)

1. What is the unit of the rate constant of a first order reaction ?
2. What is the unit of the rate constant of a second order reaction ?
3. Name any two factors which influence the rate of reaction.
4. The hydrolysis of ester in acid medium is a first or second order reaction ?
5. The rate of a reaction increases or decreases with the increase in temperature ?
6. Give an example of zero order reaction.
7. What is the half life period of a reaction having rate constant 6.93×10^{-4} sec^{-1}?
8. What is the unit of second order rate constant?
9. What is the unit of first order rate constant?
10. What is the reaction order if the unit of rate constant is litre mol^{-1} sec^{-1}?
11. Calculate the order of reaction having the rate expression rate = $k[A]^{1/2} [B]^{3/2}$.

B. Short answar type questions : (2 marks each)

1. What is half-life period ? How is it related to the rate constant for a first-order reaction ?
2. (a) The half-life period of a first order reaction is 30 seconds. Calculate its rate constant.
   (b) What is the value of rate constant of a first order reaction having half life period 10 minutes ?

3. (a) The rate constant of a first order reaction is 0.60 sec^{-1}. What is its half-life period?
   (b) If the rate constant of a first order reaction is 6.93×10^{-4} per second, what is its half-life period ?
4. Radioactive decay is a first order rate process. Two-third of a radioactive isotope disintegrates in 30 minutes. What is the rate constant of the disintegration ?
5. The rate constant of a first order reaction is, $k = 7.39 \times 10^{-5}$ sec^{-1}. Find the half-life of the reaction.
6. What is the difference between order and molecularity of a reaction ?
7. Derive the half-life period from the 1st order rate equation.
8. Distinguish between order and molecularity of a reaction.
9. What is zero order reaction ? Give one example.
10. Name any two factors which influence the rate of a reaction.
11. Half-life period of a substance is 20 days. After 30 days what percentage of the substance will be left.
12. Calculate the rate constant of a reaction (1st order) which is 90% complete in 10 minutes.

C. Short answer type questions : (3 marks)

1. State and explain how the molecularity and rate of reaction may be different. Give an example of pseudo unimolecular reaction.
2. What do you mean by activation energy ? How the activation energy can be determined ?
3. Show that in a first order reaction, the time taken for the completion of some fraction of change or any fraction of change is independent of the initial concentration of the reactant.
4. 75% of a reaction of the first order was completed in 32 minutes. When was it half completed ? (Ans: 16 minutes)
5. Thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 minutes how long would it take for 90% of the compound to decompose ? (Ans : 400 minutes)
6. First order reaction, $A \longrightarrow B$ requires activation energy energy of 70 kJ $mole^{-1}$. When a 20% solution of A was kept at 25^0C for 30 miniutes, 25% decomposition took place. What will be percentage decomposition in the same time in a 30% solution maintained at 40^0C ? Assume that activation energy remains constant in this range of temperature. (Ans : 67.21%)
7. A first order reaction is 20% complete in 10 minutes. Calculate the specific rate constant of the reaction and the time taken for the reaction for 75% completing ?

8. At 380^0C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mole^{-1}. Calculate the time required for 75% decomposition at 450^0C. (Ans : 20.36 min)

9. The decomposition of N_2O_5 according to the equation

$$2N_2O_5(g) \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reactions. (Ans : $3.70 \text{ x } 10^{-4}$ sec^{-1})

10. The ionization constant of NH_4^+ in water is 5.6×10^{-10} at 25^0C. The rate constant for the reaction of NH_4^+ and OH^- to from NH_3 and H_2O at 25^0C is 3.4×10^{-10} lit mol^{-1} sec^{-1}. Calculate the rate constant for proton transfer from water to NH_3

(Ans : $k = 6.07 \times 10^{-5}$ sec^{-1})

D. Long questions : (7 marks each)

1. Derive an expression for rate constant of first order reaction. Give an example for first order reaction.

2. Explain the terms molecularity and order of a reaction. Give one example from each of first and second order reactions.

   A 0.1 M HCN solution contained 0.2 moles of KCN per litre of the solution. What was the hydronium ion concentration of the solution. (K_a for HCN = 7.2×10^{-10})

3. State the rate equation for a first order reaction. Derive the half-life period from the rate equation.

   A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion ?

4. Write short notes on :
   a) Activation energy.
   b) Half-life period.
   c) Order and molecularity of a reaction.

5. Write notes on distinction between molecularity and order of reaction.

6. Derive the expression for first order rate constant. A first order reaction takes 69.3 minutes for 50% completion. How long will it take for 80% completion?

7. What do you mean by molecularity and order of reaction? Give one example each of the first and second order reaction.

E. Multi Choice Questions :

1. The unit of the rate constant for the second order reaction is :
   - (a) Mol^{-1} litre sec^{-1}.
   - (b) Mol. litre^{-1} sec^{-1}
   - (c) Sec^{-1}
   - (d) Mol litre^{-1} sec.
2. In which of the following cases, does the reaction go farthest to completion ?
   - (a) $k = 10^2$
   - (b) $k = 10^{-2}$
   - (c) $k = 10$
   - (d) $k = 1$
3. The specific rate constant of a first order reaction depends upon the,
   - (a) concentration of the reactant.
   - (b) concentration of the product.
   - (c) time
   - (d) temperature.
4. Half-life period of any first order reaction is,
   - (a) Directly proportional to intial concentration of reactant.
   - (b) Half of the rate constant.
   - (c) Same for all reactions.
   - (d) Independent of initial concentration of reactant.
5. The rate law for the reaction.

   $RCI + NaOH_{(aq)} \longrightarrow ROH + NaCl$ is given by, Rate = k_1 [RCl]. The rate of reaction will be :
   - (a) Doubled on doubling the concentration of NaOH.
   - (b) Halved on reducing the concentration of alkyl halide to one half.
   - (c) Increasesed on increasing the temperature of the reaction.
   - (d) Unaffected by increasing the temperature of the reaction.
6. What will be amount of $_{53}I^{128}$ ($t_{1/2}$ = 25 minute) left after 50 minutes ?
   - (a) One half
   - (b) One fourth
   - (c) One third
   - (d) One eight.

7. 75% of a first order reaction was completed in 32 minutes. 50% of the reaction will be completed in.
   - (a) 24 minutes.
   - (b) 16 minutes.
   - (c) 8 minutes.
   - (d) 22 minutes.

8. A large increase in the rate of reaction for a small rise in temperature is due to.
   - (a) Increase in number of collision.
   - (b) Increase in the number of activated molecules.
   - (c) Lowering of activation energy.
   - (d) Shortening of the mean free path.

9. For an endothermic reaction where ΔH represent the enthalpy of the reaction in kJ/mol, the minimum value for energy of activation will be.
   - (a) Less than ΔH
   - (b) Zero.
   - (c) Equal to ΔH
   - (d) More than ΔH

10. The half-life of a radioactive element is 1580 years. How long will it take to reduce to 1/4th of its original mass ?
    - (a) 3160 years
    - (b) 796 years
    - (c) 1580 years
    - (d) 6320 years

11. The isotope ${}_{19}K^{42}$ has a half life of about 12 hours. What fraction of the initial concentration of ${}_{19}K^{42}$ remains after 48 hours.
    - (a) 1/4
    - (b) 1/8
    - (c) 1/12
    - (d) 1/16

12. The hydrolysis of ethyl acetate in acid medium is a reaction of the
    - (a) Zero order
    - (b) First order
    - (c) Second order
    - (d) Third order.

13. The rate constant k'_a of one reaction is found to be double that of the rate constant k''_a of another reaction. Then the relation between the corresponding activation energies of the two reactions Ea' and Ea$''$ can be represented as,

(a) $E'_a > E''_a$ (b) $E'_a < E''_a$

(c) $E'_a = E''_a$ (d) $E'_a = 4E''_a$

14. When a graph is plotted between lnk and 1/T for a first order reaction, we get a straight line. The slope of the line is equal to

(a) $-E_a/2.303$ (b) $-\frac{2.303}{Ea.k}$

(c) $E_a/2.30k$ (d) $-E_a/k$

15. The temperature coefficient of most of the reactions lies between.

(a) 1 and 3 (b) 2 and 3

(c) 1 and 4 (d) 2 and 4

16. $t_{1/2}$ for zero order reaction is

(a) $\propto a$ (b) $\propto a^{1/2}$

(c) $\propto a^2$ (d) $\propto a^3$

17. The decomposition of N_2O_5 by

$2N_2O_5 \longrightarrow 4NO_2 + O_2$ follows first order kinetics.

Hence,

(a) The reaction is bimolecular
(b) The reaction is unimolecular
(c) $t_{1/2} \propto a^0$ (d) None of the above

18. The hydrolysis of ester in alkaline medium is

(a) Bimolecular reaction
(b) Termolecular reaction.
(c) First order reaction.
(d) Second order reaction.

19. The reaction $2Na + Cl_2 = 2NaCl$ is found to follow 3rd order kinetics, its molecularity is

(a) 1 (b) 2

(c) 3 (d) 4

20. If 'a' is the initial concentration of a substance which reacts according to zero order kinetic and 'k' is rate constant the time for the reactant to go to completion is,

(a) $\frac{a}{k}$ (c) $\frac{k}{a}$

(b) $\frac{2}{ka}$ (d) $\frac{2k}{a}$

21. Which one of the following does not influence the rate of reaction.
    - (a) Nature of reactant
    - (b) Concentration of reactant
    - (c) Temperature
    - (d) Molecularity,

22. When $AgNO_3$ solution is added to aqueus NaCl, a white precipitate is obtained. This reaction is :
    - (a) Slow
    - (b) With measurable speed
    - (c) Instantaneous
    - (d) None of the above.

23. The rate law for the single step reaction

    $2A + B \longrightarrow 2C$ is given by
    - (a) Rate = k[A] [B]
    - (b) Rate = $k[A]^2 [B]$
    - (c) Rate = k[A] [B]
    - (d) Rate = $k[A]^2 [B]^0$

24. The rate law of the reaction,

    $2A + B \longrightarrow 2C$ is represented as,

    Rate = $k [A]^2[B]$. If A is taken in large excess, the order of the reaction will be,
    - (a) Three (b) Two
    - (c) One (d) Zero.

25. If the rate of reaction between A and B is given by, rate = $[A][B]^2$, then the reaction is,
    - (a) First order with respect to A
    - (b) Second order with respect to B
    - (c) Third order overall
    - (d) all are correct.

26. The rate at which a substance reacts is proportional to.
    - (a) equivalent weight
    - (b) Molecular weight
    - (c) number of moles
    - (d) number of moles per litre.

27. Rate Expression of a chemical change is $\frac{dx}{dt} = k[A]^2 [B] [C]^0$

The order of the reaction is

(a) 2 (b) 3 (c) 1 (d) 0

28. A zero order reaction is one

(a) In which the difference of concentration of product and reactant is zero.
(b) In which concentration of the reactants do not change with time.
(c) In which one of the reactants is in large excess.
(d) In which reactants do not react.

29. The half-life period of a reaction is 100 minutes. In 400 minutes the initial concentration of 2.0g will become.

(a) 0.25g (b) 0.75g
(c) 0.125g (d) 0.1g

30. Which of the following rate law applies to a second order reaction involving only one reactant ?

(a) Rate is directly proportional to concentration.
(b) Rate is directly proportional to the square root of concentration.
(c) Rate is equal to square of concentration.
(d) Rate is proportional to the square of concentration.

31. In a second order reaction $2A \longrightarrow$ products, the concentration is halved. The half life of the reaction is,

(a) Halved (b) Doubled
(c) Becomes four fold (d) Unaltered

ANSWERS TO MULTIPLE CHOICE TYPE QUESTIONS

1. a
2. a
3. d
4. d
5. b,c
6. b
7. b
8.b
9. c
10. a
11. d
12. b
13. b
14. c
15.b
16. a
17. c
18. a,d
19. c
20. a
21. d
22.c
23. b
24. c
25. d
26. d
27. b
28. b
29.c
30. d
31. b

* * *

UNIT - V

CHAPTER - 5

SURFACE CHEMISTRY

5.1 ADSORPTION :

Introduction :

It is a known fact that there are unbalanced residual forces acting along the surface of a liquid or a solid. This is because if we consider a molecule present within the bulk of a liquid or solid we will find that the molecule is uniformly attracted from all sides by the molecules that are present in the neighbourhood and the net force of attraction that this molecule experiences is nil. On the otherhand if we consider a molecule present on the surface of the liquid or solid we will find that this molecule is subjected to some sort of inward pull by the molecules that are present in the bulk. The molecule has some unutilized valencies because there are no neighbouring molecules above the surface to which it can be bonded. As a result of these unbalanced residual forces the surface of the liquid or solid is always under strain and it has a tendency to attract and retain molecules of other substances preferably gases with which they are brought into contact. This ultimately results in higher concentration of the gas molecules on the surface of liquid or solid than in the bulk.

This phenomenon of higher concentration of molecular species on the surface of the solid or liquid than in the bulk is known as adsorption. The branch of chemistry dealing with the processes or the reactions taking place on the surface of the substances is known as **Surface chemistry.**

Adsorbent :

It is the substance upon whose surface the phenomenon of adsorption takes place. Colloids due to their small dimensions possess large surface area & act as good adsorbents, Examples include charcoal, silica gel, clay etc. (See Fig. 5.1)

Adsorbate :

The substance which is taken up on the surface is known as **adsorbate.**

Interface :

The common surface between the two phases where the adsorbed molecules concentrate is known as the **interface.**

Desorption :

It is reverse of adsorption. The process of removal of adsorbed substance from the surface of the adsorbent is known as **desorption.** The process is brought about either by heating or by reducing the pressure.

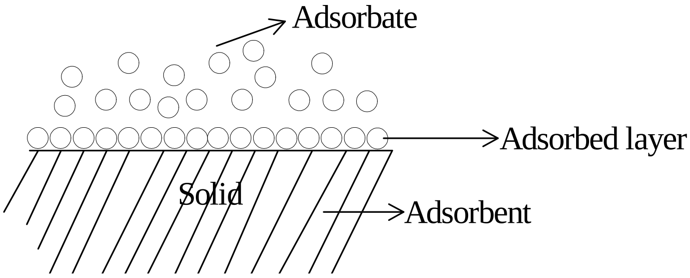


Fig. 5.1

Adsorption and Absorption :

Both adsorption and absorption are to be distinguished carefully. In adsorption the substance is retained only on the surface, it does not pass on to the interior or bulk of the solid or liquid. It is simply a surface phenomenon. But in case of absorption the substance in uniformly distributed throughout the body of the solid or liquid. Thus,

(i) Water vapour is absorbed by anhydrous calcium chloride but adsorbed by silica gel.

(ii) Ammonia is absorbed by water but adsorbed by charcoal.

The difference between adsorption and absorption is illustrated in the following Fig. 5.2 and Table - 5.1

Adsorption **Absorption**

Fig. 5.2

Table - 5.1 Distinction between adsorption and absorption

Adsorption	Absorption
1. It is a surface phenomenon and therefore occurs only on the surface	1. It occurs throughout the body of the material.
2. It is rapid in the beginning but slows down later at equilibrium.	2. It occurs at a uniform rate.
3. There is unequal distribution of the material at the surface and in the bulk.	3. There is uniform distribution of the molecular species throughout the bulk.

Sorption :

It is a term used to describe a process in which both absorption and adsorption take place simultaneously. This term has been introduced by Mc Bain. For example dyes get adsorbed as well as absorbed by the cotton fibre. Hydrogen is adsorbed as well as absorbed by charcoal.

TYPES OF ADSORPTION

Positive and Negative Adsorption :

If the concentration of adsorbate is more at the surface than in the bulk the adsorption is known as positive adsorption. On the otherhand if the concentration of adsorbate is less at the surface than in the bulk the adsorption is negative adsorption. Negative adsorption is observed only in case of solutions.

Basing on the nature of forces existing between adsorbate and adsorbent, the process of adsorption may be classified into two types namely (i) Physical adsorption or vanderWaals' adsorption (ii) Chemical adsorption or Langmuir adsoption.

(i) Physical adsorption :

The adsorbate is held on the surface of the adsorbent by weak intermolecular attractive forces known as vanderWaals' forces. This type of adsorption is also known as vanderWaals' adsorption or physisorption. Between solid and gas the equilibrium is established rapidly and it is reversible. Adsorption is temporary because of weak forces of attraction between the adsorbate and the adsorbent. This type of adsorption can be reversed by increasing the temperature or by decreasing the pressure.

Example – Adsorption of gases on charcoal.

(ii) Chemical adsorption or Chemisorption :

The adsorbate is held on the surface of the adsorbent by forces of attraction of almost the same strength as chemical bond. This type of adsorption is also known as Langmuir adsorption or chemisorption. Compared to physical adsorption it is more permanent and can not be easily reversed. Example– Adsorption of hydrogen by metals like Ni, Pd, Pt etc.

Heat of adsorption and Free Energy change :

As a result of adsorption the residual forces acting along the surface of the adsorbent go on decreasing. There is decrease in surface energy which appears as heat. Therefore, adsorption is necessarily exothermic and is accompanied by evolution of heat.

Molar heat of adsorption is the amount of heat evolved when 1 mole of gas or vapour is adsorbed on the surface of solid

We know the thermodynamic equation

$\Delta G = \Delta H - T\Delta S$ where

ΔG = change in Free Energy
ΔH = change in Enthalpy
ΔS = change in Entropy

Again ΔG should be negative for a feasible process. Since adsorption is an exothermic process ΔH is –ve. Again since the adsorbate changes from more random gaseous state to less random adsorbed state on the surface of the solid ΔS is –ve. Adsorption is thus accompanied with decrease in enthalpy so also decrease in entropy of the system. Since ΔH and ΔS are both –ve, it is clear that ΔH should have a high –ve value so as to make ΔG –ve. The heat of adsorption per mole of the adsorbate goes on decreasing i.e. ΔH becomes less and less –ve as adsorption proceeds further and further. At a particular stage ΔH becames equal to TΔS and ΔG becomes zero. This is the case of equilibrium.

Table - 5.2 Comparison between physical adsorption and chemical adsorption

Physical adsorption.	Chemical adsorption.
1. Forces of attraction are weak vanderWaals' forces.	1. Forces of attraction are strong chemical bond forces.
2. Occurs at low temperature.	2. Occurs at high temperature.
3. It is not specific.	3. It is highly specific.
4. Heat of adsorption is low, usually it is in the range of 20–40 kJ mole^{-1}.	4. High heat of adsorption, in the range of 40-400 kJ mole^{-1}
5. It is multilayer adsorption. The adsorbed layer is several molecules thick.	5. It is single layer adsorption. The adsorbed layer is only of unimolecular thickness.
6. It is a reversible process.	6. It is highly irreversible.
7. Rate of adsorption increases with increase of pressure of the adsorbate.	7. Rate of adsorption decreases with increase of pressure of the adsorbate.
8. It does not require any activation energy.	8. It requires activation energy.

5.2 ADSORPTION OF GASES ON SOLIDS :

The adsorption of gas on the surface of solid is known as **occlusion.** The extent of adsorption of a gas on solid adsorbent depends on the following factors.

1. Nature of the gas (Adsorbate) :

Physical adsorption is non specific. So a gas gets adsorbed on the surface of the solid to a greater or lesser extent. It has been observed that readily soluble and easily liquefiable gases like NH_3, HCl, Cl_2, SO_2 etc are adsorbed more than the so called permanent gases like H_2, N_2, O_2 etc. This is because the vanderWaals' forces involved in the adsorption are more predominant in the former category than in the latter category.

On the otherhand chemical adsorption is highly specific. So adsorption of gas on the surface of solid can take place only if it can form a chemical bond with it.

2. Nature of the solid (Adsorbent) :

Easily liquefiable gases can be adsorbed on the surface of most commonly used adsorbent activated charcoal. Metals like Ni, Pt & Pd are also used as adsorbents for adsorption of permanent gases like H_2, O_2, N_2 etc. Activated charcoal is used in gas masks for adsorption of poisonous gases.

3. Specific area of the solid (adsorbent) :

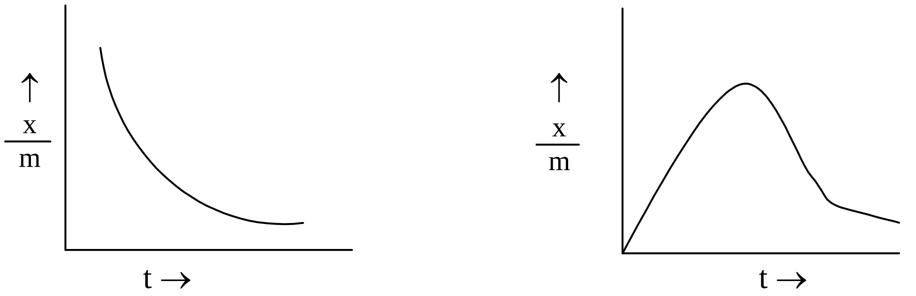
The extent of adsorption also depends upon the surface area of the adsorbent. The greater the surface area per unit mass of the adsorbent (specific surface area), the greater is the extent of adsorption. This is the reason why the porous or finely divided forms of the adsorbents adsorb effectively.

4. Effect of temperature :

Adsorption is associated with evolution of heat. According to Lechateliers' principle the extent of adsorption increases with fall in temperature. In adsorption an equilibrium is established between the gas in contact with the solid and the gas on the surface.

$$\text{Gas + Solid} \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Gas adsorbed on the surface of the solid.} \Delta H \text{ is –ve.}$$

Adsorption isobar is the graph drawn between the extent of adsorption (x/m) and temperature 't' at constant pressure. The adsorption isobars for both physical and chemical adsorption are shown below in Fig-5.3.



(Physical adsorption) (Chemisorption)

x = mass of the adsorbate m = mass of adsorbent

Fig-5.3

In physical adsorption there is continuous fall in $\frac{x}{m}$ with rise in temperature. But in chemisorption there is rise in $\frac{x}{m}$ value in the beginning and then a fall in value with rise in temperature. Like chemical reactions, chemisorption requires energy of activation, hence there is rise in $\frac{x}{m}$ value in the beginning.

5. Effect of pressure of the gas.

We know that adsorption is a reversible process and is accompanied with decrease of pressure. Thus increase of pressure tends to increase the magnitude of adsorption. The variation of adsorption with pressure at constant temperature is generally represented gaphically as in Fig-5.4. The plot is called the **adsorption isotherm**.

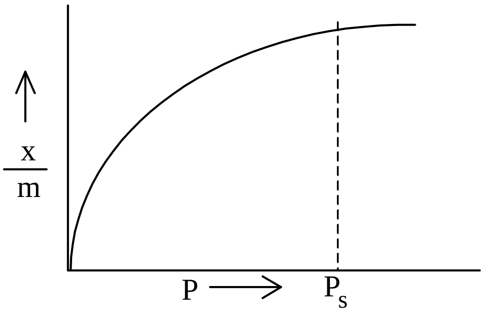


Fig-5.4 Adsorption isotherm

6. Activation of adsorbent :

Increasing the adsorbing power of the adsorbent is otherwisely known as activation of adsorbent. The more the activation of adsorbent the more is the extent of adsorption. Activation can be made by the following methods :

(a) by mechanical rubbing or making the surface of adsorbent rough and porous.

(b) by using adsorbent in finely divided form. This increases the surface area and also the extent of adsorption.

(c) by the action of super heated steam on the adsorbent. Charcoal is activated by this method.

5.3 FREUNDLICH'S ADSORPTION ISOTHERM :

At equilibrium pressure P_S, $\frac{x}{m}$ attains its maximum value and no more adsorption occurs even if the pressure is increased further. This is called saturation state and P_S is referred to as saturation pressure. Such type of isotherm can be obtained if

(i) The adsorbed gas forms a unimolecular layer on the surface of the solid.

(ii) The adsorbed gas behaves ideally is the vapour phase.

Freundlich gave the following relationships between $\frac{x}{m}$ and p

(a) **At low pressure**

The graph is almost linear and sloping, which indicates that $\frac{x}{m}$ is directly proportional to pressure (P) is

$$\frac{x}{m} \propto P$$

or, $$\frac{x}{m} = KP, \text{ where K is a constant.}$$

(b) **At high pressure** (beyond saturation pressure P_S)

The graph is a straight line parallel to the pressure axis. Hence $\frac{x}{m}$ becomes independent of P.

$$\frac{x}{m} \propto P^o$$

or, $$\frac{x}{m} = KP^o, \text{ where K is a constant.}$$

(c) **At intermediate pressure :** Hence $\frac{x}{m}$ depends upon pressure raised to the powers between 0 and 1. This is represented mathematically as

$$\frac{x}{m} \propto P^{\frac{1}{n}}$$

or, $$\frac{x}{m} = KP^{\frac{1}{n}}$$ where 'n' is constant that depends on the nature of adsorbate and adsorbent. The value of $\frac{1}{n}$ lies in between 0 and 1.

The above relationship is known as **Freundlich's adsorption isotherm.**

Taking logarithms of both the sides of above equation,

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P.$$

If log $\frac{x}{m}$ is plotted against log P, a straight line will be obtained having a slope $\frac{1}{n}$ and the intercept on log ($\frac{x}{m}$) axis will correspond to logK. (see Fig-5.5)

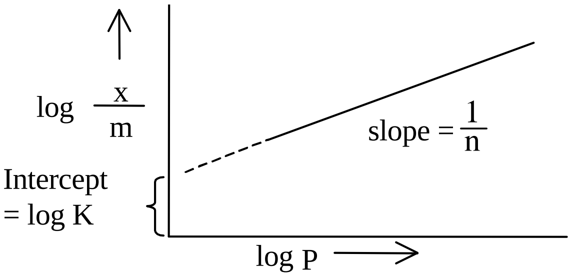


Fig. 5.5 Graph of log $\frac{x}{m}$ vs log P

From the graph it is possible to find out the value of K and n.

5.4 LANGMUIR ADSORPTION ISOTHERM :

The theory of adsorption of gas on the surface of a solid was proposed by **Langmuir**. The surface of the solid is considered to be made up of a number of elementary sites. Each site adsorbs one gas molecule. All the adsorption sites are assumed to be equivalent. It is also assumed that a dynamic equilibrium exists between the adsorbed molecules and the free molecules. If A is the gas molecule and X is the surface of the solid.

$$A_{(g)} + X\ (\text{surface}) \underset{K_d}{\overset{K_a}{\rightleftarrows}} A\,X$$

Where, K_a ⟶ Rate constant for forward reaction i.e absorption.

K_d ⟶ Rate constant for backward reaction i.e desorption.

If N ⟶ Total number of sites on the surface

θ ⟶ Fraction of the surface sites occupied by gas molecules

$(N - N\theta)$ i.e $N(1-\theta)$ ⟶ Number of vacant sites on the surface

P_A ⟶ Pressure of A

Then, the rate of adsorption = $K_aP_A N(1-\theta)$ ....(1)

and the rate of desorption = $K_d N\theta$ ....(2)

At equilibrium the rate of adsorption is equal to the rate of desorption

So, from equ. (1) & (2)

$$K_a P_A N(1-\theta) = K_d N\theta \text{...............(3)}$$

or $$KP_A(1-\theta) = \theta \text{..................(4)}$$

where $K = \frac{K_a}{K_d}$

Equation (4) can be written as

$$\frac{1-\theta}{\theta} = \frac{1}{KP_A} \text{ .... (5)}$$

or, $\frac{1}{\theta} - 1 = \frac{1}{KP_A}$ .... (6)

or, $\frac{1}{\theta} - = \frac{1}{KP_A} + 1 = \frac{1 + KP_A}{KP_A}$ ....(7)

$\boxed{\theta = \frac{KP_A}{1 + KP_A}}$ ....(8)

Equ. (8) is called the **Langmuir Adsorption isotherm.**

Assumptions involved in the derivation of Langmuir Adsorption isotherm

(i) The gas adsorbed forms a monolayer on the surface of the adsorbent.

(ii) The adsorbed gas behaves ideally in the vapour phase

(iii) Each binding site on the surface of the adsorbent has same affinity for the gas molecules, The surafce of the solid in thus homogeneous.

(iv) The molecules adsorbed on different sites do not interact with each other.

(v) Adsorption is localised and takes place on collision of the gas molecules with the vacant sites on the surface of the solid.

(vi) For all sites the heat of adsorption is the same. It is independent of pressure and fraction of the surface of the adsorbent covered by gas molecules.

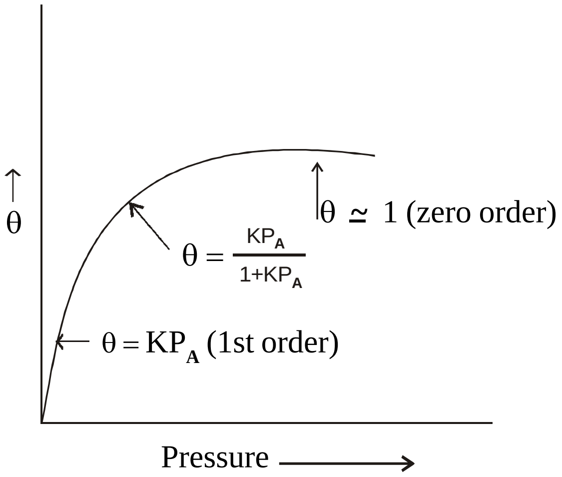
Study of adsorption isotherm

Consider equation (8) . $\theta = \frac{KP_A}{1 + KP_A}$

(a) At low pressure $KP_A << 1$, so that

$\theta = KP_A$ ....(9)

Thus, the fraction of the surface covered is directly proportional to the partial pressure of the gas molecules. This corresponds to 1st order reaction. When θ is plotted against pressure the nature of the curve is as depicted below. (Fig. 5.6)



(Fig. 5.6)

(b) **At high pressure,** $KP_P >> 1$, so that

$$\theta = \frac{KP_A}{KP_A} = 1 \text{ .... (10)}$$

Thus at high pressure θ tends to become unity. The surface sites are completely covered with gas molecules. The reaction rate becomes independent of pressure and therefore the reaction becomes zero - order.

(c) **At intermediate pressure**

From equation (9) & (10)

At high pressure $\theta = 1$

At low pressure $\theta = KP_A$

Hence, at intermediate pressure $\theta = KP_A^{1/n}$

where $\frac{1}{n}$ is a value lying between zero and one.

Since there is adsorption of single layer of molecules on the surface, the fraction θ is proportional to the amount of gas adsorbed per unit mass of adsorbent.

Representing this quantity by 'a',

we have, $a \propto \theta$ or, $a = K_1 \theta$ where K_1 is another constant.

So , $a = \frac{x}{m} = K_1 \theta = K_1 KP_A^{1/n} = kP_A^{1/n}$ .... (11)

where, x = amount of gas adsorbed and

m = gram of adsorbent

Equation (11) is the same as Freundlich adsorption isotherm.

Limitations

(i) Langmuir's theory of adsorption holds good only at high temperature and low pressure

(ii) As the pressure increases or temperature decreases some additional layers are formed. The adsorption becomes multimolecular, it no longer remains monomolecular.

5.5 APPLICATIONS OF ADSORPTION :

The phenomenon of adsorption has a wide range of applications. A few applications are given below.

1. **Removal of poisonous gases :** Activated charcoal is used in gas masks in which all poisonous gases and vapours like CH_4, CO etc are adsorbed by charcoal leaving the pure air through its pores.
2. **Removal of colouring matter :** Animal charcoal is used as a decolouriser in the manufacture of cane-sugar.

3. **Control of humidity :** Silica and alumina gels are used as adsorbents for removing moisture and controlling humidity.
4. **Creation of high vacuum :** If a bulb of charcoal cooled in liquid air is connected to a vessel which has already been evacuated by a vacuum pump, the remaining traces of air are adsorbed by charcoal and a high vacuum is created.
5. **Chromotographic analysis :** Chromatographic purification of compounds is based upon adsorption.
6. **Supply of nutrients to the plants :** Colloidal particles of clay present in the soil adsorb certain amount of moisture in which the nutrients such as compounds of nitrogen, phosphorus and potassium dissolve and pass onto the plants through roots.
7. **Catalysis :** The phenomenon of adsorption plays an important role in heterogenous catalysis. The use of finely divided iron in the manufacture of ammonia and finely divided Nickel in hydrogenation of oils are the examples.
8. **Removal of hardness of water :** The use of ion exchange resins for removal of hardness of water is based on adsorption.
9. **Medicines :** Various drugs can be adsorbed by body tissues. The effectiveness of medicines is controlled by their selective adsorption.
10. **Analytical chemistry :** In volumetric analysis adsorption indicators are used. Also there are selective adsorption of certain ions on some precipitate. For example $Ba(NO_3)_2$ can not be used for the precipitation of $BaSO_4$ because of the adsorption of NO_3^- ion on $BaSO_4$ precipitate.

5.6 CATALYSIS :

A substance that alters the rate of a chemical reaction without itself undergoing a change is known as a **catalyst**. At the end of the chemical reaction the catalyst can be recovered unchanged.

A catalyst may accelerate or retard the rate of a chemical reaction. When it accelerates the rate it is known as a positive catalyst whereas in case of retardation it is known as a –ve catalyst.

eg. In the Haber's process for synthesis of Ammonia Iron acts as a positive catalyst where as in the process of decomposition of H_2O_2, acetanilide acts as a negative catalyst.

5.6.1 Characteristics of a Catalyst

1. The catalyst remains unaffected in amount, so also in chemical compostion at the end of a chemical reaction.

   eg. Consider the manufacture of H_2SO_4 in lead chamber process. In this case nitric oxide acts as a catalyst.

$$NO_{(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons NO_{2(g)}$$

$NO_{2(g)}$ reacts with oxygen to form sulphur trioxide. At the end of the process Nitric oxide is regenerated.

$$NO_{2(g)} + SO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$

2. The catalyst in a very small quantity is required for the reaction.

e.g. Colloidal platinum at a concentration of 10^{-8} mol dm^{-3} catalyses the decomposition of H_2O_2.

However in certain cases the rate of the reaction depends upon the concentration of catalyst.

e.g. (i) Rate of inversion of cane sugar depends upon the concentration of H^+ used as catalyst.

(ii) In some heterogeneous reaction the rate of the reaction increases with increase in surface area of the catalyst. This is the reason why the efficiency of a solid catalyst increases when it is present in finely divided state.

3. In a reversible reaction, a catalyst can not alter the state of equlibrium.

A catalyst catalyses both forward and backward reaction to the same extent in a reversible reaction and therefore does not have any effect on equilibrium constant.

4. A catalyst gets termporarily involved in the reaction providing an alternative reaction path of comparatively lower activation energy than that for uncatalysed reaction.

5. Tha catalyst can not initiate the reaction. The reaction can occur, though slowly, even in the absence of catalyst.

6. The catalyst is gnerally specific in action.

e.g. MnO_2 catalyses the decomposition of $KClO_3$ but not $KClO_4$ or KNO_3.

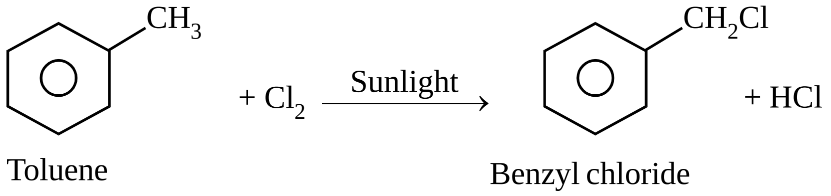
Enzymes have also specific catalytic action.

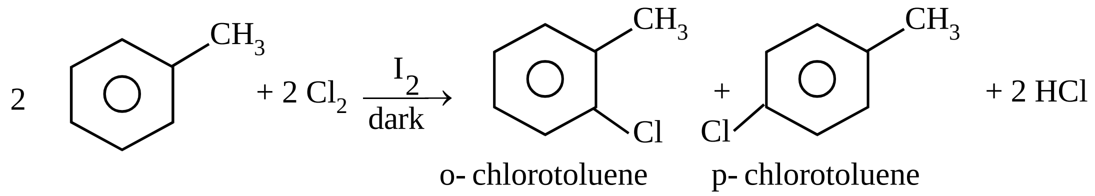
7. The catalyst can not alter the nature of the products of the reaction.

e.g. $KClO_3$ on decomposition gives oxygen. This thing happens in the presence or in the absence of catalyst MnO_2. Similarly the combination of H_2 and N_2 always results in the formation of NH_3 whether a catalyst is added or not.

However, there are certain exceptions.

(i) Chlorination of toluene in the absence of catalyst and in the presence of sunlight results in the formation of benzyl chloride where as in the presence of halogen carrier like Fe or I_2 and in the absence of sunlight forms o – & p – chlorotoluene.





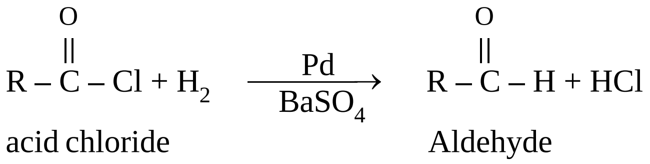
8. A catalyst is poisoned by certain substances.

e.g. (i) The rate of formation SO_3 in the contact process can be slowed down considerably in the presence of some arsenic compounds, even in traces.

(ii) In the hydrogenation of ethene the catalytic activity of Cu can be reduced by the presence of Hg even in traces.

(iii) But in certain cases it is necessary to poison the catalyst so as to get the required product.

Acid chlorides can be reduced to aldehydes by catalyst Pd suspended on $BaSO_4$.



$$\underset{\text{acid chloride}}{R-\overset{\overset{\large O}{||}}{C}-Cl} + H_2 \xrightarrow[BaSO_4]{Pd} \underset{\text{Aldehyde}}{R-\overset{\overset{\large O}{||}}{C}-H} + HCl$$

The function of $BaSO_4$ is to poison the catalyst Pd thereby not allowing the reaction to proceed further to alcohols.

9. A catalyst has an optimum temperature at which its efficiency becomes maximum.

10. The catalytic activity can be enhanced by the presence of certain substances known as promoters.

e.g. In the synthesis of NH_3 by Haber's process molybdenum acts as promoter to the catalyst iron.

5.6.2 Types of catalysis

There are two types of catalysis

(a) Homogeneous catalysis

(b) Heterogeneous catalysis

Besides the above two there is a third category known as Enzyme catalysis which is due to its own characteristics.

(a) Homogeneous Catalysis

In this case the reactants and the catalyst form a single phase. Examples are summerized in the following table - 5.3.

Table - 5.3

Homogeneous Catalysis

Process	Products	Typical Catalyst
1. Lead chamber process for manufacturer of H_2SO_4 $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$	$SO_3(g)$	NO
2. Oxidation of CO(g) by $O_2(g)$	$CO_2(g)$	NO
3. Inversion of Cane sugar	Glucose and Fructose	H^+
4. Hydrolysis of an ester	Carboxylic Acid and Alcohol	H^+
5. Decomposition of CH_3CHO	CH_4	I_2 Vapour

(b) Heterogeneous Catalysis

In this case the catalyst is in a different phase than that of the reactants. The catalyst is usually a metal or an oxide

It is present in finely divided state to provide large surface area. The reactants are usually liquids or gases. Most commonly used catalysts are metals like Pt, Ni, Fe, Cu & metal oxides like ferric oxide, zinc oxide and molybdenum oxide. Examples are summarised in the following Table - 5.4.

Table - 5.4

Heterogeneous catalysis

Process	Products	Typical Catalyst
1. Polymerization of Propylene	Polypropylene	Ti (IV) chloride
2. Contract process for manufacture of H_2SO_4	SO_3	Pt.
3. Bosch process for manufacture of H_2	CO_2 and H_2	Fe
4. Ammonia Synthesis	$NH_3(g)$	Fe with Al_2O_3, MgO, CaO, K_2O etc.
5. Alkylation of Benzene	$C_6H_5 - CH_3$	H_3PO_4 on SiO_2
6. Hydrogenation of oils	Vegetable (fat) ghee	Ni

5.7 ENZYME CATALYSIS :

Enzymes are complex nitrogeneous substances (proteins) with high relative molar mass of the order of 10,000 or even more and are derived from living organisms. Certain reactions may be catalysed either by the organisms in the bulk like yeast or by the chemical synthesised by and extracted from them like yeast extract. Most of the biochemical processes such as digestion and biosynthesis are catalysed by enzymes.

Characteristics of enzyme catalysis

1. Reactions catalysed by enzymes are highly specific. Each reaction is catalysed by a specific enzyme. For example the enzyme urease catalyses the hydrolysis of urea and no other reaction.

$$NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

2. In case of enzyme catalysis the rate of the reaction is more dependant on the amount of the catalyst (enzyme) than it is in case of other type of catalysis.
3. There exists an optimum temperature for all reactions catalysed by the enzymes. At this temperature the efficiency of the catalyst is maximum. The enzyme loses its catalytic activity above this temperature and below this temperature the rate of the reaction becomes slow due to temperature effects. The optimum temperature for maximum enzyme activity varies between 15°C to 25°C.
4. The catalytic activity of the enzymes is due to their capacity to lower the activation energy needed for a particular reaction.
5. The enzyme lose their catalytic activity in the presence of electrolytes and on exposure to ultraviolet radiations. The addition of electrolyte results ultimately in coagulation of enzymes.
6. For each enzyme there is one specific co-enzyme. Co-enzymes are the activators or promoters for enzyme reactions. The activity of enzymes gets paralysed in case the co-enzyme is separated from the enzyme.
7. Enzyme reactions are far more sensitive to catalysitc poisons than any other type of catalytic reactions. Some typical poisons are HCN, H_2S, CS_2 etc.
8. The rate of a chemical reaction catalysed by an enzyme in maximum at a particular value of pH called optimum pH value which is between 5-7. The following table summarizes the examples of reactions catalysed by particular enzymes.

Table - 5.5
Enzyme Catalysis

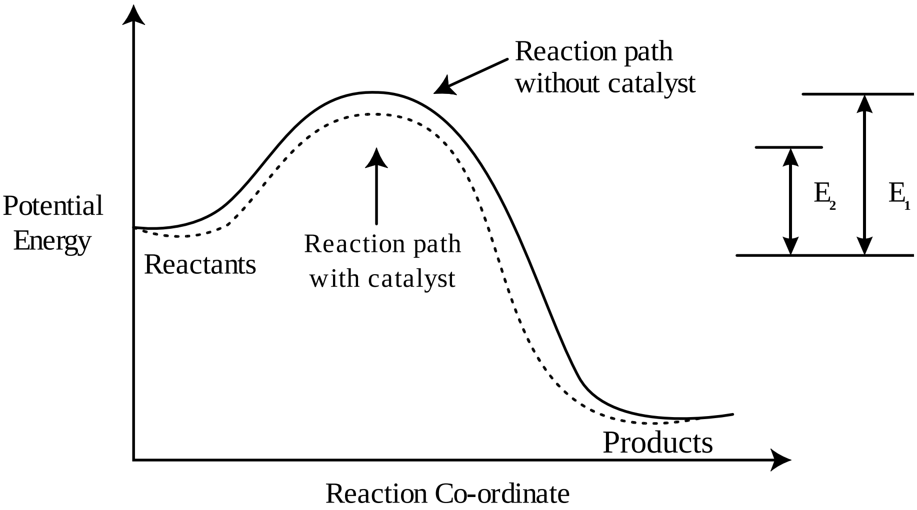
Reaction	Catalyst
1. $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_5H_{12}O_6$ sucrose glucose fructose	Invertase
2. $(C_6H_{10}O_5) + nH_2O \rightarrow C_{12}H_{22}O_{11}$ starch maltose	Diastase
3. $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$ glucose	Zymase
4. $NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$ urea	Urease

5.8 EFFECT OF THE CATALYST ON ACTIVATION ENERGY :

The effect of catalyst can be explained by intermediate complex theory. Consider the following reaction.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

In this case MnO_2 catalyses the reaction so as to increase the rate considerbly. According to this theory the catalyst forms temporary bonds with reactants forming an intermediate complex. The complex formed has transitory existence and it decomposes to yield the products and the catalyst. The catalyst provides an alternative pathway involving lower activation energy. The potential energy barrier is thus lowered in presence of the catalyst as is evident from the following figure 5.7.



E_1 → Energy of activation without catalyst.

E_2 → Energy of activation with catalyst.

Fig. 5.7 Effect of catalyst on activation energy

The lower the value of activation energy of a reaction the faster will be its rate. This is also evident from Arrhenius equation $k = A.e^{-Ea/RT}$

5.9 ADSORPTION THEORY OF HETEROGENEOUS CATALYSIS :

According to this theory when the reactant molecules in gaseous state or in solution are adsorbed on the surface of solid catalyst, the rate of the reaction is increased due to greater accumulation of reactant molecules on the surface of the catalyst. Since adsorption is an exothermic process, the heat of adsorption is used in increasing the rate of the reaction. The catalytic activity is localised on the surface of the catalyst and this can be explained by a suitable machanism. The mechanism involves a number of steps.

1. Reactant molecules are diffused to the surface of the catalyst.
2. Reactant molecules get adsorbed on the surface of the catalyst.

3. Formation of an intermediate.
4. Desorption of reaction products from the surface of the catalyst.
5. Diffusion of reaction products away from the catalyst's surface.

The above five steps can be pictorially summarised by the following figure 5.8.

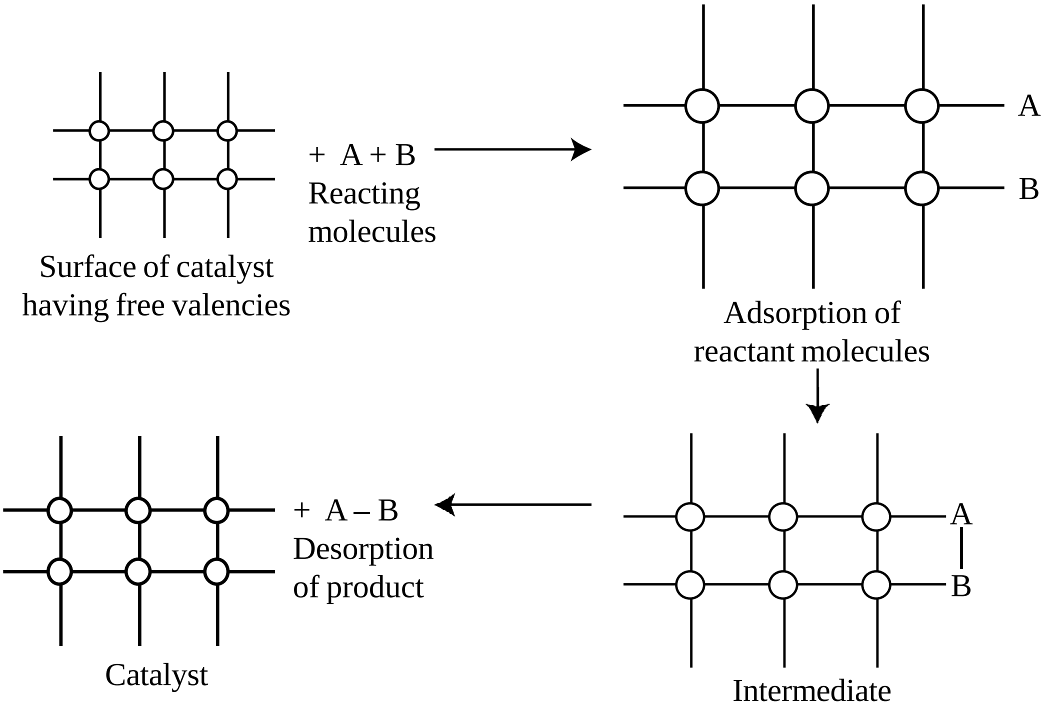


Fig. 5.8 Adsorption of reacting molecules, formation of intermediate and desorption of product

5.10 IMPORTANT FEATURES OF SOLID CATALYSTS :

1. Activity : We know that the reactant molecules are to be adsorbed on the surface of the catalyst. The activity of a catalyst depends upon the strength of chemisorption to a greater extent. The reactant molecules must get adsorbed reasonably strongly on the surface of the catalyst to become active. But the adsorption must not be that strong enough to make the reactant molecules immobile.

e.g. In case of hydrogenation reaction the catalytic activity increases from Gp5 to Gp11 metals with maximum activity shown by Group 7-9 elements.

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$$

Activity is thus the ability of the catalyst to increase the rate of a chemical reaction, the degree of increase can be as high as 10^{10} times in certain cases.

2. **Selectivity :** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. The same reactants may lead to form different products in presence of different catalysts.

e.g. (a) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

(b) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(c) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Thus the action of a catalyst is highly selective in nature. A substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

5.11 COLLOIDAL STATE :

Introduction :

Thomas Graham while working on diffusion observed that solutions of some substances diffused easily through a parchment membrane whereas others did not. He divided the soluble substances into two categories namely **crystalloids** and **colloids**. This observations led to the development of a new branch of knowledge known as **colloid science.**

Crystalloids :

There are substances the solutions of which can diffuse rapidly through vegetable or animal membrane. Such substances are called crystalloids. Examples of crystalloids include salt, sugar, urea, acids and bases.

Colloids :

There are substances the solutions of which show little or no tendency to diffuse through vegetable or animal membranes. Such substances are called **colloids.** Examples include gelatin, glue, albumen, silicic acid etc.

After careful observation Thomas Graham and other investigators came to a conclusion that between crystalloid and colloid there was no rigid distinction since the same substance could behave both as crystalloid and colloid when dispersed in different medium. For example, soap forms a colloidal solution in water but behaves as a crystalloid in alcohol. NaCl is a crystalloid when dissolved in water but acts as a colloid in benzene. The term "colloidal substance" has therefore lost its importance and **"colloidal state"** is most commonly used for all purposes since almost all substances can be brought into colloidal state by suitable means.

5.12 TYPES OF COLLOIDAL SYSTEM :

(i) A colloidal system consists of finely divided particles of any substance with diameters lying within the range 1 to 100 nm (*i.e* 10 to 2000 A^0) dispersed in any medium.

(ii) A colloidal system is a two phase system comprising of dispersed phase and dispersion medium.

(iii) The continuous phase is known as dispersion medium in which extremely minute particles of discontinuous phase or dispersed phase lying within the colloidal range are suspended.

(iv) The dispersed phase and dispersion medium may be solid, liquid or gas. Thus different colloidal systems are possible depending upon the nature of dispersed phase and dispersion medium. (as shown in table- 5.6)

Table - 5.6 (Different Colloidal systems)

Dispersed phase	Dispersion medium.	Colloidal system.	Examples
Solid	Solid	Solid Sol	Mineral, gem stones
Solid	Liquid	Sol	Paints, Proteins, gold sol, Ink.
Solid	Gas	Aerosol of solid	Smoke, dust storm
Liquid	Solid	Gels	Butter, Jellies, Boot polish
Liquid	Liquid	Emulsion	Milk, medicines. Cod-liver oil.
Liquid	Gas	Aersol of liquid	Fogs, clouds, mists Fine insecticide sprays.
Gas	Solid	Solid foam	Rubber, Pumice stone.
Gas	Liquid	Foam or Froth	Soap suds, lemonad froth

True solutions, Colloidal solutions and Suspensions

Depending upon the size of particles constituting the dispersed phase and dispersion medium the solutions are divided into three categories.

(i) **True solutions :** Water soluble substances like sugar or sodium chloride when added to water dissolve giving a homogeneous solution. The particles of the solute are of molecular size, invisible and do not settle down on standing. True solutions are therefore called molecular solutions.

(ii) **Suspensions :** Insoluble substances like barium sulphate or clay when added to water settle down on standing for sometime. The particles are large enough to be visible in naked eye. Suspensions are known as coarse dispersions.

(iii) **Colloidal solutions :** In between the two extremes lie particles which are bigger than molecules but are too small to be visible even under a most powerful microscope. They have a little or no tendency to settle down when suspended in a liquid. Colloidal solutions are known as colloidal dispersions.

The properties of true solution, suspension and colloidal solution are summarised in Table-5.7.

Table - 5.7 Properties of True solution, colloidal solution and suspension

	Properties	True solution	Colloidal solution	Suspension.
1.	Size	Less than 1 nm	Between 1 nm & 100nm.	> 100 nm.
2.	Diffusion.	Diffuse readily through parchment membrane.	Diffuse slowly through parchment membrane.	No diffusion
3.	Visibility	Invisible even under ultramicroscope	Visible under ultramicroscope	Visible even in naked eye.
4.	Scattering of light	No scattering	Scattering takes place (Tyndall effect)	Do not show Tyndall effect.
5.	Filtration	Possible through filter paper & parchment membrane	Possible through filter paper but not through parchment paper.	Neither possible through filter paper nor through parchment paper.

5.13 CLASSIFICATION OF COLLOIDS :

On the basis of affinity of dispersed phase for dispersion medium the colloidal solutions may be classified as follows.

(a) **Lyophilic Colloids**

- (i) These are solvent loving.
- (ii) These are stable colloids.
- (iii) They have strong attraction for the dispersion medium.
- (iv) On evaporation of the dispersion medium from colloidal sol, the residue can pass into colloidal state on mere addition of the liquid. Hence these are also known as **reversible colloids.**
- (v) Examples are proteins, starch and rubber.

(b) **Lyophobic Colloids**

- (i) These are solvent hating.
- (ii) These are less stable.
- (iii) They have very little attraction for the dispersion medium.
- (iv) The residue left on evaporation can not readily be reconverted to a sol. Hence these are also known as Irreversible colloids.
- (v) Examples are Ferric hydroxide, Arsenic sulphide, Gold and other metals.

Colloidal solutions in water are called hydrosols and those in alcohol are called **alcosols**. Hydrosols may be hydrophilic or hydrophobic depending upon their affinity for water. Gelatin, gum etc. are hydrophilic colloids where as metal sulphides and metal hydroxides are hydrophobic colloids.

Difference between lyophilic and lyophobic colloids are summarised in Table-5.8.

Table – 5.8 Distinction between lyophilic and lyophobic sols

Property	Lyophilic sols	Lyophobic sols.
1. Surface Tension	Lower than that of dispersion medium.	Same as that of the dispersion medium.
2. Visibility	Particles can not be detected even under ultramicroscope.	Particles can be readily detected under ultra-microscope.
3. Viscosity	Much higher than that of the medium.	Same as that of the medium.
4. Reversibility	Reversible	Irreversible.
5. Stability	More stable	Less stable.
6. Action of electrolytes	Addition of small quantity of electrolytes has very little effect and larger amount is needed to cause coagulation.	Addition of small quantity is sufficient to cause coagulation.
7. Migration in an electric field.	Particles may migrate in either direction or not at all in an electric field.	Particles migrate either towards anode or towards cathode in an electric field.
8. Hydration	Particles are extensively hydrated.	No hydration.

5.14 CLASSIFICATION OF COLLOIDS ON THE BASIS OF MOLECULAR SIZE :

On the basis of molecular size colloids have been classified into three types.

(i) Multimolecular colloids

The dispersed phase consists of aggregate of a large number of a small molecules having molecular size less than 1 nm i.e 10^{-9} m. The aggregate has dimensions of colloidal size. The particles are held together by weak forces of attraction like vander Waals forces. They are usually lyophobic in nature. Examples include platinum sol, gold sol, sulphur sol etc.

(ii) Macromolecular colloids

The dispersed phase consists of macromolecules or polymers having very high molecular mass. The molecular size is of colloidal dimensions. They are usually lyophobic in nature. Examples include starch, cellulose, plastic, protein etc.

(iii) Micelles or Associated colloids

The dispersed phase consists of aggregates of large number of particles of colloidal size in concentrated solutions. The aggregated particles are called **micelles** at higher concentration. The molecules contain both lyophilic and lyophobic groups. Examples include soaps and synthetic detergents.

5.15 PREPARATION OF COLLOIDAL SOLUTION :

Colloidal state ($10\ A^o$ to $10^3\ A^o$) is an intermediate state between suspension ($> 10^3\ A^o$) and a true solution ($1 - 10\ A^o$). Two types of methods are generally employed for preparation of colloidal solution.

1. **Dispersion methods :** These methods involve the breaking of coarse particles into colloidal dimensions. The dispersion methods may be of following types.

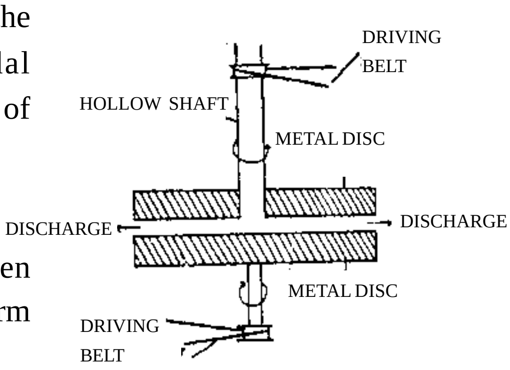


Fig -5.9

(a) **Mechanical dispersion :**

(i) The substance is finely ground and then shaken with the dispersion medium to form a coarse suspension.

(ii) The Coarse suspension is broken down to particles of colloidal dimensions in a colloid mill.

(iii) In the colloid mill there are two metal discs nearly touching each other and rotating in opposite direction with very high speed.

(iv) The suspension is allowed to pass through the rotating disc and broken down to particles of colloidal size

(b) **Electro-dispersion. (Bredig's arc method)**

(i) This method is suitable for preparing colloidal solutions of metals like silver, gold, platinum etc.

(ii) An electric arc is struck between the metal electrodes that are immersed in the dispersion medium. The dispersion medium is placed in the freezing mixture.

(iii) The electrodes should be made up of the same metal whose colloidal solution is to be prepared.

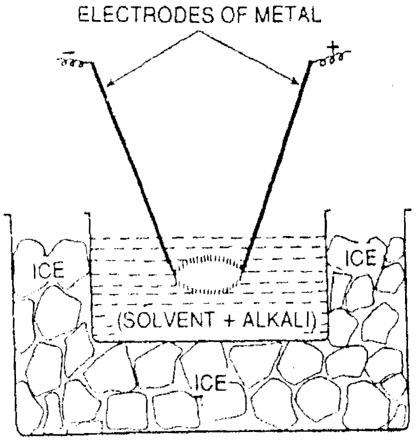


Fig-5.10

(iv) The enormous heat of the arc turns the metal into vapour which get condensed by the ice cold water to give particles of colloidal dimensions. (Fig-5.10)

(v) A little KOH is added to the dispersion medium to stabilise the sol.

(c) **Peptisation :**

(i) The process of conversion of a precipitate into colloidal dispersion by chemical means is known as *peptisation.*

(ii) An electrolyte having an ion in common with the material to be dispersed is necessary for the formation of sol. The electrolyte added is known as the *peptising agent.*

(iii) The peptising action is due to the preferential adsorption of one of the ions of the electrolyte on the surface of particles of the material.

(iv) When a small amount of $FeCl_3$ is added to freshly prepared $Fe(OH)_3$, a dark reddish brown colloidal solution results. Here $FeCl_3$ is the peptising agent. Fe^{3+} ions from $FeCl_3$ get adsorbed on the surface of $Fe(OH)_3$. Since like charges repel each other, colloidal particles of the type $[Fe(OH)_3]Fe^{3+}$ get separated. Similarly $Al(OH)_3$ sol is obtained when dilute HCl is added to freshly prepared $Al(OH)_3$.

2. Condensation or Aggregation Methods.

In these methods particles of atomic and molecular dimensions are allowed to aggregate to form bigger particles of colloidal dimensions. The method includes the following.

(a) **Double decomposition :** Arsenous sulphide sol is prepared by passing H_2S gas through a dilute solution of As_2O_3 and removing excess H_2S by boiling.

$$As_2O_3 + 3H_2S \rightarrow \underset{\text{yellow.}}{As_2S_3} + H_2O$$

(b) **Oxidation :**

When H_2S gas is passed through an aqueous solution of SO_2, colloidal sulphur is formed. It is a light yellow coloured aquosol.

$$SO_2 + 2H_2S \rightarrow 2H_2O + \underset{\text{(colloidal)}}{3S.}$$

(c) **Reduction :**

When gold chloride solution is treated with $SnCl_2$, a violet gold sol is obtained.

$$2AuCl_3 + \underset{\substack{\text{Reducing}\\\text{agent}}}{3SnCl_2} \rightarrow 3SnCl_4 + \underset{\text{(colloidal gold sol)}}{2Au}$$

(d) **Hydrolysis :**

A colloidal solution of $Fe(OH)_3$ is obtained by boiling a dilute solution of $FeCl_3$.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

Similarly, by hydrolysis of $AlCl_3$ and sodium silicates, colloidal solutions of $Al(OH)_3$ and silicic acid are also obtained.

(e) **Exchange of solvents :**

Sulphur and phosphorus are soluble in alcohol. When an alcoholic solution of sulphur is poured in excess of water hydrosol is formed. The substance present in molecular state in alcohol precipitate out in water in the form of particles of colloidal size.

Purification of colloidal solutions

The colloidal solutions are rendered unstable by the presence of impurities. These impurities are therefore removed by suitable methods which are discussed below.

(1) Dialysis :

The process of separating a crystalloid from a colloid by diffusion through a parchment membrane is known as **dialysis** and the apparatus used to this effect is known as **dialyser.** There are two types of dialysers.

(a) Graham's dialyser :

An impure colloidal solution is taken in the dialyser made up of parchment or cellophane paper. It is suspended in a beaker containing running distilled water. The rate of flow of water is adjusted so as to keep the level of water constant. The impurities in the form of crystalloid pass through the parchment membrane leaving behind the colloidal solution in the pure form inside the dialyser (parchment bag) (Fig - 5.11).

For example, Sodium silicate is allowed to react with dilute HCl and the mixture is taken in the parchment bag immersed in water to get a colloidal solution of silicic acid (H_2SiO_3)

$$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl$$

In this case NaCl and unused HCl pass through the membrane leaving behind pure colloidal solution of silicic acid.

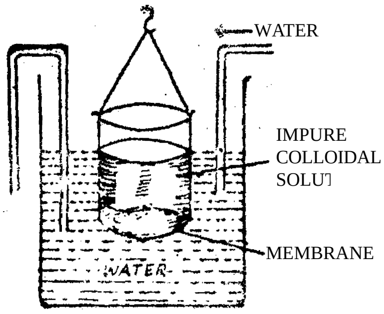


Fig-5.11

(b) Electrodialyser :

The process of dialysis is ordinarily quite slow but it can be hastened by the application of electric field. The impure colloidal solution is taken in a parchment bag suspended in a vessel through which fresh water in continuously passing. The ions of the electrolyte in the bag migrate faster under the influence of electric field towards the oppositely charged electrodes leaving behind the colloidal solution in the bag. The process is known as **electrodialysis**. (Fig-5.12)

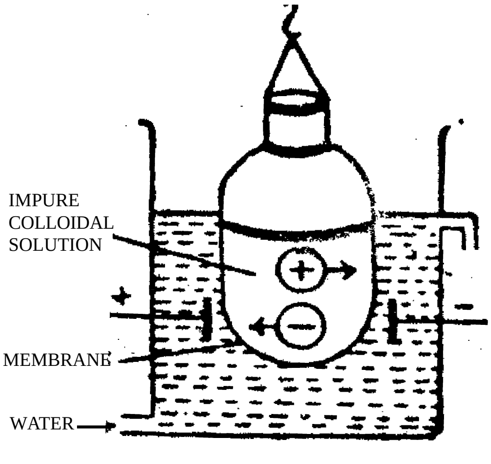


Fig-5.12

(2) Ultrafiltration :

The separation of colloids from crystalloids can also be made by ultrafiltration. Ordinary filter paper have pores larger than 1μ i.e 10^{-6}m through which colloidal solution along with the impurities (crystalloids) can easily pass. The pores of the filter paper can be made smaller by soaking it in a solution of gelatin or collodion and then hardening them by soaking in formaldehyde.

The pores thus become very small so as not to allow the colloidal particles to pass through them. Only the crystalloids can pass through such filter paper leaving behind the colloidal solution. The filter paper is known as ultrafilter and the process is known as **ultrafiltration.**

This process is very helpful in removing soluble impurities from colloidal solution. Cellophane membranes are the best ultrafilters.

5.16 PROPERTIES OF COLLOIDAL SOLUTION :

(i) **Heterogeneous nature :** A colloidal solution is heterogeneous in nature. It consists of two phases : the dispersed phase and dispersion medium.

(ii) **Diffusibility :** The colloidal particles constituting the dispersed phase do not diffuse through the parchment paper. This property forms the basis of colloid chemistry.

(iii) **Filtrability :** The colloidal particles can readily pass through ordinary filter paper. However the particles can be filtered through ultrafilters.

(iv) **Colour :** The colour of the colloidal particles is not always the same as colour of the substance taken in bulk. For example colloidal sulphur is colourless whereas sulphur is yellow. Colloidal gold is red whereas gold is yellow.

(v) **Visibility :** Even by the help of most powerful microscope the colloidal particles can not be seen. However in recent times u.v rays or cathode rays are used for seeing these particles. The electron microscope may also be used for the purpose.

(vi) **Colligative properties :** Colligative properties are those which depend upon the number of solute particles that are present in the given mass of solvent. These properties include lowering of vapour pressure, depression in freezing point, elevation in boiling point etc. Colloidal particles are not simple molecules, these are physical aggregation of molecules. So the number of particles present in the sol is always less than the number of particles present in true solution. Hence all the colloidal dispersions show a low value of colligative properties.

(vii) **Surface area :** Since colloidal particles are very small in size they provide a large surface area.

(viii) **Optical properties**

Tyndall effect : Tyndall observed that a beam of light passing through a true solution could be seen only if the eye is placed directly on its path. But the same beam of light when passed through a colloidal solution became visible as a bright streak. This phenomenon is know as Tyndall effect and the illuminated path is known as Tyndall cone (Fig-5.13)

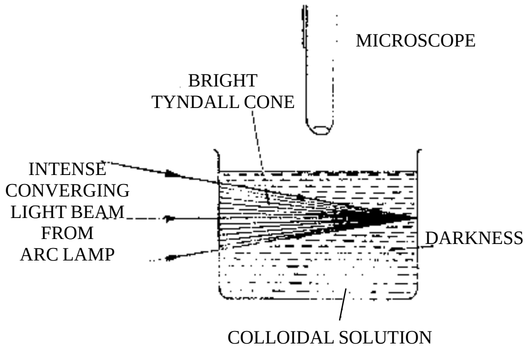


Fig-5.13

Tyndall effect is due to scattering of light from the surface of colloidal particles. The effect is shown if the following conditions are satisfied.

(i) The wavelength of light used must be greater than the diameter of the particles constituting the dispersed phase.

(ii) The difference in value of refractive indices of the dispersed phase and dispersion medium must be appreciable.

In true solution the beam is invisible because there are no particles of sufficiently large diameter to scatter light.

Tyndall effect is well defined in case of lyophobic sol since the difference between the values of refractive indices of the dispersed phase and dispersion medium is appreciable. On the other hand in case of lyophilic sols the particles are largely solvated and as a result the difference in refractive indices of the two phases is lowered and the effect becomes much weaker.

Example of Tyndall effect

A beam of light entering a dark room lights up the dust particles present in the air. The dust particles are large enough to scatter light rendering the path of light visible.

Uses : (i) The effect distinguishes between the lyophilic and lyophobic colloids.

(ii) Colloidal particles which are invisible can be made visible by using dark background illumination.

(iii) The effect has been used by Zsigmondy and Sicdentopf in devising ultramicroscope.

(ix) Mechanical property

Brownian movement :

An English botanist Robert Brown observed that pollen grains in aqueous suspension were in a state of constant rapid zigzag motion. When viewed under ultramicroscope it was found that the particles of hydrophobic sols executed similar type of ceaseless random motion. (Fig-5.14)

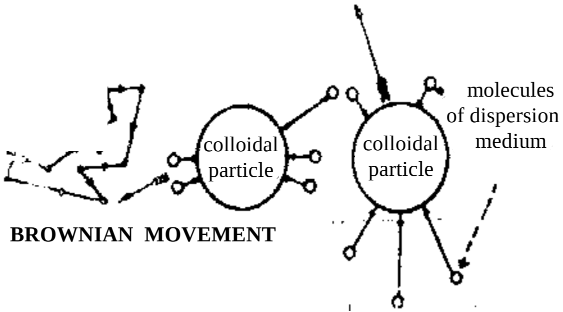


Fig -5.14

This kinetic activity of particles suspended in a liquid is called **Brownian movement.**

Cause : The movement is due to unequal bombardment of the molecules of dispersion medium with the colloidal particles. Brownian motion is inversely proportional to the size of the colloidal particles. The movement slows down with the increase in particle size. The reason for slow movement in case of bigger particle is decrease in chance of unequal bombardment on it. As a result of the movement the colloidal particles acquire almost the same amount of energy as possessed by the molecules of dispersion medium.

Applications :

(1) Diffusion of particles from solution of higher concentration to solution of lower concentration can be explained on the basis of the Brownian movement of colloidal particles.

(2) The motion offers an explanation for the random kinetic motion of molecules of a liquid.

Origin of charge on Colloidal particles.

The sols are associated with little amount of electrolytes and without the presence of electrolytes the sols become highly unstable. The charge on the colloidal particles is due to preferential adsorption of a particular type of ion on their surface. If the particles prefer to adsorb positive ions they acquire positive charge and if they have a preference to adsorb negative ions they become negatively charged.

For example–

(i) Ferric hydroxide sol is positively charged. Since it is formed by the hydrolysis of Ferric chloride, the +ve charge on the sol is due to preferential adsorption of Fe^{3+} ion on the surface of the particles of $Fe(OH)_3$. The Fe^{3+} ions are generated due to ionisation of $FeCl_3$ which is present in traces.

(ii) In Arsenic sulphide sol traces of H_2S are present. There is preferential adsorption of sulphide ion on the surface of particles of Arsenic sulphide. Hence the sol is –vely charged. The sulphide ions are furnished by the dissociation of H_2S.

(iii) Stannic oxide sol carries a +ve charge if peptised by a small amount of HCl. But if it is peptised by small amount of NaOH it carries a –ve charge. This is because in the former case a small amount of $SnCl_4$ is formed and Sn^{4+} ions are adsorbed on the surface of stannic oxide particle and the sol carries +ve charge. In the latter case small amount of Na_2SnO_3 is formed and the SnO_3^{2-} ions are adsorbed giving the sol –ve charge.

(iv) Another interesting example is furnished by silver iodide sol which may be +vely or –vely charged. If a dilute solution of $AgNO_3$ is added to slight excess of dilute solution of sodium iodide, the AgI sol formed is –vely charged. This is due to adsorption of I^- ions. Again if a dilute solution of sodium iodide is added to slight excess of $AgNO_3$, the AgI sol formed is +vely charged. This is due to adsorption of Ag^+ ion (Fig-5.15), However, if silver nitrate and sodium iodide are mixed in equivalent amounts, AgI is precipitated, but no sol is formed.

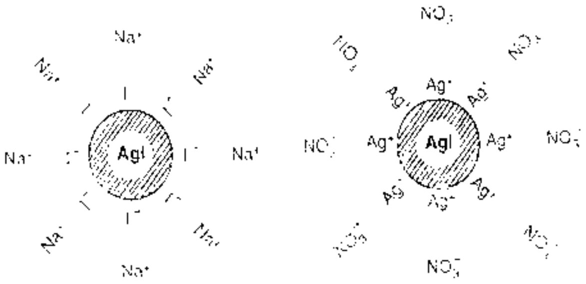


Fig - 5.15

Conclusion :

(a) The ion which is more nearly related chemically to the colloidal particle is adsorbed preferentially. (Ref. example (i) & (ii))

(b) The ions adsorbed by the colloidal particles are those which are common to them. (Ref.. example (iv))

(c) On the surface of colloidal particle there is an electrical double layer of opposite charges. (Ref. example iv)

(x) Electrokinetic Properties :

ZETA POTENTIAL

A colloidal particle is a charged particle and is surrounded by ions of opposite charge. Hence an electrical double layer is formed at the surface of separation between two phases. Consider solid-liquid interface. The double layer formed at the interface is made up of a layer of ions in aqueous solution which are firmly held to the solid (fixed layer) and a more diffused mobile layer extending into the solution. The fixed layer may consist of +ve or –ve ions but the mobile or diffused layer consists of ions of both the signs. The resultant charge of the diffused layer is equal in magnitude but of opposite sign to that of the fixed layer. (Fig-5.16)

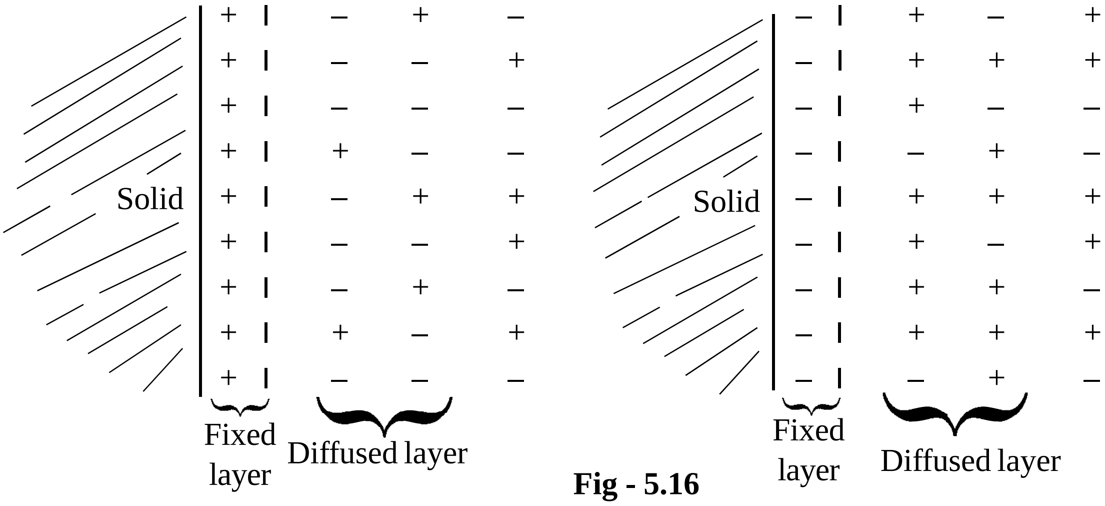


Fig - 5.16

Since separation of charge is a seat of potential, there develops a difference in potential between the fixed and the mobile layer.

This difference in potential between the fixed layer and the diffused layer having opposite charge is known as **electrokinetic potential** or **Zeta potential.**

Zeta potential (Z) is given by the relationship. $Z = \frac{4\pi\eta\mu}{D}$

where η = Coefficient of viscosity of dispersion medium.

μ = Electrophoretic mobility of particles

D = Dielectric constant of the medium.

The value of Z is about 50 millivolts. when Z approaches zero, coagulation of sol particles takes place.

Since solid particles and the liquid medium carry opposite charges, on application of an electric field, the solid particles and the liquid medium will move in opposite directions.

(a) If experiments are so arranged that only the particles move and not the medium, the phenomenon is known as **Electrophoresis** or **Cataphoresis.**

(b) On the otherhand if the experiments are designed such that only the medium moves and not the particles, the phenomenon is known as **Electro-osmosis.**

Electrophoresis :

The migration of electrically charged sol particles under the influence of an applied electric field is known as **Electrophoresis or Cataphoresis**. This phenomenon can be demonstrated in a U-tube. (Fig 5.17)

(i) The U-tube is provided with a stop cock through which it is connected to a reservoir of funnel shape.

(ii) Small amount of water is taken in the U-tube and sol of Arsensic sulphide is taken in the reservoir.

(iii) Stop cock is opened slightly and the sol is allowed to enter the U-tube by gradually raising the reservoir. Water is displaced upwards and a sharp boundary is produced in each arm.

(iv) Two platinum electrodes are dipped in water layer and a voltage of 50 to 200 volts is then applied.

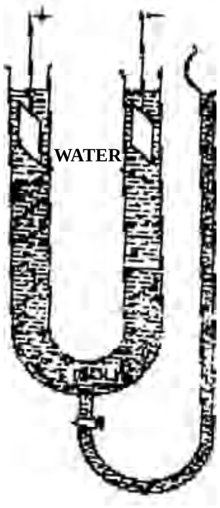


Fig-5.17

(v) The position of boundary in both the arms is marked by means of a lens or cathetometer. In the present case the boundary on the negative electrode side is seen to move down and that on the +ve electrode side is seen to move up indicating that the particles migrate towards the positive electrode.

(vi) The direction of motion of the particles determines the charge carried by the particles. Since Arsenic sulphide sol is –vely charged, in this case the flow is towards the +ve electrode.

Electrophoretic mobility of colloidal particles :

The rate at which the colloidal particles move under the influence of electric field can be expressed in terms of their electrophoretic mobilities. The electrophoretic mobility of colloidal particles is defined as the distance travelled by them in one second under a potential gradient of 1 volt per centimetre.

Advantages

(i) It is possible to separate the colloidal materials from their mixtures since different colloidal materials are associated with different mobilities. For fractionation of proteins, polysaccharides, nucleic acids etc this method is very helpful.

(ii) It is used in precipitation of smoke from chimney gases.

(iii) It is used to determine the charge on colloidal particles.

(iv) It is used in removal of dirt from sewage.

COAGULATION OF COLLOIDAL SOL (Flocculation)

The stability of colloidal particles is due to the charge present on them. In lyophobic colloids the stability is due to their electric charge where as in case of lyophilic colloids the stability is due to their charge and extensive solvation. Tendency of sol particles to settle render them unstable.

In lyophobic sols the particles carry same type of charge and repel each other and resist the tendency to combine or settle. In lyophilic sol same type of electrostatic repulsion operates along with another added factor of solvation. There is attraction between the solvent molecules and the suspended particles which results in solvation of particles and prevent the particles from coming closer.

If by some means the charge on the colloidal particles can be destroyed then such particles settle down in the form of a precipitate. The precipitation of particles of the dispersed phase is known as **Coagulation or Flocculation**. When the charges on the colloidal particles are destroyed the zeta potential around the particles drops below 0.02V and this results in reduction of repulsion between the colloidal particles leading to coagulation or flocculation.

Coagulation of lyophobic sol : The removal of charges can be done in different ways.

(1) **By addition of other electrolytes :**

Although traces of electrolytes are required for the stability of the sols, the presence of large amount of electrolytes cause their coagulation. The reason is that the colloidal particles take up the ions carrying charge opposite to that present on them and as a result the charge on them get neutralised and the sol gets coagulated or precipitated. For example,

(i) Arsenous sulphide sol gets precipitated upon addition of sodium chloride to it. Na^+ ion is the flocculating ion, it neutralises the –ve charge carried by the sol particles. As_2S_3 sol can also be coagulated by addition of positive ions like Mg^{2+}, Ca^{2+}, Ba^{2+} etc.

(ii) $Fe(OH)_3$ sol which is +vely charged can be coagulated by negative ions such as Cl^-, NO_3^-, SO_4^{2-} etc.

(2) **By mutual precipitation :** When two sols having opposite charges are mixed together in suitable proportions, mutual precipitation takes place. For example, when +vely charged sol $Fe(OH)_3$ and –vely charged sol As_2S_3 are mixed in suitable proportions their charges are neutralised with each other and both are partially or completely coagulated or precipitated.

(3) **By persistent dialysis :** On prolonged dialysis the traces of electrolytes present in the sol are removed and the sol becomes unstable.

(4) **On boiling the sol :** On boiling the sol, the amount of electrolyte present in the sol is reduced and in some cases the sol may precipitate.

(5) **On freezing the sol :** If freezing of sol is carried out for enough time there is removal of medium and the sol becomes unstable.

(6) **By mechanical means :** Stirring the sol for a long time may coagulate it. Also the vibratory action caused by ultrasound may result in coagulation.

Hardy-Schulze Rule :

According to this rule coagulation is brought about by the ions having opposite charge to that carried by the sol particles. Hence –ve ions cause coagulation of +ve sol and +ve ions cause the coagulation of –ve sol.

The quantity of the electrolyte necessary to coagulate a definite amount of the sol depends upon the valency of the ion carrying a charge opposite to that of colloidal particles. This is known as Hardy-Schulze rule. For the coagulation of As_2S_3 sol flocculating power of the cations decreases in the order $Al^{3+} > Ba^{2+} > Na^+$. Also for the coagulation of $Fe(OH)_3$ the flocculating power of anions is in the order

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^- .$$

Flocculation value : The minimum concentration of an electrolyte required to cause coagulation or flocculation of a sol is called its flocculation value. This is expressed in millimoles per litre of the electrolyte. The following table represents the flocculation values of different elctrolytes for As_2S_3 and $Fe(OH)_3$ sols.

Coagulation of Lyophilic sols :

(1) **By adding electrolytes (Salting out)**

The coagulation of lyophilic sol by the addition of electrolyte is not due to neutralisation of charge on the particle as in case with the lyophobic sol. The electrolyte added binds part of the water and get hydrated. As a result the polymer molecules in lyophilic sol get dehydrated and there is reduction in values of their zeta potential. The dehydration results in coagulation. The effect is called *salting out.* The salting out effect depends upon the nature of the ions and salts of a given metal. Various ions are arranged in order of their effectiveness in a series known as **Lyotropic series or Hofmeister series.**

The order of cations is

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Na^+ > K^+$$

The order of anion is

$$Citrate^{3-} > Tartrate^{2-} > SO_4^{2-} > CH_3COO^- > Cl^- > NO_3^- > ClO_3^- > I^- > CNS^-$$

(2) **By addition of a suitable solvent :**

Solvents like alcohol and acetone have large affinity for water. When these solvents are added to lyophilic sols, the dispersed phase undergoes dehydration and therefore the stability of such particles is due to their charge only. If in this condition small amount of electrolyte is added that results in coagulation of the sol.

Protection of Colloid :

It is a fact that the lyophobic sols are easily coagulated as compared to lyophilic ones by the addition of small quantity of electrolyte. But the lyophobic sol becomes less sensitive to coagulation when a large amount of lyophilic sol is added to it. The presence of lyophilic colloid thus inhibits the flocculating action of an electrolyte on a lyophobic colloid. For example, the coagulation of gold or silver sol can be prevented by the addition of lyophilic sol like gelation or albumin. The lyophilic sol is known as the **protective colloid** and its effect on lyophilic one is known as **protective action.** Hence the process by which the sol particles are prevented from coagulation by the addition of electrolyte is known as protection of colloid. The reason for protection is due to the fact that the sol particles adsorb the protective colloid particles forming a protective layer around them. This layer prevents the flocculating ion from reaching the sol thereby not allowing the sol to precipitate.

Gold Number

Zsigmondy introduced the principle of gold number in order to measure the relative protective power of lyophilic colloids. It is defined as **the number of milligrams of protective colloid which prevents the coagulation of 10 ml of a given gold sol when 1 ml of a 10% solution of NaCl is added to it.**

The protective action of a lyophilic sol depends upon factors like dispersity and the molar mass of the sol and also the pH of the solution at which the experiment is carried out. The smaller the gold number the greater is the protective action of the protective colloid. For example, gelatin is having a small gold number (Table - 5.9), hence acts as a very good protective colloid.

Table -5.9 Protective action of lyophilic colloids on some hydrophobic sols.

Protective colloids	Gold number
Gelatin	0.1
Dextrin	20
Saponin	115
Potato starch	20
Haemoglobin	0.03-0.07
Egg albumin	2.5
Gum arabic	0.5

5.17 APPLICATIONS OF COLLOIDS :

Colloids play a vital role in our day to day life as well as in agriculture, medicine, industry etc. Some of the applications in various fields are discussed below.

1. **Medicines :** Most of the medicical preparations are emulsions that are colloidal in nature. Medicines in the form of emulsions are easily assimilated and therefore more effective.
2. **Foods :** Most of our foods are colloidal in nature. Milk is an emulsion which is stabilised by casein, a lyophilic colloid. The smoothness of icecream can be preserved by the addition of gelatin, a protective colloid. Similarly jelly, jam, whipped creams etc are of colloidal nature.
3. **Rubber plating :** Rubber plating can be carried out by the process of electrophoresis for the porpose of insulating various tools. The article to be rubber plated is made anode. Upon application of an electric field the rubber particles being –vely charged, migrate towards anode and get deposited on the article.
4. **Sewage disposal :** For sewage disposal the electrophoretic property of colloidal particles is of great use. Particles of dirt, mud etc of colloidal size are contained in sewage water. These particles carry electric charge and therefore do not settle down easily. On application of an electric field in the sewage tank these particles migrate towards oppositely charged electrode, get neutralized and settle down in the form of a precipitate at the bottom.
5. **Artificial rain :** Electrified sand is thrown from aeroplanes on the clouds which consist of charged particles of water dispersed in air. The colloidal water particles of the clouds get neutralised and coagulate to bigger water drops which ultimately results in artificial rain.

6. **Purification of water :** The presence of –vely charged fine particles of clay causes slight turbidity in water. The addition of potash alum ie Al^{3+} ions neutralises the –ve charge carried by the collodal clay particles and cause their coagulation. The clay particles settle down leaving water in clear state.

7. **Smoke precipitation :** In industrial areas the smoke coming out of the chimneys contains electrically charged colloidal particles of carbon dispersed in air. Principle of electrophoresis is employed for the removal of these particles. In cottrell precipitator (Fig-5.18), the smoke is allowed to pass through chambers fitted with highly electrically charged plates. The colloidal carbon particles present in smoke are discharged and deposited on the oppositely charged electrode leaving the gas to escape through the chimney.

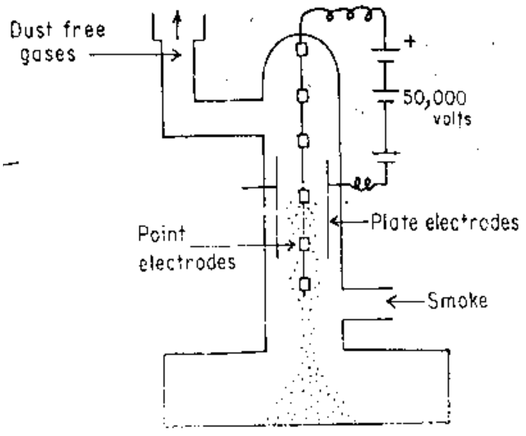


Fig-5.18

8. **Detergent action of soap :** Soap solutions are used to remove the dirt and dust particles sticking to the fabric. But most of the dirt or dust sticks on the oily or greasy materials which ultimately gather on cloth. It is difficult to wash the cloth simply by water since grease is not readily wetted by water. The interfacial tension existing between water and grease can be lowered upon addition of soap and this causes the emulsification of grease in water. Mechanical action such as rubbing helps in removal of dirt.

9. **Formation of delta :** River water contains negatively charged colloidal particles of sand and clay. Sea water contains a large number of dissolved salts and therefore serves as electrolyte containing Na^{+}, Ca^{2+}, Mg^{2+} etc. When river water touches sea water coagulation of clay particles takes place at the point of contact because of charge neutralisation. As a result the clay particles coagulate and settle down raising the river bed. The river water adopts a separate coarse and this results in formation of delta.

10. **Smoke screens :** Smoke screens consist of fine particles of titanium oxide dispersed in air. These are used in warfare for the purpose of concealment and camouflage. When ejected from aeroplanes smoke screen containing heavy particles of titanium oxide drops down rapidly forming a curtain of dazzling whiteness.

11. **Blue colour of the sky :** It is due to scattering of blue light by the colloidal dust and water particles present in the sky.

5.18 EMULSION :

The colloidal systems in which both dispersed phase and dispersion medium are liquids are otherwise known as **emulsions**. Any two immiscible liquids can thus form an emulsion. Emulsions are usually unstable and upon standing form two separate layers. Examples are milk, cod-liver oil etc.

Types of Emulsions

There are two types of emulsions

(a) Oil in water type (o/w)

Here oil is the dispersed phase and water is the dispersion medium. Water is the continuous medium in which oil droplets are dispersed.

Example-Milk is an emulsion of this type since fat globules are dispersed in water.

(b) Water in oil type (w/o)

Here water is the dispersed phase and oil is the dispersion medium. Oil is the continuous medium in which water droplets are dispersed.

Example- Butter is an emulsion of this type

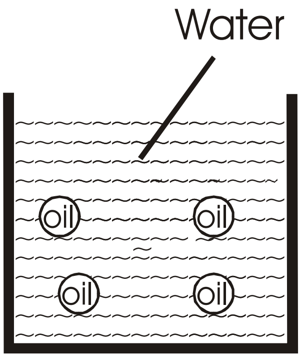


Fig. 5.19 Oil in water (o/w) type

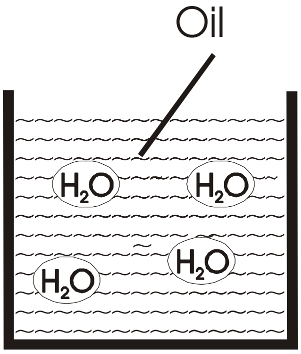


Fig.5.20 Water in oil (w/o) type

Identification of emulsions

(i) **Dye test -** Add a small amount of oil soluble dye to the emulsion under examination. If it is of w/o type i.e if oil is the continuous medium then it acquires the colour of the dye immediately. On the otherhand if the emulsion is of o/w type the dye will not mix and the emulsion remains colourless.

(ii) **Electrical conductivity -** If water is in excess, more will be the electrical conductvity. In o/w type emulsion or aqueous emulsion the electrical conductivity is more than w/o type emulsion or oily emulsion.

(iii) **Dilution test -** If on adding water the emulsion character is retained then the emulsion is identified as o/w type. On the otherhand by adding oil if the emulsion character is retained then the emulsion is identified as w/o type.

Emulsifiers

(i) Emulsifiers are the agents required for stabilising the emulsions.

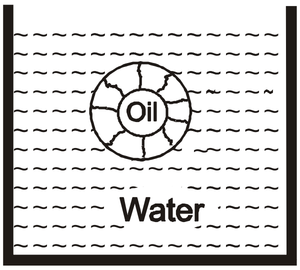
(ii) They lower the interfacial tensions between the constituents of emulsion.

(iii) They form thin films around the droplets of dispersed phase thereby not allowing them to come closer preventing their coagulation.

(iv) Examples of emulsifiers or emulsifying agents include soaps, detergents and lyophilic colloids.

Role of Emulsifier

Consider two immiscible liquids such as a hydrocarbon oil and water . If we shake the two solutions vigorously, a milky solution results. This is an emulsion of o/w type. The emulsion is highly unstable. It is necessary to add a small amount of another substance i.e an emulsifier or emulsifying agent to stabilise the emulsion.



The emulsifier consists of both ionic as well as non -ionogenic surfactants. The ionic surfactants which act as emulsifiers include soaps, long chain sulphonic acids and alkyl sulphates. These ionic surfactants are long chain organic compounds with polar groups. These surfactants get adsorbed at the interface between the dispersed phase and the dispersion medium forming a monomolecular layer thereby lowering the interfacial tension between oil and water facilitating the mixing of two liquids. The soap molecules contain polar groups (–COONa) and non polar end hydrocarbon chain. The concentration of soap at the interface is made in such a way that the polar end interacts with water and nonpolar end with oil. The emulsion thus gets stabilised.

The non –ionogenic surfactants include lyophilic colloids such as proteins, gums, gelatin etc. In milk, a protein is there known as casein. Casein forms a multimolecular protective layer around the droplets of fat dispersed in water. Milk is therefore a stable emulsion.

Properties of Emulsions

(i) Emulsions are colloidal systems.

(ii) They exhibit all the electrical and optical properties of colloids like Brownian movement, Tyndall effect, Electrophoresis, Coagulation etc.

(iii) Size of particles range from 1000 A^0 to 10,000 A^0.

Use of Emulsions

(i) They find use in concentration of ore particularly in Froth floatation process.

(ii) Digestion of fats in the intestine involves emulsification.

(iii) Various medicines like lotions, creams and ointments are available in the form of emulsions.

(iv) The cleansing action of soaps and detergents is based on formation of w/o type emulsion.

(v) Milk which acts as an important part of our diet is an emulsion of o/w type.

CHAPTER (5) AT A GLANCE

1. **Crystalloids :** Substances the solutions of which can readily diffuse through animal or vegetable membrane. Example– salt, sugar, urea, acids, bases.
2. **Colloids :** Substances the solutions of which show little or no tendency to diffuse through animal or vegetable membrane. Example– gelatin, albumin, glue etc.
3. Size of colloidal particles lie within the range 1 to 100 nm i.e. 10 to 2000 A^o.
4. A colloidal system consists of dispersed phase and dispersion medium.
5. **Lyophilic colloids** are solvent loving and stable colloids. Example- Proteins, starch, rubber etc.
6. **Lyophobic colloids** are solvent hating and less stable colloids. Example– Ferric hydroxide, Arsenic sulphide sols.
7. **Dialysis :** The process of separating a crystalloid from a colloid by diffusion through a parchment membrance is known as dialysis.
8. **Tyndall effect is** due to scattering of light from the surface of colloidal particles.
9. The difference in potential between the fixed layer and the diffused layer having opposite charge is known as **electro kinetic potential or zeta potential.** (Z)

$$Z = \frac{4\pi\eta\mu}{D}$$

10. **Electrophoresis :** The migration of electrically charged sol particles under the influence of an applied electric field is known as Electrophoresis.
11. **Coagulation :** The precipitation of particles of dispersed phase is known as Coagulation or Flocculation.
12. **Hardy-Schulze Rule**

    Coagulation is brought about by the ions having opposite charge to that carried by the sol particles.
13. **Flocculation value :** The minimum concentration of an electrolyte required to cause coagulation or floculation of a sol is called its flocculation value.
14. **Gold number :** The number of milligrams of protective colloid which prevents the coagulation of 10 mL of a given gold sol when 1 mL of a 10% solution of NaCl is added to it.
15. **Adsorption :** The phenomenon of higher concentration of molecular species on the surface of the solid or liquid than in the bulk is known as adsorption.

16. **Adsorbate :** The substance which is taken up on the surface of the adsorbent.
17. **Adsorbent :** The substance upon whose surface the phenomenon of adsorption takes place.
18. **Desorption :** It is reverse of adsorption. The process of removal of adsorbed substance from the surface of the adsorbent is known as desorption.
19. **Absorption :** The substance is uniformly distributed throughout the body of the solid or liquid.
20. **Sorption :** Both adsorption and absorption take place simultaneously.
21. **Positive and negative adsorption :** When the concentration of adsorbate is more at the surface than in the bulk the adsorption is positive adsorption. But if the concentration of adsorbate is less at the surface than in the bulk it is a case of negative adsorption.
22. **Physical adsorption :** The adsorbate is held on the surface of adsorbent by weak vanderWaals' forces. It is reversible.
23. **Chemical adsorption :** The adsorbate is held on the surface of adsorbent by forces of attraction of almost the same strength as chemical bond. It is irreversible.
24. **Molar Heat of adsorption :** It is the amount of heat evolved when 1 mole of gas or vapour is adsorbed on the surface of the solid.
25. **Extent of adsorption** increases with fall in temperature and increase of pressure.

QUESTIONS

Very short answer type questions. (1 mark each)

1. Distinguish between crystalloid and colloid.
2. What is the binding force in physisorption ?
3. What is gold number ?
4. By what method a colloid can be separated from crystalloid.
5. What is the name of the process of removing an adsorbed substance from the surface on which it is adsorbed.
6. Liquid-liquid colloidal systems are termed ———
   (sols, hydrosols, emulsoids, suspensoids)
7. Why animal charcoal is used for purification of sugar ?
8. A colloidal solution has two phases namely ——— phase and ——— phase.
9. Why colloids can not be filtered by ordinary filter paper ?
10. A colloidal solution is called a ———
11. What is the size of a colloidal particle ?

12. Why does a colloidal solution coagulate on addition of an electrolyte ?
13. What is the cause of Tyndall effect ?
14. Why are the colloidal particles charged ?
15. Why colloidal solution is heterogeneous.
16. What is desorption ?
17. Define molar heat of adsorption.
18. Give an example of emulsion

Short answer type questions. (2 marks each)

1. Explain Gold number.
2. Give a method of preparing colloidal solution of arsenous sulphide. Give equation.
3. What is Tyndall effect ? What is it due to ?
4. What is adsorption ?
5. What is electrophoresis ?
6. What is colloidal solution ?
7. Why alum is used for clearing muddy water.
8. Name the factors (any four)that govern the adsorption of a gas on a solid.
9. What is detergent ? How it works ?
10. What is a colloidal solution ? How does it differ from a true solution ?
11. Give two examples of lyophilic sols and how are they formed ?
12. Why animal charcoal is used for purification of sugar ?
13. What is the difference between adsorption and absorption ?
14. A powerful beam of light is passed through two beakers, one containing a solution and the other a colloidal solution. How each of the solution acts towards the beam of light ?
15. Why some colloidal particles migrate to electrodes in an electric field ?
16. Why are colligative properties almost negligible in case of colloidal solutions ?
17. Why is adsorption exotheromic ?
18. Explain why the gases like NH_3, HCl, CO_2 etc can be liquefied easily than the permanent gases like H_2, N_2, O_2 etc.
19. Among $[Fe(CN)_6]^{4-}$, PO_4^{3-}, SO_4^{2-} which is more effective in coagulating $Fe(OH)_3$ sol ?
20. Distinguish between adsorbent and adsorbate.
21. Distinguish between lyophilic and lyophobic colloids.
22. When a river meets the occan, it generally form delta. Give reasons.
23. Why cannot colloidal sol be filtered by ordinary filter paper ?
24. Name any two/four applications of adsorption (four)
25. When rivers meet the ocean, they generally form delta, give reasons.
26. Distinguish between homogeneous and heterogeneous catalysis.
27. What is meant by selectivity of a catalyst ?

Long answer type questions. (10 mark each)

1. Write notes on
   (a) Tyndall effect
   (b) Soap and Detergent
   (c) Gold number
   (d) Brownian movement
2. Explain different types of adsorption. Write any four applications of colloids.
3. Give one method of preparation of colloidal solution. Give an account of electrical and optical properties of colloidal solution.
4. Give a brief account of soap and detergent.
5. Explain the terms adsorption and absorption with examples. Name the factors on which the extent of adsorption of a gas on solid depends.
6. How are colloids classified ? Discuss any two properties of colloidal solution.
7. State and discuss Hardy-Schulze rule.
8. Explain the following
   (a) Brownian movement (b) Gold number (c) Dialysis.
9. What is adsorption ? Distinguish between physical adsorption and chemisorption.
10. Explain various applications of colloidal solution
11. Discuss the factors that affect the phenomenon of adsorption.
12. What do you understand by the term "Electrophoresis" ? How would you demonstrate this phenomenon.
13. What is a colloid ? How does colloid differ from crystalloid ? "Colloid is a state of matter, not a class of matter" – discuss the statement.
14. Explain three of the following.
   (a) Peptisation (b) Dialysis (c) Emulsions (d) Lyophobic sols.
15. Give a note of the following.
   (a) Origin of charge on colloidal particles.
   (b) Zeta potential.
16. Write a note on Cataphoresis. (5 marks)
17. Discuss important features of solid catalysts with reference to activity and selectivity.
18. Explain adsorption theory of heterogeneous catalysis.
19. Discuss effect of catalyst on activation energy with examples.
20. What is enzyme catalysis ? Discuss its characteristics with suitable examples.
21. What is a catalyst ? Discuss the characteristics of a catalyst with examples.

MULTIPLE CHOICE QUESTIONS WITH ANSWERS

1. A mixture of colloid and crystalloid can be separated by
   (a) diffusion (b) cataphoresis (c) dialysis (d) filtration
2. Tyndall effect in colloidal solution is due to
   (a) Scattering of light (b) Reflection of light (c) Absorption of light
   (d) Presence of electrically charged particles
3. The capacity of an ion to coagulate a colloidal solution depends on
   (a) its shape (b) the amount of its charge (c) the sign of the charge
   (d) both of the amount and the sign of charge.
4. The Brownian motion is due to
   (a) Temperature fluctuation within the liquid phase
   (b) Attraction and repulsion between the charges on the colloidal particles.
   (c) Impact of the molecules of the dispersion medium on the colloidal particles.
   (d) Convection current.
5. Lyophilic sols are more stable than lyophobic sols because
   (a) The colloidal particles have +ve charge
   (b) The colloidal particles have –ve charge.
   (c) The colloidal particles are solvated
   (d) There are strong electrostatic repulsion between the negatively charged colloidal particles.
6. An Arsenous sulphide sol carries a –ve charge. The maximum precipitating power for this sol is possessed by
   (a) K_2SO_4 (b) $CaCl_2$ (c) Na_3PO_4 (d) $AlCl_3$
7. Which of the following substances gives a positively charged sol ?
   (a) Gold (b) A metal sulphide (c) Ferric hydroxide (d) An acidic dye
8. On adding a few drops of dil HCl to freshly precipitated $Fe(OH)_3$, a red colour colloidal solution is obtained. The phenomenon is known as
   (a) Peptisation (b) Dialysis (c) Protective action (d) Dissolution
9. Which of the following will have high coagulating power for As_2S_3 colloid ?
   (a) PO_4^{3-} (b) SO_4^{2-} (c) Al^{3+} (d) Na^+
10. The sky looks blue due to
    (a) Dispersion of light (b) Reflection (c) Transmission (d) Scattering
11. Which of the following is not a colloid
    (a) Chlorophyll (b) Smoke (c) Transmission (d) Milk
12. Fog is an example of colloidal system of
    (a) liquid dispersed in gas (b) gas dispersed in gas
    (c) solid dispressed in gas (d) solid dispersed in liquid
13. ——— is an example of emulsion.
    (a) milk (b) jelly (c) boot polish (d) froth

14. Gold number gives
    (a) The amount of gold present in the colloid
    (b) The amount of gold required to break the colloid
    (c) The amount of gold required to protect the colloid
    (d) None of the above.
15. Which of the following can adsorb large volume of hydrogen gas.
    (a) Finely divided platinum (b) Colloidal solution of palladium.
    (c) Finely divided nickel (d) colloidal Ferric hydroxide
16. Which of the following can act as a protective colloid.
    (a) gelatin (b) silica gel (c) oil in water emulsion (d) all correct.
17. The blue tinge of smoke is due to
    (a) Scattering (b) Coagulation (c) Brownian motion (d) Electro osmosis.
18. Tyndall effect is not observed in
    (a) true solution (b) suspension (c) emulsion (d) colloidal solution.
19. The migration of +vely charged colloidal particles under the influence of an electric field towards the cathode is called
    (a) Electro-osmosis (b) Electrophoresis (c) Dialysis (d) Coagulation
20. When the dispersion medium is water, the colloidal system is called
    (a) Sol (b) Aerosol (c) Organosol (d) Aquasol
21. Which of the following is a hydrophobic sol ?
    (a) Starch solution (b) Gum solution
    (c) Protein solution. (d) Arsenic sulphide sol
22. A colloidal solution in which a solid is dispersed in a liquid is called
    (a) Gel (b) Emulsion (c) Sol (d) Precipitate
23. Which of the following is a homogeneous system
    (a) Muddy water (b) Bread (c) Concrete (d) A solution of sugar in water
24. Which of the following is not represented by sols ?
    (a) Adsorption (b) Tyndall effect (c) flocculation (d) Paramagnetism
25. Maximum coagulation power is in
    (a) Na^+ (b) Ba^{2+} (c) Al^{3+} (d) Sn^{4+}

ANSWERS TO MULTIPLE CHOICE QUESTIONS

1.c 2.a 3.d 4.c 5.c 6.d 7.c
8.a 9.c 10.d 11.a 12.a 13.a 14.d
15.a 16.a 17.a 18.a 19.b 20.d 21.d
22.c 23.d 24.d 25.d

❑❑❑

UNIT - VI

CHAPTER - 6

GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

6.1 INTRODUCTION :

All the known elements have been divided into four classes and each category occupies a definite place in the long form of the Periodic Table.

1. Inert gases
2. Metals
3. Non-metals
4. Metalloids.

1. **Inert Gases:** Six elements namely Helium, Neon, Argon, Krypton, Xenon and Radon are known as inert gases. They occupy Zero group of the periodic table. Except Helium they have eight electrons in their valence shells, so atoms of these elements neither gain nor lose electrons. As they are unable to share electrons with other elements, they are not given any electro negativity value. They are colourless and monoatomic.

2. **Metals:** Atoms of the metals have the tendency to donate electrons in chemical reactions. They possess low electronegativity (1.7 down)

Properties:

(a) Soluble metallic oxides (Na_2O, K_2O etc,) yield OH^- ions when treated with water.

(b) Both soluble and insoluble metallic oxides are known as basic oxides as they are good proton acceptors and they form OH^- (proton acceptor ion) in water.

(c) Metals are malleable (can be spread into thin sheets) and ductile, (can be drawn into wires) have high electrical conductivity, high thermal conductivity and metallic lusture when freshly cut.

3. **Non-Metals:** Atoms of non-metals have the tendency to accept electrons from metals in chemical reactions. Covalent bonds are formed when they combine with one another. Their electronegativity ranges from 2.4 to 4.0.

Properties:

(a) Non-metallic oxides yield H_3O^+ (hydronium ion) when treated with water. Hence they are called acidic oxides.

(b) They are non-malleable, non-ductile and have no metallic lustre.

(c) Non-metals which are gases at ordinary conditions exist as diatomic molecules.

4. **Metalloids:** Metalloids are borderline elements. They exhibit both metallic and non-metallic properties to some extent. They usually act as electron donors with non-metals and electron acceptors with metals. Example : Boron, Silicon, Germanium, Arsenic, Antimony and Tellurium.

Properties:

(a) Metalloids form acidic oxides

(b) They are solids at room temperature.

(c) They are poor conductors of heat and electricity and brittle in character.

(d) The compounds of metalloids are mostly covalent in nature.

Electrochemical Series:

Elements arranged in the decreasing order of their chemical reactivity in a table is termed as Electrochemical series.

Example: Li, K, Ba, Sr, Ca, Na, Mg, Al, Mn, Zn, Cr, Cd, Fe, Co, Ni, Sn, Pb, H, Sb , Bi, As, Cu, Hg, Ag, Pt, Au… (arranged in the decreasing order)

Significance:

Decreasing order of chemical reactivity signifies the following:

a) Li is the most reactive one while Au is the least reactive.

b) Metals from Li to Na, produce H_2 from cold water, steam and acids.

c) Metals from Mg to Fe produce H_2 from steam and acids.

d) Metals from Co to Pb produce H_2 from acids.

e) Ag, Pt and Au do not produce H_2 from water and acids but form oxides by indirect method.

f) Metal oxides from Cu to Au can be easily reduced by hydrogen.

6.2 OCCURRENCE OF METALS IN NATURE :

Metals are available in nature either in

1) Free state or native state.

2) Mineral state, or

3) Form of an ore.

1. **Free State –** A metal is said to occur 'free' or 'native' when it is found in nature in the metallic state.

   Example: Cu,Ag, Au

   Significance: Such metals are less electropositive than Hydrogen.

2. **Mineral:** Metals which exist in the form of compounds with impurities like sand are called minerals.

   Example Zincite (ZnO), Horn Silver(AgCl), Cuprite(Cu_2O)etc).

3. **Ores:** An ore is a naturally occurring substance from which the metal may be extracted economically and profitably.

   Example: Galena(PbS), Copper glance(Cu_2S), Zinc oxide(ZnO), Calcium phosphate [$Ca_3(PO_4)_2$]etc.

   All ores are minerals, but all minerals are not ores.

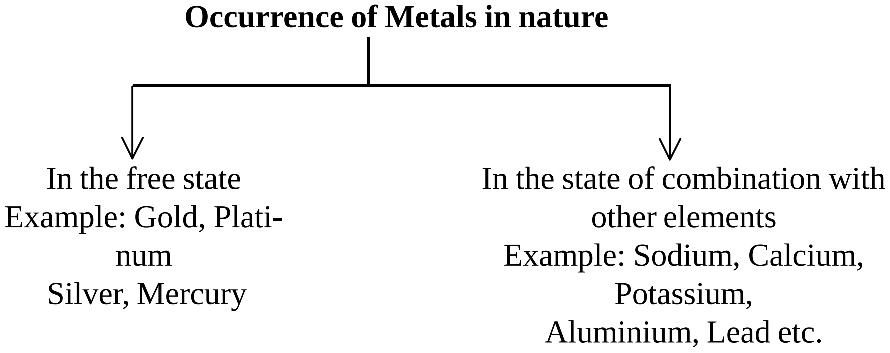


Table - 6.1

Metals and their important Minerals

Metal	Mineral	Chemical Formulae
Sodium	Rock Salt	NaCl
	Chile Saltpetre	$NaNO_3$
	Borax	$Na_2B_4O_7$
Potassium	Carnallite	$KCl, MgCl_2.6H_2O$
	Nitre	KNO_3
	Kainite	$K_2SO_4, MgSO_4, MgCl_2.6H_2O$
Magnesium	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3.CaCO_3$

	Epsom salt	$MgSO_4.7H_2O$
	Kieserite	$MgSO_4.H_2O$
	Carnallite	$MgCl_2KCl, 6H_2O$
Calcium	Limestone	$CaCO_3$
	Dolomite	$MgCO_3, CaCO_3$
	Gypsum	$CaSO_4, 2H_2O$
Copper	Copper pyrites	$CuFeS_2$
	Copper glance	Cu_2S
	Malachite	$Cu(OH)_2, CuCO_3$
	Azurite	$Cu(OH)_2, 2CuCO_3$
	Cuprite	Cu_2O
Silver	Horn Silver	$AgCl$
	Silver glance	Ag_2S
Zinc	Zincite	ZnO
	Zinc Blende	ZnS
	Calamine	$ZnCO_3$
Mercury	Cinnabar	HgS
Aluminium	Bauxite	$Al_2O_3.2H_2O$
	Cryolite	Na_3AlF_6
	Alunite	$K_2SO_4, Al_2(SO_4)_3, 4Al(OH)_3$
	Spinel	MgO, Al_2O_3
Tin	Tin Stone	SnO_2
Lead	Galena	PbS
Manganese	Pyrolusite	MnO_2
Chromium	Chromite	FeO, Cr_2O_3
Iron	Magnetite	Fe_3O_4
	Haematite	Fe_2O_3
	Limonite	$Fe_2O_3, 3H_2O$
	Iron pyrites	FeS_2

6.3 EXTRACTION OF METALS OR METALLURGY :

Metallurgy:

It is the process or processes by which metals are extracted from their respective ores.

Gangue or Matrix:

The rocky or earthy materials almost always found to be associated with the ores as impurities and looked upon as waste materials are called gangue or Matrix. (Latin word Matte = Mother i.e. earthy or stony substance in which minerals are found embedded)

6.3.1. Concentration of the ore:

In any metallurgical operation, concentration means to remove impurities (gangue) form the ore. It is effected by many processes like:

(i) **Breaking and Crushing:** Big masses of rocks containing the ore must be reduced to small lumps so that they may be completely exposed to the action of the subsequent operations. It is usually done by machines like crushers etc.

(ii) **Grinding and Pulverizing:** Some times the concentration and further treatment of some ores demand their reduction into very fine state. This is also effected by machines like grinding and pulverizing mills.

(iii) **Washing:** This process includes all methods of concentration in which water in motion is used. Washing machines are generally used for such purpose.

(iv) **Floatation:** Here concentration of the powdered ore is effected by taking advantage of difference in the behaviour towards oil or water. Sulphides, for example, do not get wet, as do silica and most oxides when treated with water. They will, therefore, float on the surface when silica etc. will sink.

(v) **Froth Floatation Process :** This method is used for the concentration of sulphide ores, as sulphide ores get preferentially wetted compared to the gangue materials.

The powdered sulphide ore is added to a tank containing water and eucalyptus oil or turpentine oil. Then the suspension is violently agitated with a rotating paddle. This paddle draws air in it and froth is formed. The sulphide ore particles stick to the froth and rise to the surface with froth. The gangue particles left behind in the tank. The froth is dried for recovery of the ore particles.

Pine oils, fatty acids, xanthates etc. known as “collectors” enhance non-wettability of the mineral particles and “froth stabilises” e.g. cresols, aniline etc. stabilise the froth.

“Depressants” are used to separate two sulphide ores. For example, in case of an ore containing ZnS and PbS, NaCN is used as a depressant. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

(vi) Magnetic Separation: This method is applicable for concentrating ores, which differ from their impurities in magnetic character.

Example: The main impurity of Tinstone (SnO_2) is ferrous tungstate ($FeWO_4$). It is also known as Wolfram. To remove the impurity from tinstone, it is to be powdered first and then the powdered ore is to be dropped over a belt revolving round the two rollers, out of which one roller is a magnet.

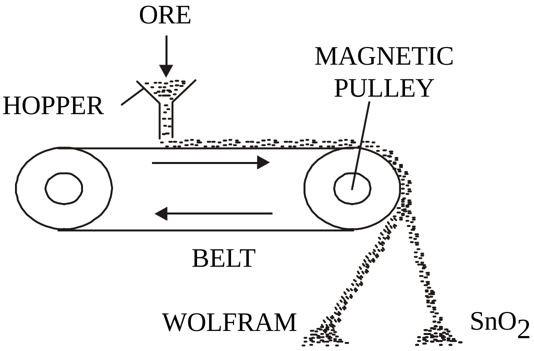


Fig. 6.1 Magnetic separation

The magnetic part of the ore is attracted by the magnetic roller and separates out, whereas the non-magnetic part of the ore is separated out a little away from the magnetic impurities.

(vii) Leaching : "The process of treating the powdered ore with a suitable reagent which can selectively dissolve the ore but not the impurities" is known as **leaching**.

(a) Leaching of alumina from bauxite : The bauxite ore contains aluminium in the form of Al_2O_3 along with SiO_2, iron oxides and titanium oxide as impurities. The powdered ore is heated with a concentrated solution of NaOH at 473 – 523K and 35–36 bar pressure. Alumina is leached out as sodium aluminate and SiO_2 as sodium silicate leaving behind the impurities.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na\,[Al(OH)_4]\,(aq)$$

$$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$

The resulting solution is filtered to remove the undissolved impurities. Then it is cooled and its pH is adjusted either by dilution of by neutralization with CO_2 when aluminium hydroxide gets precipitated. In this stage, the solution is seeded with freshly prepared samples of hydrated alumina to get it precipitated leaving behind sodium silicate in the solution.

$$2Na\,[Al(OH)_4]\,(aq) + CO_2(g) \rightarrow Al_2O_3 . x\,H_2O(s) + 2NaHCO_3(aq)$$

The hydrated alumina is filtered, dried and heated to give back pure Al_2O_3.

$$Al_2O_3 . x\,H_2O(s) \xrightarrow{1470K} Al_2O_3(s) + x\,H_2O\,(g)$$

(b) Leaching of silver and gold: Some metals like gold and silver are extracted from their concentrated ores by leaching. They are dissolved in suitable reagents like acids or bases leaving behind insoluble impurities. The metal is recovered from the solution by precipitation or crystallization. For example, silver ore is leached with dilute solution of sodium cyanide. Silver dissolves forming a complex, sodium dicyanoargentate(I). The solution is further treated with scrap zinc to get the precipitate of silver.

$$Ag_2S + 4\,NaCN \longrightarrow \underset{\text{Sodium dicyanoargentate(I)}}{2\,Na\,[Ag\,(CN)_2\,]} + Na_2S$$

$$2\,Na\,[Ag\,(CN)_2\,] + Zn \longrightarrow \underset{\text{Sodium tetracyanozincate (II)}}{Na_2\,[Zn\,(CN)_4\,]} + \underset{\text{ppt.}}{2Ag\downarrow}$$

Similarly, native gold is leached with potassium cyanide solution and it is recovered from the solution by addition of scrap zinc.

$$4\,Au + 8KCN + O_2 + 2H_2O \rightarrow 4\,K[Au\,(CN)_2] + 4\,KOH$$

$$2\,K\,[Ag\,(CN)_2\,] + Zn \rightarrow K_2\,[Zn\,(CN)_4] + \underset{\text{ppt}}{2\,Au\downarrow}$$

Flux:

It is the substance added to the ores, before heating, with the object that it will react chemically with the impurities (**gangue**) present in the ores and form a fusible slag.

The nature of flux depends upon the impurity to be removed. Accordingly three kinds of fluxes are generally used.

(a) Acidic Flux:

Sand is an example under this category. It is used to remove basic impurities such as metallic oxides.

Example: $$\underset{\text{(Impurity)}}{FeO} + SiO_2 \longrightarrow \underset{\text{(Fusible slag)}}{FeSiO_3}$$

(b) Basic Flux:

Calcium oxide(CaO) is an example under this category. It is used to remove acidic impurities such as sand(SiO_2)

$$\underset{\text{(Impurity)}}{SiO_2} + \underset{\text{(Flux)}}{CaO} \longrightarrow \underset{\text{(Fusible slag)}}{CaSiO_3}$$

$$\underset{\text{(Impurity)}}{P_2O_5} + \underset{\text{(Flux)}}{3CaO} \longrightarrow \underset{\text{(Fusible slag)}}{Ca_3(PO_4)_2}$$

(c) Neutral Flux: Fluorspar(CaF_2)

Slag :

The fusible compounds formed by the union of flux and the impurities especially when it is the waste product of an operation is termed as **slag**.

Slag = Flux + Impurities(gangue)

6.3.2. Extraction of crude metal from the concentrated ore :

Calcination and Roasting:

These two terms are related to the process of extraction of metals from their concentrated ores. Before the concentrated ores are subjected to the final metallurgical operations to get the metals in the free state preliminary chemical treatment is necessary. The objective of this treatment is to (i) get rid of impurities, which would cause difficulties in the later stages and (ii) convert the ore into its oxide

Calcination:

It is a process of heating the concentrated ore in absence of air but at a temperature insufficient to melt it with a view to driving off the volatile matters.

Example:

1. When calamine ($ZnCO_3$), an ore of Zn is calcined, carbon dioxide is expelled and zinc oxide (ZnO) is formed.

$$ZnCO_3 \xrightarrow{\text{calcination}} ZnO + CO_2$$

2. Bauxite ($Al_2O_3, 2H_2O$), an ore of Aluminium, when subjected to calcination, anhydrous aluminium oxide (Al_2O_3) is formed

$$Al_2O_3, 2H_2O \xrightarrow{\text{calcination}} Al_2O_3(s) + 2H_2O$$

3. $Fe_2O_3, 3H_2O \longrightarrow Fe_2O_3 + 3H_2O$
4. $PbCO_3 \longrightarrow PbO + CO_2$
5. $CaCO_3, MgCO_3 \longrightarrow CaO + MgO + 2CO_2$
6. $CuCO_3 \longrightarrow CuO + CO_2$
7. $4FeO + O_2 \longrightarrow 2Fe_2O_3$
8. $2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

Roasting :

It is the process of heating the concentrated ore in excess of air but at a temperature insufficient to melt it(i.e. below the point of fusion) with a view to oxidising it.

Example:

1. Zinc sulphide when roasted, gives zinc oxide

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$

2. Cuprous sulphide when roasted gives cuprous oxide

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

3. $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2\uparrow$

Calcination or roasting process is generally carried out in a specially designed furnace called reverberatory furnace (Fig.6.2)

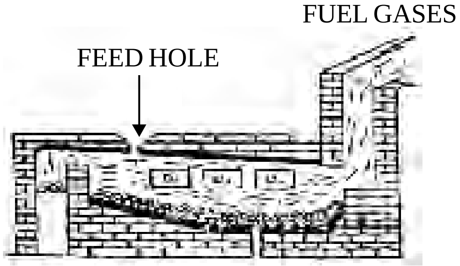


Fig. 6.2 Reverberatory Furnace

Distinction between Calcination and Roasting:

	Calcination		**Roasting**
1	It is the process of heating an ore in absence of air.	1	It is process of heating an ore in presence of air.
2	It is usually employed for carbonate and hydrated oxide ores.	2	It is usually employed for sulphide ores.
3	It renders the ore dehydrated and spongy. Also decomposes carbonate ores. $CaCO_3 \xrightarrow{Heat} CaO + CO_2$	3	It renders the ore into its oxide form. $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

Smelting :

It is an operation in metallurgy in which a metal is extracted in the state of fusion.

During roasting, the ore is converted to the oxide of the metal. But it is still mixed with some gangue which is not removed in the processing. To remove the last of the gangue, the roasted ore is now smelted. Therefore, smelting is regarded as the process of reduction of the ores in a fused state. Coke or charcoal is therefore used which acts as the reducing agent. Further an additional substance called flux is also used to get the fusible product called slag after heating to a high temperature above its melting point.

Impurities + Flux = Fusible slag
(in the ore)

The selection of flux depends upon the nature of impurities. If the impurities are basic (like CaO, FeO, MnO_3 etc.) then the flux employed is acidic (i.e. Silica)

$$\underset{\text{Basic impurity}}{CaO} + \underset{\substack{\text{Flux}\\ \text{(acidic)}}}{SiO_2} = \underset{\text{Slag}}{CaSiO_3}$$

On the other hand if the impurities are acidic (like SiO_2, P_2O_5 etc) then the flux used is basic (i.e. CaO)

$$\underset{\text{Acidic impurity}}{P_2O_5} + \underset{\substack{\text{Flux}\\ \text{(acidic)}}}{3CaO} = \underset{\text{Slag}}{Ca_3(PO_4)_2}$$

The smelting of ores is carried out in different types of furnaces depending upon the raw materials used.

Reduction of the metal oxide to the free metal :

The roasted or calcined ore is then reduced to the metal by using a suitable reducing agent. Some metal oxides get reduced easily while others are very difficult to be reduced. For both the cases heating is required. To understand the pyrometallurgy (variation in temperature requirement for thermal reductions) and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibb's energy interpretations are made.

6.4 THERMODYNAMIC PRINCIPLES OF METALLURGY :

The theory of metallurgical transformations can be understood from the thermodynamic concepts of Gibb's free energy change.

According to thermodynamics : $\Delta G = \Delta H - T\Delta S$ (i)

Where, ΔG = Gibb's free energy change.

ΔH = Change in enthalpy

and 'T' is the specified temperature in Kelvin scale.

For a reaction of equillibrium : $\Delta G° = - RT \ln K$ (ii)

where 'K' is the equilibrium constant for the reversible reaction at specified temperature 'T'. A study of above two equations leads to following conclusions.

(1) Feasibility of a reaction :

A reaction is feasible only when 'ΔG' is –ve. As is evident from equation (i), if 'ΔS' is +ve for a process (for all spontaneous processes ΔS is +ve), on increasing the temperature 'T', the value of $T\Delta S$ will increase and when $T\Delta S$ becomes greater than ΔH, ΔG will be negative and the reaction will proceed in the forward direction.

(2) Coupling of reactions :

A reaction with 'ΔG' value '+ve' can be made to occur by coupling it with another reaction having large negative ΔG, so that net ΔG of the two reaction will be –ve.

Explanation : Let for a reaction $A \rightarrow B$ ΔG_1 = +ve.

and $C \rightarrow D$ ΔG_2 = –ve

After coupling both the reactions : $A + C \rightarrow B + D$ and

$\Delta G = \Delta G_1 + \Delta G_2 = -$ ve, when $\Delta G_2 > \Delta G_1$

So the coupling of two reactions enables the system to produce the products. Such coupling reactions can be easily understood in terms of Ellingham diagram which plots standard free energy of formation of oxides (i.e. $\Delta_f G°$) per mole of O_2, as a function of absolute temperature.

6.4.1 Ellingham Diagram :

Ellingham diagram (Fig. 6.3) is a plot of $\Delta_f G°$ vs T for formation of oxides of elements. Similar diagrams can also be constructed for sulphides and halides of elements. This diagram helps in predicting the feasibility of thermal reduction of an ore (ΔG = –ve). We can study the Ellingham Diagram in two steps.

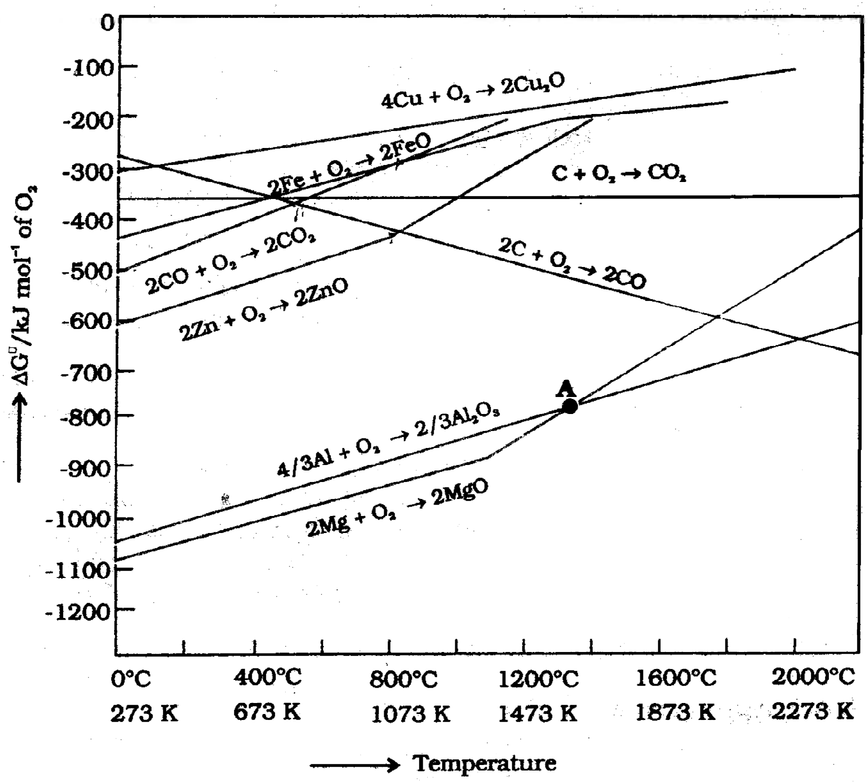


Fig. 6.3 : Gibbs energy (ΔG°) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

Step-1 : Formation of metal oxide :

Let us consider a reaction of the type

$2xM(s) + O_2(g) \rightarrow 2M_xO(g)$

for formation of a metal oxide.

Here dioxygen in gaseous state is used in giving M_xO, a solid as the product.

For gas → solid phase change ΔS is –ve. With increase in value of T, TΔS becomes more and more –ve, hence leading to ΔG value less –ve, i.e. with rise in temperature, ΔG value increases.

So $\Delta_f G°$ vs T graph gives a +ve slope for most of the reactions involving the formation metal oxides, $M_xO(s)$ (Fig. 6.3)

Step-2 : Phase Change :

When there is a phase change (i) solid to liquid or (ii) liquid to gas, there is an increase in the slope on the +ve side as ΔS becomes +ve.

For example : In the Zn – ZnO plot, at the boiling point of Zn (1180K), there is an abrupt increase in the +ve slope of the curve. Similarly, in Mg – MgO curve the +ve slope increases abruptly at boiling point of Mg i.e. at 1380K. The small circles on the left indicate the M.Pts and on the right indicate the B.Pts.

Limitations :

(1) This diagram only suggests whether the reduction of a metal oxide with a particular reducing agent is possible or not. But it does not tell anything about the rate of the reaction.

(2) The interpretation of $\Delta G°$ is based upon equillibrium constant 'K' (i.e. $\Delta G° = RT \ln K$), thus presuming that there is an equillibrium between reactant and product.

$M_xO + A$ (reducing agent) $\rightleftharpoons$ $xM + AO$ (oxidising agent). But this is not always true because reactants and/or products may be in solid state.

6.4.2 Theory of Pyrometallurgy :

The thermodynamic principles as well as the Ellingham diagram together can explain the feasibility of reduction of a metal oxide with reducing agents like carbon or any other metal.

(a) Reduction by carbon :

The process of extraction of a metal by reduction of its oxide with carbon is called smelting. This process takes place in following steps :

(i) Reduction : $M_xO(s) \rightarrow xM \text{ (s or l)} + \frac{1}{2} O_2(g)$ .... (i)

(ii) Oxidation : $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ .... (ii)

Equation (i) is actually reverse of equation (iii) representing the oxidation of the metal.

$$x M \text{ (s or l)} + \frac{1}{2} O_2(g) \rightarrow M_xO(s); \Delta G°_{(M,\, M_xO)} \text{ .... (iii)}$$

If complete oxidation of C to CO_2 occurs,

$$\frac{1}{2} C(s) + O_2(g) \rightarrow \frac{1}{2} CO_2(g); \frac{1}{2} \Delta G°_{(C,\, CO_2)} \text{ .... (iv)}$$

Similarly, if CO is used as reducing agent.

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g); \Delta G°_{(CO,\, CO_2)} \text{ .... (v)}$$

On subtracting (iii) from each of the three equations (ii), (iv) and (v), we have,

$$M_xO(s) + C(s) \rightarrow x M \text{ (s or l)} + CO(g) \text{ .... (vi)}$$

$$M_xO(s) + \frac{1}{2} C(s) \rightarrow x M \text{ (s or l)} + \frac{1}{2} CO_2(g) \text{ .... (vii)}$$

$$M_xO(s) + CO(g) \rightarrow x M \text{ (s or l)} + CO_2(g) \text{ .... (viii)}$$

These three equations (vi), (vii) and (viii) describe the actual reduction of the metal oxide, M_xO to the free metal M.

The $\Delta_fG°$ values for these reactions, in general, can be obtained by subtraction of the corresponding $\Delta_fG°$ value from the Ellingham diagram (Fig 6.3). The –ve value of $\Delta_fG°$ predicts feasibility of the reduction process.

So, it can be understood that, at any given temperature, any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram, because the free energy change ($\Delta_f G°$) for the combined redox reaction will be negative.

Magnesium can reduce Al_2O_3, ZnO, FeO and Cu_2O more readily than Aluminium can reduce ZnO, FeO, Cu_2O. This is because the $\Delta_f G°$ values in the former cases are more –ve. Thus the relative tendency of these metals to act as reducing agents is : Mg > Al > Zn >Fe > Cu. For Ag_2O and HgO, as it is seen from the diagram, $\Delta_f G°$ becomes +ve at higher temperature. This suggests that these oxides are unstable at high temperature and hence decompose to liberate the corresponding metal.

$$2\,Ag_2O\,(s) \xrightarrow{\text{Heat}} 4Ag(s) + O_2(g).$$

$$2\,HgO\,(s) \xrightarrow{630K} 2Hg(l) + O_2(g).$$

6.4.3 Effect of temperature on the Free Energy Change ($\Delta_f G°$) of a Reduction process :

As we know that $\Delta G = \Delta H - T\,\Delta\,S$,. If a reaction does not occur at low temperature, it can occur at high temperature, if $\Delta_f G°$ for the redox reaction becomes –ve at that temperature. In the Ellingham diagram (Fig. 6.3), this temperature is indicated by the intersection of the two curves :

(a) Curve for formation of M_xO

and (b) The curve for oxidation of the reducing agent.

At the point of intersection of the two curves, $\Delta G° = O$. Below this temperature, the $\Delta G°$ is –ve and the oxide is stable. But above this temperature $\Delta G°$ is +ve and the oxide being unstable breaks to give metal and oxygen. Al can reduce MgO to Mg above 1623K.

6.5 EXTRACTION OF IRON FROM ITS OXIDE ORES :

6.5.1 Occurrence

The different ores of iron are oxide ores, carbonate ores and sulphide ores.

1. **Oxide ores**
   - **(a) Haematite, Fe_2O_3** (Red in colour)
   - **(b) Magnetite, Fe_3O_4** (Richest ore of iron, black in colour)
   - **(c) Limonite, $Fe_2O_3.3H_2O$, (hydrated ferric oxide)** (yellow, brown or red in colour)
2. **Carbonate ore**

   Siderite or spathic iron, $FeCO_3$
3. **Sulphide Ores**
   - (a) I**ron pyrites, FeS_2**
   - (b) **Chalcopyrites, $CuFeS_2$**

   Iron pyrite is usually used for the preparation of SO_2, chalcopyrite is used for the extraction of copper.

6.5.2 Extraction

The actual process employed in the extraction of iron from its ores depends on the type of iron desired. Different types of iron arise out of varying carbon content. The three important types are

1. Pig or Cast iron (About 2 to 4% carbon)
2. Wrought iron (0.1 to 0.25% carbon)
3. Steel (0.15 to 1.5% carbon)

The metal is extracted (as cast or pig iron) usually from haematite ore. Haematite ore contains siliceous impurities with a little P,S, Al_2O_3 etc. The process of extraction involves the following three steps.

1. Concentration of the ore.
2. Conversion of the ore to pig iron.
3. Refining (Conversion of pig iron to steel).

1. **Concentration of the ore :** In order to increase the efficiency of the extraction process, the ore obtained directly from mines is subjected to concentration.Concentration increases the percentage of iron oxide in the raw ore.

   The ore is crushed into small pieces and washed with stream of water to remove earthy and siliceous impurities. The ore may be subjected to froth floatation process to carry the real haematite ore into the froth. Since the iron ores are magnetic in nature,the powdered ore can be allowed further to travel on a running belt in a magnetic field so the the magnetic haematite is deposited close to the magnetic field leaving the gangue (impurities) farther away.

2. **Conversion of ore to pig iron (Manufacture of pig iron) :** The process involves two steps.

   1. Calcination and Roasting
   2. Smelting

   Calcination and Roasting : The concentrated ore is heated in excess or air with a little coke (C) in shallow kilns. The ore undergoes following changes.

   (a) Moisture is removed : $2Fe_2O_3.3H2O \longrightarrow 2Fe_2O_3 + 3H_2O\uparrow$
   If ferrous carbonate is in the ore : $FeCO_3 \longrightarrow FeO + CO_2\uparrow$

   (b) Impurities such as P,S, As, Sb etc. are removed as their volatile oxides.
   $S_8 + 8O_2 \longrightarrow 8SO_2\uparrow$ $P_4 + 5O_2 \longrightarrow 2P_2O_5\uparrow$ $4As + 5O_2 \longrightarrow 2As_2O_5\uparrow$

   (c) Ferrous oxide is oxidised to ferric oxide.
   $4FeO + O_2 \longrightarrow 2Fe_2O_3$

   (d) During the process the entire mass becomes porous so that the ore can be easily reduced during smelting.

   Smelting : The extraction of a metal from its ore by a process involving melting is known as *smelting.* It is also referred to as *chemical reduction.*

For extracting iron, smelting is carried out in a blast furnace (Fig. 6.4) A blast furnace is a huge cylinder made of steel. Its height may vary from 120 to even 200ft and width is about 30 ft. in diameter. The inside of the furnace is lined with very high melting refractory bricks. the calcined and roasted ore along with limestone ($CaCO_3$) and coke (C) (ore 8 parts, lime stone 1 part and coke 4 parts) are lifted to the top of the furnace and released at the mouth of the furnace provided with a cup and cone arrangement. Near the bottom of the furnace blast of hot air is forced into the furnace through water cooled nozzles called **tuyers.**

The following reactions take place in different zones of the blast furnace within the temperature range 480 - 1575K. Near the bottom, hot air in contact with falling coke reacts to give

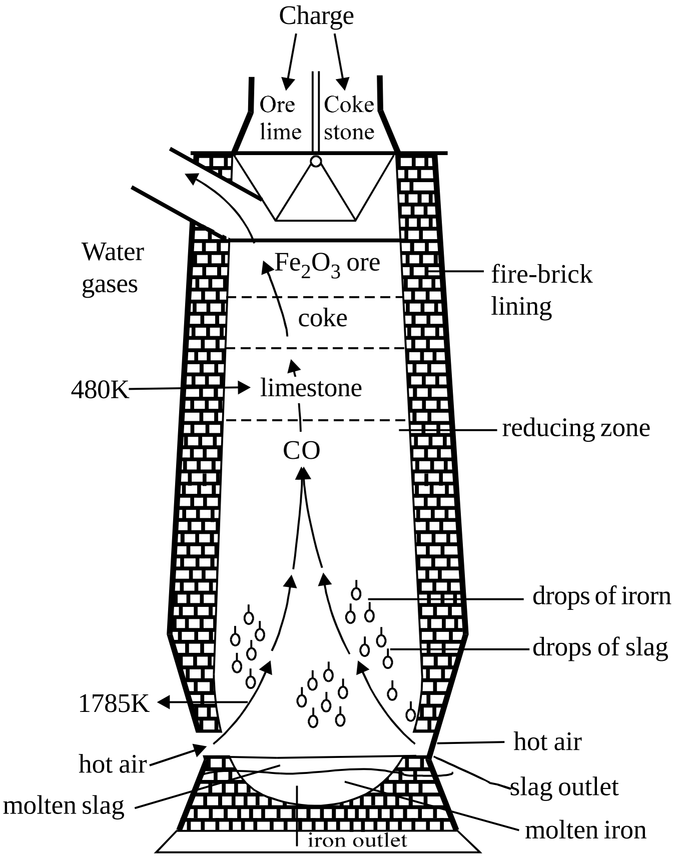


Fig. 6.4 The Blast Furnace

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$

The reaction is exothermic. The upward carbon dioxide comes in contact with layers of coke and gets reduced to carbon monoxide.

$$CO_2 + C \longrightarrow 2CO - \text{heat}$$

Now carbon monoxide acts as a reducing agent and reduces iron oxides to iron.

$$Fe_2O_3 + 3CO \longrightarrow \underset{\text{(Molten)}}{2Fe} + 3CO_2\uparrow \quad (675 - 975K)$$

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2\uparrow$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2\uparrow$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2\uparrow$$

$$FeO + CO \longrightarrow \underset{\text{(Molten)}}{Fe} + CO_2\uparrow$$

$$2FeO + C \longrightarrow \underset{\text{(Molten)}}{2Fe} + CO_2\uparrow$$

Molten iron, thus formed is collected at the bottom of the furnace.

Lime stone acts as flux and removes siliceous impurities in the form of slag.

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ $\quad$ $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag)
Calcium silicate
(1075 - 1275K)

$CaO + Al_2O_3 \longrightarrow Ca(AlO_2)_2$ (slag)
Calcium aluminate

The molten slag is lighter than the molten iron and floats on the top which can be removed through the outlet-holes provided. Carbon monoxide, coming out of the furnace is used to heat the air-blast initially given to the furnace.

The silicates, phosphates, manganates and aluminates present as impurities in the ore are converted to the corresponding oxides of Si, P and Mn. These oxides are finally reduced to their corresponding elements. These elements are partly absorbed by molten iron and partly by molten slag.

$SiO_2 + 2C \longrightarrow Si + 2CO$ $\quad$ $2P_2O_5 + 10C \longrightarrow 4P + 10CO$

$MnO_2 + 2CO \longrightarrow Mn + 2CO$

Some of the phosphate impurities react with sand and carbon.

$2Ca_3(PO_4)_2 + 3SiO_2 + 10C \longrightarrow 3(2CaO.SiO_2) + 4P + 10CO$

Molten metal may combine with phosphorus and carbon as follows.

$3Fe + P \longrightarrow Fe_3P$ $\quad$ $3Fe + C \longrightarrow Fe_3C$
(Cementite)

Molten iron is tapped off from the furnace and solidified into blocks known as **pigs.** Molten iron on sudden cooling is converted to **white cast iron** and on slow cooling to **grey cast iron.** Cast iron is either converted to **wrought iron** or **steel.**

It is possible to manufacture 1000-3000 tons of pig iron per day using blast furnace of suitable dimension. A blast furnace may work non-stop for about five years. Thereafter operation is stopped and the furnace is overhauled.

3. Refining : Conversion of Pig iron to Steel (Manufacture of Steel) :

Steel is more useful than iron. Various steels are prepared by regulating the carbon content. Steel is softer and more malleable than pig or cast iron. Conversion of pig iron to steel is a purification process.

There are three methods for the manufacture of steel.

1. Bessemer process
2. Open Hearth process
3. Electric Furnace process.

(a) Bessemer process

Molten pig or cast iron is poured into the Bessemer converter (Fig 6.5) The converter is a pear-shaped furnace about 20ft. high and 10ft. in diameter and lined with refractory silica (SiO_2) bricks. If the pig iron contains appreciable amount of phosphorus, the converter is lined with lime (CaO) and Magnesia (MgO) instead of silica. Some lime is added to the molten pig iron. Air or air mixed up with oxygen is forced through the bottom of the converter into the molten pig iron. The temperature inside the converter is about 1880K.

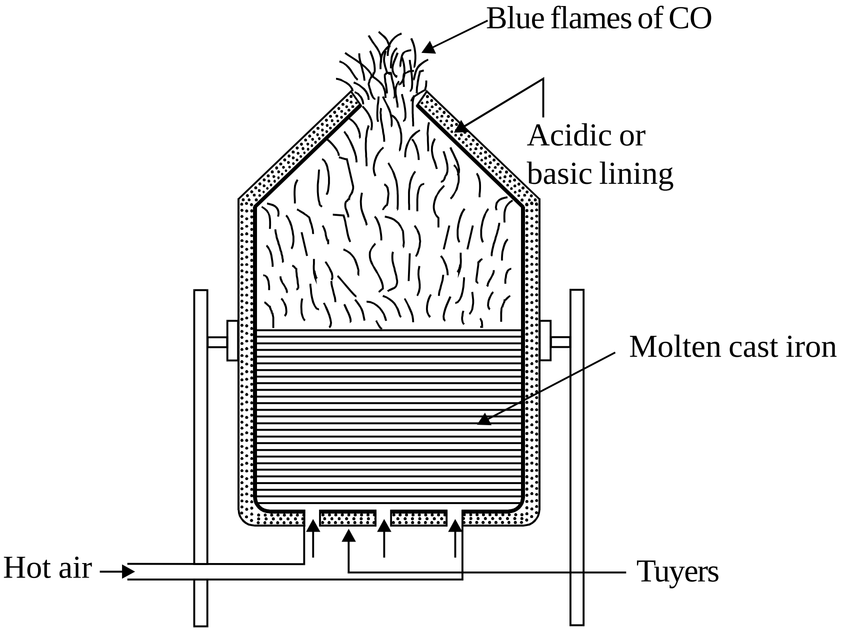


Fig. 6.5 Bessemer's converter used for the manufacture of steel from cast iron.

The following reactions take place.

$Si + O_2 \longrightarrow SiO_2$ $\quad 2Mn + O_2 \longrightarrow 2MnO$ $\quad 2Fe + O_2 \longrightarrow 2FeO$

$MnO + SiO_2 \longrightarrow \underset{\text{manganese silicate}}{MnSiO_3 \text{ (slag)}}$ $\quad FeO + SiO_2 \longrightarrow \underset{\text{ferrous silicate}}{FeSiO_3 \text{ (slag)}}$

If phosphorus is present as an impurity it is oxidised to phosphorus pentoxide and then to calcium phosphate.

$4P + 5O_2 \longrightarrow 2P_2O_5$ $\quad P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2 \text{ (slag)}$

The slag calcium phosphate, called **Thomas slag** is used as an important fertiliser.

Carbon mostly present in the form of Fe_3C further reacts with FeO and O_2.

$FeO + Fe_3C \longrightarrow 4Fe + CO$ $\quad 2Fe_3C + O_2 \longrightarrow 6Fe + 2CO$

Free carbon also burns with oxygen to carbon monoxide

$$2C + O_2 \longrightarrow 2CO$$

The evolved CO reacts with air (oxygen) to form CO_2 and a blue flame is seen at the mouth of the converter. As soon as the blue flame dies down, it is evident that all the carbon is oxidised.

At this stage no further air is supplied into the converter. Then requisite amount of carbon (charcoal) along with manganese (in the form of *spiegeleisen:* 15–20% Mn and rest iron) is added to molten iron. The steel thus prepared in the Bessemer converter has the approximate composition: Fe 98.4%, C 0.4%, Mn 0.9%, P 0.1%, Si 0.1%).

This steel in its molten state is called **Bessemer steel** which is poured directly into moulds and high quality pipes, tubes, etc. are made out of it.

The L.D. process

In the Bessemer process nitrogen present in the air blast badly affects the mechanical properties of steel. Therefore in the L.D. (**Lintz** and **Donawitz**) process (Fig. 6.6) blast of pure oxygen in place of air is blown into the molten pig iron from the top.

In this process impurities like sulphur and phosphorus are quickly oxidised and the oxidation of carbon is regulated. This process manufactures better quality of steel than the Bessemer process.

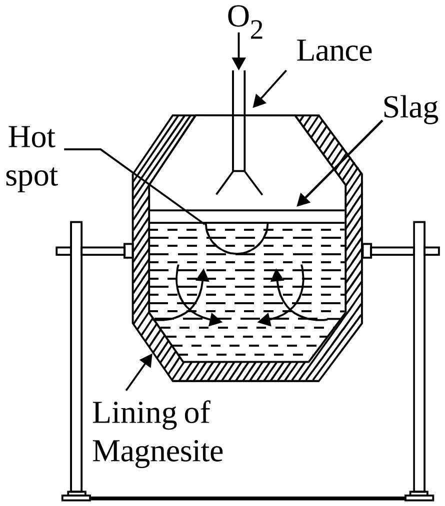


Fig. 6.6. Converter for L.D. process

(b) Open Hearth process or Siemens – Martin process

This is the modern process in which a steel of exact composition is obtained. The furnace used consists of an open hearth (Fig.6.7) lined with silica or calcined dolomite (CaO.MgO) depending upon the nature of impurities present in the pig or cast iron. If the impurities are of Mn, Si, etc., silica lining is used. Calcined dolomite lining is used if P is present in appreciable amount.

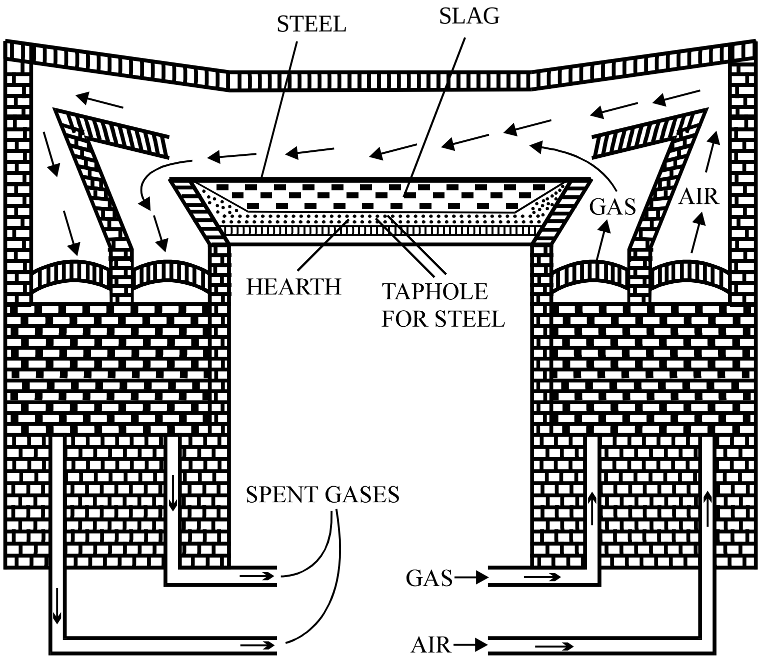


Fig. 6.7. Open Hearth Furnace

In this process, a mixture of pig or cast iron, scrap iron, iron ore (Haematite) and lime is melted in an open hearth furnace. The furnace attains a temperature of about 1870K by burning fuel gas and air.

Impurities like Si and Mn are oxidised to their respective oxides by haematite (Fe_2O_3). Both Mn and Si are removed as manganous silicate (slag).

$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2$ $3Mn + Fe_2O_3 \longrightarrow 2Fe + 3MnO$

$MnO + SiO_2 \longrightarrow MnSiO_3$ (slag) $CaO + SiO_2 \longrightarrow CaSiO_3$ (slag)

Phosphorus present reacts with lime and is removed as calcium phosphate slag.

$12P + 10Fe_2O_3 \longrightarrow 6P_2O_5 + 20Fe$ $2P_2O_5 + 6CaO \longrightarrow 2Ca_3(PO_4)_2$ (slag)

Carbon and sulphur are oxidised to volatile gases.

$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2$$

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$$

Iron containing Fe_3C reacts with Fe_2O_3 to form steel.

$$3Fe_3C + Fe_2O_3 \longrightarrow 11Fe + CO$$

Samples of steel prepared are drawn from time to time and tested for carbon content. Finally *spiegeleisen* is added to the molten mass to get the desired steel. The slag formed over the surface protects the steel from oxidation. The process is much slower than Bessemer's process, but **a better quality of steel is formed.** This process has added advantage for the following reasons.

(i) Scrap is re-used.

(ii) Economy of fuel is achieved by using regenarative system.

(iii) The temperature can be controlled as the heating is done externally.

(c) Electric Furnace process :

The electric furnance method differs from the open hearth process primarily in the method of heating. This process of making steel is costly and is carried out in those countries where electricity is cheap. The furnance (Fig.6.8) is made of steel with inside refractory bricks and has a good lining of dolomite or magnesite. The Bessemer steel alongwith some lime and ferric oxide are charged into the furnace.

An arc is then struck between the graphite electrodes and the surface of the charge. The enormous heat produced in the furnace melts the charge. The impurities such as P, S, Si and Mn react with the basic lining to form slag. Carbon is oxidised to CO.

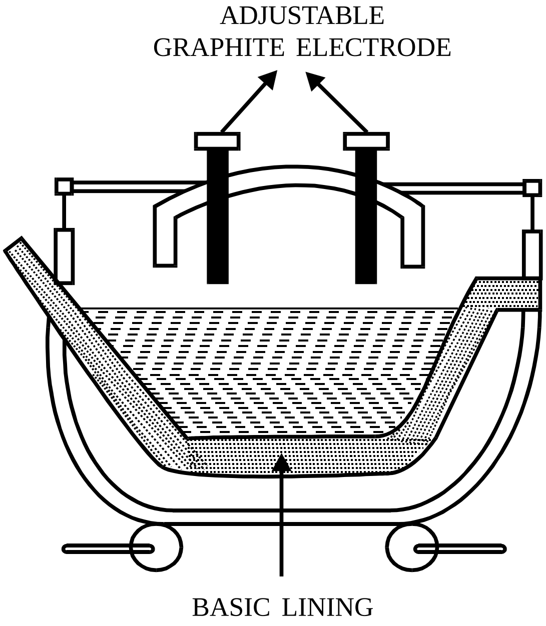


Fig. 6.8. Electric steel furnace

This process is used to manufacture high melting alloy-steels, since high temperature is maintained in the furnace.

Manufacture of Wrought iron

Wrought iron is manufactured from pig or cast iron by **puddling process.** The cast iron is melted on the hearth of a special type of reverberatory furnance (Fig.6.9) by hot gases and stirred with long iron rods. The furnance is lined with haematite (Fe_2O_3) which oxidises the impurities and subsequently they are removed as slag.

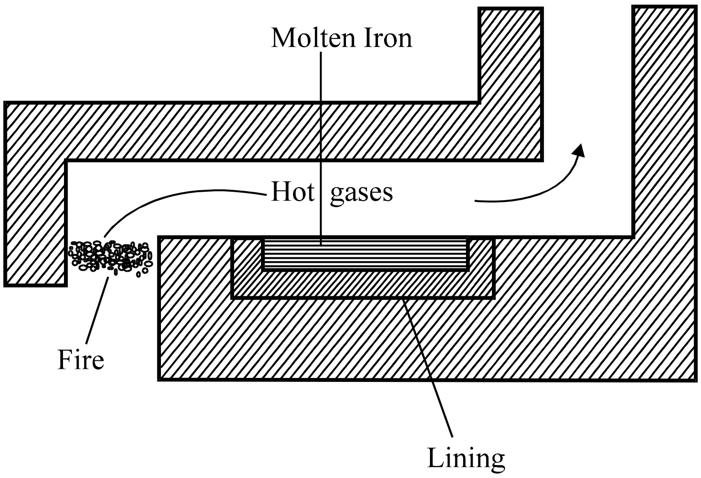


Fig. 6.9. Preparation of wrought iron in a reverberatory furnace.

$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO$ $\qquad$ $3Si + 2Fe_2O_3 \longrightarrow Fe + SiO_2$

$3Mn + Fe_2O_3 \longrightarrow 3MnO + 2Fe$ $\qquad$ $MnO + SiO_2 \longrightarrow \underset{\text{(slag)}}{MnSiO_3}$

$6P + 5Fe_2O_3 \longrightarrow 10Fe + 3P_2O_5$ $\qquad$ $P_2O_5 + Fe_2O_3 \longrightarrow 2FePO_4$ (slag)

When impurities are removed, the melting point of iron metal rises and it becomes a semi-solid mass. The semi-solid mass is taken out in the form of balls and beaten under steam hammers to squeeze out as much of slag as possible.

Wrought iron, thus manufactured is almost pure iron.

6.5.3 Types of iron :

There are three commercial varieties of iron depending upon the percentage of carbon content.

Pig or Cast iron: It is the most impure form of iron containing highest percentage of carbon (about 4%). 2% of other combined impurities such as S, P, Si and Mn are also present. Molten pig iron from the blast furnace when cast into moulds by cooling and remelting, cast iron is prepared.

Properties :

1. Cast iron is hard and brittle.
2. It cannot be forged or welded by hammering.
3. When molten cast iron solidifies, it expands slightly.
4. Cast iron is succeptible to rusting.

Uses :

1. Cast iron finds extensive applications in casting articles of various shape.
2. Cast iron is used to manufacture toys, stoves, cooking-range, stools, radiators, pipes and agricultural implements.
3. It is also used to make wrought iron and steel.

Wrought iron:

It is the pure form of iron and contains 0.1 to 0.25% of carbon.

Properties:

1. Wrought iron is soft, ductile and malleable.
2. It is tough and resistant towards rusting and corrosion due to presence of a very small percentage of slag in it.
3. Since it softens at about 1280 K it can be forged and welded.
4. It has fibrous structure and thus can withstand high stresses.

Uses:

1. Wrought iron is used to make magnets in dynamos and electric cranes.
2. Since it can withstand sudden stress, it is used to manufacture chains, nails, bolts, hooks, wires, bars and railways carriage couplings.

Steel:

Steel is the most commercial variety of iron containing 0.15 to 1.5% carbon. In steel this percentage of carbon remains in between that of cast iron and wrought iron.

Properties :

1. Steel is extremely hard due to presence of 10% manganese.
2. It melts at about 1650K and can be welded.
3. **Heat treatment on steel :** The hardness of steel depends on its carbon content and heat treatment.

(a) **Quenching :** Hard steel can be further hardened by heating it to bright redness (1125K) and suddenly cooling it by plunging into cold water or oil. The steel becomes hard and brittle.

(b) **Tempering :** If the quenched steel is reheated to a temperature much below redness, 505K to 575K and is then cooled slowly, it retains its hardness but the brittleness considerably decreases. This process is known as *tempering.*

(c) **Annealing :** If steel is heated to red heat and then cooled slowly the process is called *annealing*. By *annealing* steel becomes soft.

(d) **Nitriding:** Nitriding is the process when steel is heated in an atmosphere of ammonia. Steel becomes hard with a coating of iron nitride on its surface.

Uses of steel :

1. Steel is used to make domestic articles, utensils, cutlery, swords, armour plates etc.
2. Extensively used for structural purposes, machineries and rail roads.
3. In making bar magnets, magnetic needles, watch springs, razors etc.

Types of steel:

(a) **Mild steel :** It has low percentage of carbon between 0.1 to 0.4 It shows the properties of wrought iron along with elasticity and hardness.

(b) **Hard steel :** Hard steel has percentage of carbon content varying in between 0.5 to 1.5. It is hard and brittle.

(c) **Special steels or alloy steels :** Steel mixed with small amounts of chromium, manganese, cobalt, nickel, molybdenum and tungsten acquires special properties. Such products are called *special steels* or *alloy steel.*

Table - 6.2 : Comparison in properties of cast iron, steel and wrought iron

Properties	Pig or Cast iron	Steel	Wrought iron
1. Carbon content	~4%	0.15 to 1.5%	0.1 to 0.25%
2. Structure	Crystalline	Crystalline	Fibrous
3. Hardness	Hard	Hard and soft	Soft
4. Malleability	Brittle	Malleable and brittle	Malleable
5. Melting point	~ 1500K	~ 1620K	~1770K
6. Welding	Cannot be welded	Can be welded	Can be welded

Table - 6.3 : Compositions, properties and uses of some alloy steels

Name of the alloy steel	Metals added to steel	Properties	Uses
1. Stainless steel	Cr 11.5%, Ni 8%	Resists corrosion	Common articles, ornamental pieces, automobile parts, cutlery
2. Chrome steel	Cr 1 to 2%	High tensile strength	Cutting machinery cutlery
3. Chrome Vanadium steel	Cr 1%, V 0.15%	High tensile strength	Springs, shafts, axles
4. Manganese steel	Mn 13%	Very had and tough, resistant to wear	Rock crushing machinery, rock drills, safes, helmets
5. Nickel steel	Ni 2 to 4%	Resistant to corrosion, Hard and elastic	Cable wires, cutting tools, automobile gears and drive shafts, aeroplane parts, armour plates.
6. Invar	Ni 36%	Small coefficent of expansion	Measuring scales and tapes, pendulum, clock pendulums, balance parts
7. Permalloy	Ni 78%	Strongly magnetised by electric current, loses magnetism when current is cut off.	Ocean cables, electromagnets.
8. Molybdenum steel	Mo 0.5 to 3%	Hard	Cutting tools and axles
9. Tungsten steel	W 5 to 20% Cr 3 to 8%	Very hard	High speed cutting tools use in lathe works.

6.6 COPPER, Cu

6.6.1 Occurrence

Copper is a fairly abundant metal. It occurs as native (in free state) copper in large quantities in Michigan (U.S.A.). Native copper is 99.9% pure.

Most copper is extracted from its ores :

1. Chalcopyrite, **$CuFeS_2$** (Metallic lustre with colour of copper metal)
2. Chalocite or Copper glance, **Cu_2S** (Dark grey colour)
3. Cuprite, **Cu_2O** (Ruby red colour)
4. Malachite, **$CuCO_3.Cu(OH)_2$**, Basic copper carbonate (Green colour)
5. Azurite, **$2CuCO_3.Cu(OH)_2$** (Blue colour)

6.6.2 Extraction of copper from cuprous oxide :

In the Ellingham diagram shown in Fig 6.3 the (Cu, Cu_2O) curve is almost at the top while (C, Cu) and (CO, CO_2) lines lie much below it, particularly in the temperature range 500 – 600K. So it is very easy to prepare metallic copper by heating cuprous oxide with coke. Therefore the sulphide ores are first change to oxide. The detailed procedure of extraction is carried out in following five steps.

1. Concentration 2. Roasting 3. Smelting 4. Bessemerisation 5. Refining

1. Concentration : The sulphide ores are concentrated by the **froth floatation process.** The ore is finely crushed in ball-mills, suspended in water containing a small quantity of pine oil and vigorously agitated by blast of air. The particles of sulphide ore remain in oil-froth and float on the surface. The gangue (impurity) particles wetted by water sink to the bottom and separated.

2. Roasting : The enriched ore is roasted in a current of air in the reverberatory furnace to remove As, Sb and much of sulphur.

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

3. Smelting : The roasted ore together with a little coke(C), and silica (SiO_2) is charged into a blast furnace and melted. As a result of smelting iron sulphide is oxidised to iron oxide and then converted into fusible ferrous silicate which is removed as a slag.

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow \quad FeO + SiO_2 \rightarrow Fe\,SiO_3 \text{ (slag)}$$

Part of ferrous sulphide melts along with cuprous sulphide at the high temperature giving rise to **matte** that contains about 50% copper.

4. **Bessemerisation :** The molten **copper matte** obtained from the blast furnace is transferred to a Bessemer converter and a blast of air is blown through the molten matte. On forcing the air blast through the melt, sulphur, arsenic, etc. are oxidised and escape as gases while ferrous oxide reacts with silica to form a slag.

Cuprous sulphide is oxidised mostly into cuprous oxide and partly into cupric oxide and cupric sulphate. Cupric oxide and cupric sulphate react with cuprous sulphide to produce metallic copper as follows.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \uparrow \quad 2\,Cu_2S + 5O_2 \rightarrow 2CuSO_4 + 2CuO$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2 \uparrow \quad CuSO_4 + Cu_2S \rightarrow 3Cu + 2SO_2 \uparrow$$

$$Cu_2S + 2CuO \rightarrow 4Cu + SO_2 \uparrow$$

After completion of the reaction the molten copper is poured into sand moulds. On cooling, the solid copper obtained assumes a blister surface. This due to the impression of evolved sulphur dioxide bubbles on the surface of molten copper during solidification. This copper metal is called **blister copper.**

5. **Refining :**

(a) By electrolytic method

The blister copper is cast into blocks and refined by electrolysis. Blister copper contains about 98% copper and very small amount of impurities like zinc, iron, nickel, silver, gold etc.

Large heavy plates of blister copper are suspended at intervals in a lead lining tank containing copper sulphate solution as electrolyte. Impure copper (blister) plates serve as anodes. The cathodes are pure and thin copper plates, coated with graphite to scrap off the deposited copper metal on it (Fig 6.10).

When electrolysis is carried out copper from the anode along with traces of Zn, Fe or Nickel dissolve into the electrolytic solution while less reactive metals i.e. silver and gold are left undissolved and settle at the bottom near the anode as **anode mud** or **anode slime** or **anode sludge**. Copper alone is deposited at cathode, leaving more active metals Zn, Fe, or Ni in solution. This is because copper ions are more easily reduced.

At the anode: $Cu \longrightarrow Cu^{2+} + 2e$ (Cu^{2+} ion passes into the solution)

At the cathode: $Cu^{2+} + 2e \longrightarrow Cu$ (Cu metal is deposited at cathode)

Copper obtained by electrolytic refining method is 99.9% pure. In the electrolytic refining process, gold and silver are also recovered.

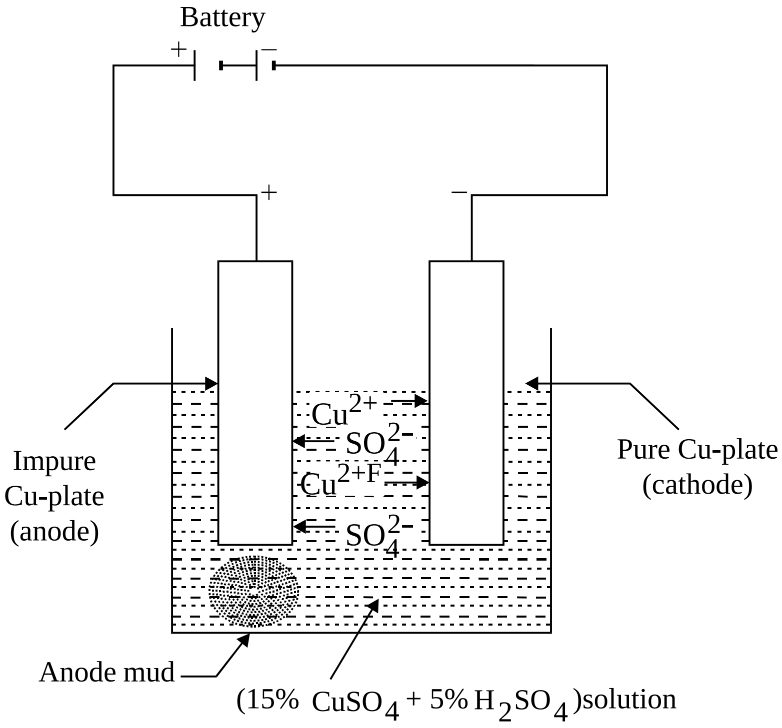


Fig. 6.10 : Electrolytic refining of blister copper.

(b) By poling

The crude blister copper is melted in the reverberatory furnace that has a silica lining. Sulphur and arsenic impurities are oxidised to their oxides. Reactive metals Fe, Zn etc. form oxides in the form of scum and are skimmed off. Some Cu_2O formed is reduced by stirring the molten metal with green wood poles. Copper refined in this process is about 99.5% pure.

Extraction of copper by Hydrometallurgical process

This process is employed to extract copper metal usually from low grade sulphide ores. A large amount of crushed ore in heaps is exposed to air and water. Copper sulphide is oxidised to copper sulphate by moist air and the process is completed in about a year.

$$2Cu_2S + 5O_2 \rightarrow 2CuSO_4 + 2CuO \qquad CuS + 2O_2 \rightarrow CuSO_4$$

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$2Fe_2S_3 + 11O_2 + 2H_2O \rightarrow 4FeSO_4 + 2H_2SO_4$$

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

The copper sulphate liquor is collected from the bottom of heaps and run into concrete pans and iron scraps are added to precipitate copper metal.

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

The precipitated copper is dried and then refined.

Extraction of copper from non-sulphide ores

The non-sulphide ores such as *malachite* and *azurite* are usually leached with dilute sulphuric acid. In the **leaching process** copper is converted to copper sulphate solution and recovered by electrolysis.

Alternatively, these oxide and carbonate ores are mixed with a flux and powdered coke and reduced in a reverberatory furnace.

$$CuCO_3 \rightarrow CuO + CO_2 \uparrow \quad ; \quad Cu(OH)_2 \rightarrow CuO + H_2O$$

$$CuO + C \rightarrow Cu + CO \quad ; \quad Cu_2O + C \rightarrow 2Cu + CO$$

6.7 ZINC, Zn

6.7.1 Occurrence :

Zinc found in different ore forms, including

Zinc spar, $ZnCO_3$	Calamine, $ZnCO_3$
Zinc Blende, ZnS	Zincite, ZnO
Willemite, 2ZnO, SiO_2	Franklinite, (ZnFe) $O.Fe_2O_3$ and Zinc Spinel, $ZnO.Al_2O_3$

6.7.2 Extraction :

Zinc is extracted using two processes

(a) Roasting of sulphide ore to obtain Zinc oxide

$$2ZnS + 3O_2 \xrightarrow{1173K} 2ZnO + 2SO_2$$

(b) Reduction with charcoal which involves release of zinc from the oxide. Carbonate ore, calamine is calcined to get oxide and CO_2 is driven off.

$$\underset{\text{(Calamine)}}{ZnCO_3} \xrightarrow[\Delta]{\text{Calcination}} ZnO + CO_2$$

Extraction of Zinc from Zinc oxide :

As seen in the Ellingham diagram in Fig. 6.3, the intersection of (Zn, ZnO) and (C, CO) curves lies at a higher temperature. So the reduction of ZnO with coke is carried out at a higher temperature.

It can also be seen that, the three curves representing the oxidation of carbon [i.e. (C, CO); (C, CO_2) and (CO, CO_2)] lie above the oxidation curve of Zn till the boiling point the Zinc (i.e. 1180K) is reached.

Above 1180K the $\Delta_f G°$ for the formation CO decreases and that for formation of ZnO increases and intersects the (C, CO_2) curve at 1270K.

So it can be concluded that above 1270K reduction of ZnO by carbon is negative and hence ZnO is easily reduced by coke.

ZnO is made into brickettes with coke and clay and heated at the temperature around 1673K and the reduction process goes to completion.

Since this temperature is above the boiling point of Zinc, the metal is distilled off and collected by rapid chilling.

6.8 ELECTROCHEMICAL PRINCIPLES OF METALLURGY :

Some molten metals are reduced by the process of electrolysis. for the process of electrolysis:

$\Delta G^\circ = -nFE^\circ$ .... (i)

where n = number of electrons involved in the process of reduction.

F = Faraday of charge.

and E° = The standard electrode potential of the redox couple (M/M^{n+}) present in the system. When two metal electrodes are coupled with each other and the difference of two E° values of them corresponds to a positive E°, then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.

Ex : $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Depending upon the reactivity of the metal produced, the materials of the electrodes are selected. Sometimes, a flux is added for making molten mass more conducting.

Electrolytic method is used for the extraction of active metals like Na, Mg, Ca, Al etc.

Metals like Na, K, Mg, Ca and Al are very reactive metals. Their oxides, chlorides and hydroxides are very stable. They cannot be reduced to free metals either by carbon or Aluminium. In such cases the metals are obtained by reduction of suitable molten salts like chlorides and hydroxides by the passage of electricity. The process is known as **Electrolytic reduction** or **Electrometallurgy**.

The metal is liberated at the cathode. The aqueous solution of salt of the metal is not taken for electrolytic reduction, since the metal liberated at the cathode reacts with water forming metal hydroxide and H_2. Hence molten salt of the metal is taken for electrolysis.

6.8.1 Occurrence and extraction of Aluminium :

Aluminium ores include Bauxite ($Al_2O_3 \cdot 2H_2O$), Diaspore ($Al_2O_3 \cdot H_2O$), Corundum (Al_2O_3) & Cryolite (Na_3AlF_6). The process of extraction of metals by electrolysis of their fused salts is called electrometallurgy. Aluminium is extracted from pure bauxite ore following the principle of electrometallurgy. The ore is concentrated by the process of leaching (discussed before). Then cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to alumina to

(i) reduce its m.pt. to around 1140K

and (ii) make it a good conductor of electricity.

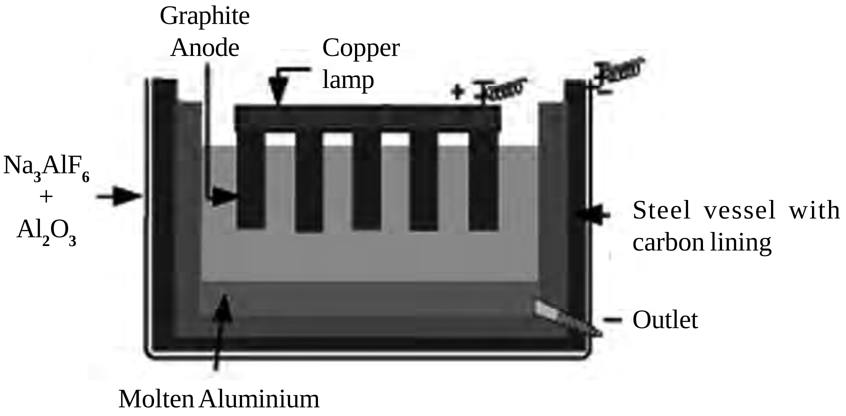


Fig. 6.11 : Electrolytic cell for extraction of aluminium

Then the electrolysis of this mixture is carried out by **Hall and Heroult process**. The electrolysis of the molten mass is carried out in an iron tank which is lined with carbon (acts as cathode) and graphite rods suspended above which serve as anode. The molten alumina is covered with a layer of powdered coke to prevent oxidation and loss of heat due to radiation. The process is carried out at about 1173K.

Cathode : Al^{3+} (melt) + $3e^- \rightarrow Al\ (l)$

Anode : $C(s) + O^{2-}$ (melt) $\rightarrow CO + 2e^-$

$C + 2O^{2-}$ (melt) $\rightarrow CO_2(g) + 4e^-$

About 0.5 kg of carbon burns during the formation of 1 kg of Aluminium. The graphite anodes are therefore changed from time to time.

At 1173K temperature the Aluminium metal liberated at cathode melts and this molten metal sinks to the bottom. This metal is collected through a tapping hole. The metal obtained by this method is 99.95% pure.

6.9 EXTRACTION OF NON-METALS BY OXIDATION :

Non-metals are generally extracted from their compound by the process of oxidation.

Isolation of chlorine :

Chlorine is extracted from brine solution by the process of oxidation.

$2\ Cl^-(aq) + 2H_2O\ (l) \rightarrow 2OH^-\ (aq) + H_2(g) + Cl_2(g)$

This extraction is done by the process of electrolysis.

$\Delta G°$ for this reaction is +422 kJ

$$\text{So, } E° = \frac{-\Delta G°}{nF} = -2.18V = -2.2V.$$

The electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl gives sodium metal along with Cl_2 gas.

For the oxides not reducible with carbon:

It must be borne in mind that in the cases of the oxides of those metals which cannot be reduced with carbon. In such cases, the halide process (Method No. 7) is adopted. For example, the oxides of calcium etc are not reducible with carbon. To get calcium from its ores we prepare the chloride first by treating the ore, the carbonate, with HCl and then either – (i) fuse the chloride with sodium or (ii) electrolyse the fused chloride.

$$CaCO_3 \xrightarrow{\text{(treated with HCl)}} CaCl_2 \xrightarrow{\text{(fused \& electrolysed)}} \begin{array}{l}\text{(Ca at the cathode)} \\ \text{(}Cl_2\text{ at the anode)}\end{array}$$

6.10 REFINING OF METALS :

The metals obtained during extraction from ores even after reduction are not always pure. They are often contaminated with slag, dissolved gases and other metals like arsenic, phosphorus, silicon, carbon etc. whose compounds happen to occur in the same ore. Hence the last step in the metallurgical process is finally carried out to get the pure metal which is known as *refining* or *purification.*

This is generally done in many ways depending upon the nature of the metal concerned. The common refining methods are listed below.

1. Liquation
2. Distillation
3. Oxidation
4. Chemical treatment
5. Electrolytic refining.
6. Vapour phase refining
7. Chromatographic methods.

1. **Liquation:** Metals with low melting points e.g. – mercury, bismuth, tin etc can be separated from most impurities – simply by melting the metal and pouring it off. The impure metal is placed on a sloping hearth of a furnace and heated gently. The metal melts and flows down leaving behind the solid impurities on the hearth.

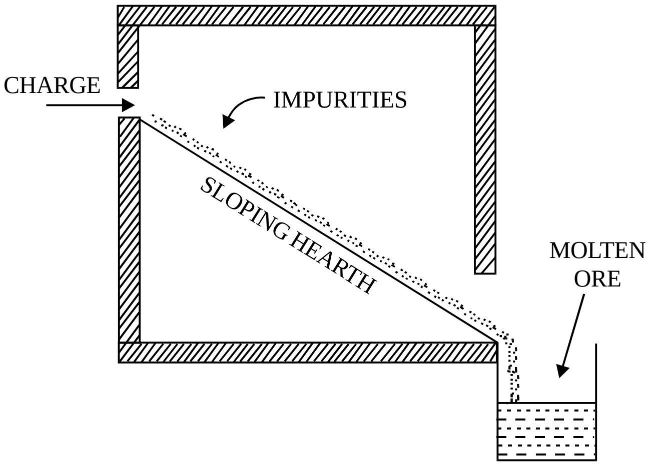


Fig. 6.12 : A Sloping hearth

2. **Distillation:** Metals with low boiling points such as zinc, cadmium, mercury and bismuth can be separated from most impurities by distilling the impure metal in a retort. The vapours of the metal so produced are condensed in a suitable receiver. The impurities are left behind in the retort.

3. **Oxidation:** This type of refining is usually employed for lead, silver, copper and such other metals. The molten metal is subjected to oxidation through application of air by (i) *tossing-* when the molten metal is tossed with the help of ladles (ii) *puddling* – i.e. stirring the molten metal with long wooden bars, (iii) *bessemerisation-* when compressed air is blown through the molten metal in specially designed furnaces, and (iv) *Cupellation-* when the molten metal is taken in small dishes made of bone ash and air passed over the melt. The impurities are oxidized and the volatile oxides thus produced escape. The pure metal remains behind.

4. **Chemical treatment :** An important example of chemical treatment of impure metals is the action of nitric acid on gold. When impure gold is treated with nitric acid. The impurities in it dissolve in the acid and the metal itself remains unattacked.

5. **Electrorefining:** Probably the most widely used refining process is the electrolytic process. A large piece of impure metal is made the anode in the electrolytic cell; a thin piece of very pure metal is made the cathode. The electrolyte is the solution of a water soluble compound of the metal concerned. On electrolysis, less active metals which may be present as impurities fall to the bottom of the electrolytic tank and are collected as ‘mud’ near anode called *anode mud*. Metals more active than the one being purified electrolytically remain in solution as ions. Thus, in the electrorefining of copper, a large piece of impure copper is made anode in the electrolytic cell; a thin piece of very pure copper is made the cathode. As the anode material dissolves slowly in the electrolyte, the less active metals such as zinc and lead go into solution and stay there as ions. The noble metals like gold and platinum, which remain unaffected, sink to the bottom and settle as *anode mud* while copper itself is deposited on the cathode.

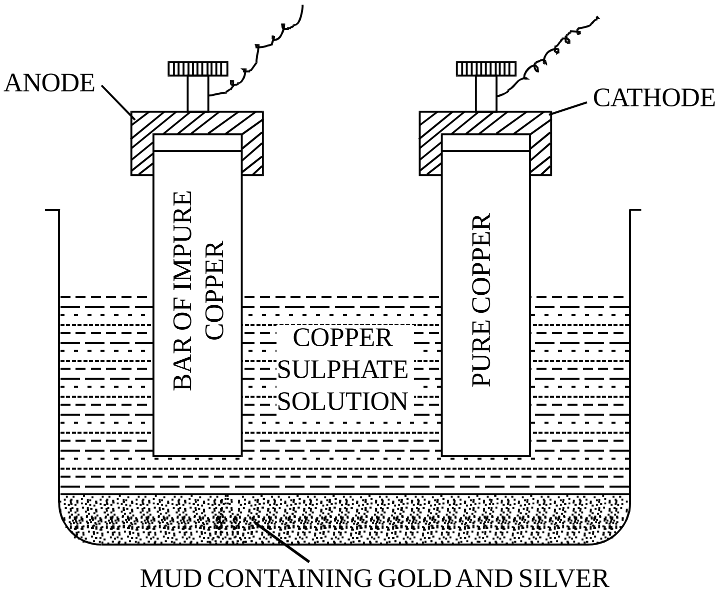


Fig. 6.13 : Electrorefining of metals

6. **Zone Refining :** It is also known as fractional crystallization method. In order to obtain metals of high purity for specific applications, this method is generally employed. Silicon and germanium used as semiconductors are obtained by this process. It is based on the principle that the impurity has greater solubility with the liquid than in solid state of the metal.

7. **Vapour Phase Refining :** In this method refining of the metal is done in vapour phase. The process is carried out only when the following two requirements are fulfilled.

   (a) The metal should form a volatile compound with an available reagent.

   (b) The volatile compound should be easily decomposable to the original metal.

Examples :

(i) **Mond process for refining Nickel :** In this process, nickel is heated in a stream of carbon monoxide forming nickel tetracarbonyl. Nickel tetracarbonyl being volatile in nature decomposes at higher temperature giving the pure nickel.

$$Ni + 4CO \xrightarrow{330\text{–}350K} Ni(CO)_4$$

$$Ni\,(CO)_4 \xrightarrow{450\text{–}470K} Ni + 4CO$$

(ii) **van Arkel method for Refining Zirconium or Titanium :** Oxygen and nitrogen are present in the form of impurity in certain metals like Zirconium and Titanium. The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, sublimes.

$$Zr + 2I_2 \rightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal get deposited on the filament.

$$Zr\,I_4 \rightarrow Zr + 2I_2$$

8. **Chromatographic methods :** As discussed in Volume I of this book, chromatographic methods are of several types depending on the station any phase used like

   (a) Paper chromatography

   (b) Column chromatography

   (c) Gas chromatography etc.

The common principle followed is that, different components of a mixture are differently adsorbed on the adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are eluted (removed) using suitable eluants.

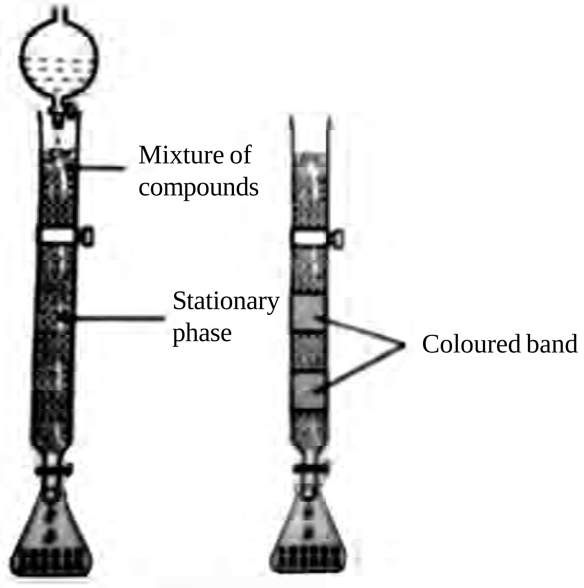


Fig. 6.14 : Schematic diagram showing column chromatography

6.11 USES OF METALS :

(A) Aluminium :

(1) Aluminium is a good conductor. So it is used for making transmission cables and for winding the moving coils of dynamos or motors.

(2) The fine dust of aluminium is used in paints and laequers.

(3) Aluminium being a reactive metal is used for extraction of metals like chromium and manganese from their oxides.

(4) Aluminium foils are used as wrappers for chocolates, medicines, photographic films etc.

Table 6.4 : Alloys Aluminium and their uses

Alloy	Composition	Uses
Aluminium Bronze	Al 95% Cu 5%	Coins, Utensils, Jewellery
Magnalium	Al 95% Mg 5%	Balance beams, Pressure cooker
Duralumin	Cu 4% Mn 0.5% Al 95%, Mg 0.5%	Aeroplanes, Automobile parts, Pressure cooker etc.

(B) Copper :

Uses of Copper :

1. Since copper has high electrical conductivity, it is extensively used in the electrical industries for making cables, wires, battery plates, generators, transformers, etc.

2. It is used in the making of cooking utensils, heating apparatus, steam pipes, boiler parts, calorimeters, etc.
3. It is used for making coins, in electroplating and electrotyping.
4. Copper salts have numerous uses in agriculture and industries.
5. Copper forms a large number of important alloys which find numerous applications.

Table - 6.5 : Alloys of Copper and their uses

Alloy	**Percentage composition**	**Uses**
1. Brass	Cu 60 to 80%, Zn 40 to 20%	Kitchen utensils, condenser tubes, musical instruments, catridges, castings, wires, parts of machinery
2. Bronze	Cu 75 to 90%, Sn 25-10%	Coins, utensils, statues, bells, propeller blades, medals.
3. German Silver	Cu 60%, Zn 25%, Ni 15%	Utensils, ornament plating, resistance coils.
4. Monel metal	Cu 30%, Ni 67%, Fe+Mn 3%	Acid container, alkali industry, acid pumps.
5. Gun metal	Cu 87%, Sn 10%, Zn 3%	Gun barrels, gears, castings.
6. Bell metal	Cu 80%, Sn 20%	Bells, Gongs, utensils.
7. Aluminium bronze	Cu 90%, Al 9.5%, Sn 0.5%	Coins, bolts, gears, statues, picture frames, cheap ornaments, paints.
8. Manganin	Cu 86%, Mn 12%, Ni 2%	Electrical apparatus.

(C) Uses of Zinc :

(1) Zinc is used for galvanising iron.
(2) Zinc-dust is used as reducing agent in the manufacture of dye-stuffs, paints etc.
(3) Zinc plates and rods are used in batteries and dry cells.
(4) Zinc forms alloys with copper which are listed above.

Alloys and Amalgams :

An alloy is a homogeneous solid obtained by melting together (i) two or more metals or (ii) metals and non-metals (usually carbon, phosphorus, silicon etc.)

Metal + Metal = Alloy

Amalgam : When one of the constituent metal of an alloy is mercury, it is known as *amalgam.*

Metal + Mercury = Amalgam.

Examples of some Alloys :

Name of the alloy	Percentage composition of metals in the alloy	Method of preparation
Brass	Cu - 90%	By fusion
	+Zn - 10%	or by electro deposition
Bronze	Cu - 90%	By fusion
	+Sn - 10%	or by electro deposition
Solder	Pb - 67%	By compression
	+Sn - 33%	
Pewter	Sn - 85%	
	+Cu - 7%	By compression
	+Bi - 6%	
	+Sb - 2%	
Ferro Chrome	Fe - 33%	By chemical process
	+Cr - 67%	
Aluminium Bronze	Cu - 90%	By chemical process
	+Al - 10%	
22Carats gold	Au - 92%	By fusion
	+Cu - 8%	
Steel alloy	Fe – 98-99.9%	By fusion & by
	+C – 0.1 to 2%	other special methods.
Type metal	Pb - 82%	By special method
	+Sb - 15%	
	+Sn - 3%	

Wood's Metal	Bi - 50%	By special method
	+Pb - 25%	
	+Sn - 12.5%	
	+Cd - 12.5%	
Stainless steel	Fe - 70%	
	+Cr - 19%	
	+Ni - 9%	
	+Cu - 1%	
	+Mo - 0.8%	
	+C - 0.2%	

Examples of some Amalgams :

Name of the amalgam	Presence of other metal with mercury	Use
Sodium amalgam	Na + Hg	Used as a good reducing agent
Copper amalgam	Cu + Hg	Used for filling dental cavities
Tin amalgam	Sn + Hg	Used for the preparation of cheap mirrors.

CHAPTER (6) AT A GLANCE

1. **Alloy :** It is a homogeneous mixture of two or more metals.

2. **Amalgam :** An alloy containing mercury as one of the constituents is called amalgam.

3. **Ferro-alloy:** An alloy containing iron as one of the constituents is called Fero-alloys

4. **Non-Ferrous alloy:** An alloy without iron content is called non-ferrous alloy.

5. **Aluminothermy:** It is a process, which involves the reduction of some metal oxides with aluminium.

6. **Calcination:** It a process of heating the concentrated ore in absence of air but at a temperature insufficient to melt it with a view to driving off the volatile matters.

7. **Concentration:** It is a process of removing impurities (gangue) from the ore.

8. **Flux:** It is the substance added to the ores before heating, with the object that it will react chemically with the impurity (gangue) present in the ore and form a fusible slag.

9. **Gangue (Matrix):** These are rocky or earthy materials associated with the ores as impurities.

10. **Ore:** It is a naturally occurring substance from which the metal may be extracted economically.

11. **Roasting:** It is the process of heating the concentrated ore in excess of air but at a temperature insufficient to melt it (i.e. below the point of fusion) with a view to oxidising it.

12. **Slag:** It is the fusible compound formed by the union of flux and gangue (impurities).

13. **Smelting:** It is the process in which the metal is extracted by reducing the oxide ore of the metal with carbon in presence of flux which combines with the impurities to form a fusible slag.

14. **Leaching :** It is the process of extracting metals like sliver, gold etc by dissolving their, concentrated ore in suitable reagent like acids or bases and then through reprecipitation or crystallisation.

15. Ellingham diagram is a plot of $\Delta_f G^\circ$ vs T for formation of oxides of elemens. The diagram helps us in predicting feasibility of thermal reduction of an ore.

****

QUESTIONS

Very Short Answer: Type (1 mark each)

1. What is calcination ?
2. What is Roasting?
3. What is the difference between flux and slag?
4. Which ore is suitable for carbon reduction?
5. What is slag?
6. Name an important ore of copper.
7. What method in employed to concentrate a sulphide ore?
8. Name one substance, which acts as a flux.
9. For a transition metal oxide, name one effective reducing agent.
10. Name a metal which can be extracted by electrolytic reduction. (Na, Cu, Ag, Zn)
11. What is formed when a flux reacts with a gangue material?
12. Can a mineral be termed as an ore?
13. The oxides of the metals are________
14. What is slag? Give an example of it.
15. Distinguish between mineral and ore.
16. What happens to the ore during roasting?
17. Distinguish between 'Calcination' and 'Roasting'.
18. What do you understand by 'carbon-reduction, in metallurgy? Give an example.
19. What type of metals are extracted electrolytically?
20. What is the compound formed from the reaction of calcium oxide and silicon dioxide?
21. Metals are ductile. The statement means that metals can be

    (a) hammered (c) drawn into wire
    (b) made to withstand high pressure (d) Magnetised

22. Which of the following is a constituent of slag?

    (a) $BaSO_4$ (b) CaF_2
    (c) $CaSiO_3$ (d) $NaAlO_2$

23. The impurity in a mineral is called___________.
24. Name two elements that occur in the nature in the native state.
25. What is the method of concentrating iron pyrite ore?
26. Froth floatation process is generally used for the metallurgy of _______.

    (oxide ore, chloride ore, sulphide ore, carbonate ore)

27. What is the function of limestone in the extraction of iron in the Blast furnace method?
28. What is formed when a flux reacts with gangue materials?
29. What are the reducing agents inside a Blast furnace?
30. Name two metals purified by electrolytic refining process.
31. What is the name of the main constituent of slag in the blast furnace during the extraction of iron?
32. In which type of ores, froth floatation process is generally used for metallurgy ?
33. Balance the following equation

    $Al + Fe_3O_4 \rightarrow Al_2O_3 + Fe$
34. Name the process by which sulphide ore is concentrated.
35. Give an example of acidic flux.

Short Answer Type (2 marks each) :

1. What is the difference between a flux and slag?
2. What is the role of lime stone in the extraction of iron from red Haematite?
3. How does roasting differ from calcination?
4. Explain with a suitable example the term cathodic reduction.
5. Name a flux which is used for removing acidic impurities.
6. Name three types of refining process.
7. Liquation is a refining process. Explain with an example.
8. Name a metal which is commonly used as a reducing agent in metallurgical operations.

    (Hint- Al)
9. Name two characteristic features of transition elements.
10. Name various methods commonly employed for the concentration of an ore.
11. What is self-reduction in metallurgy? Give example.
12. What is meant by smelting in metallurgy ?
13. Which ore is suitable for carbon reduction? Explain with one example.
14. What do you understand by carbon reduction in metallurgy? Give an example.
15. What happens to the ore during roasting?
16. What is flux? Give an example.
17. What the function of limestone in the extraction of iron ? Give equation to explain its action.

Short Answer type (3 marks each)

1. What is the significance of Leaching in the extraction of Aluminium?
2. When a metal is formed in the liquid state, then the process of reduction is easier. Comment on this statement.
3. Which one out of Zn and Cu, can be extracted by hydrometallurgy. Explain.
   [Ans : Cu, Because $E^{\circ}_{Cu^{2+}/Cu} = +0.34V$, $E^{\circ}_{2H^{+}/H_2} = 0.00\ V$ and $E^{\circ}_{Zn^{2+}/Zn} = -0.76\ V$]
4. What is the role of (a) depressant (b) froth stabilisers in ‘froth floatation process’?
5. What is the role of silica in the metallurgy of copper?
6. What is Mond’s process? Describe in detail.
7. What is ‘Leaching’?
8. How noble metals like Au and Ag are extracted from their ore?
9. Write short notes on :
   (a) Zone Refining
   (b) Column chromatography
10. State the role of silica in the metallurgy of copper.
11. What is meant by the term chromatography.

Long Answer type (7 marks each)

1. What do you understand by the terms ‘alloys and amalgams’
2. Give a brief account of the following terms as used in the extraction of metals.
   (i) Calcination (ii) Roasting
   (iii) Smelting (iv) Refining and
   (v) Magnetic separation
3. Differentiate between:
   (i) Mineral and ore (ii) Alloy and amalgam
   (iii) Calcination and roasting.
4. What do you understand by electrochemical series? Discuss the importance of electrochemical series.
5. What is the difference between
   (a) An ore and a mineral.
   (b) An alloy and amalgam.
   (c) Slag and flux (1.1.T. 1978)
   (d) Smelting and roasting (1.1.T. 1978)
6. What do you understand by concentration of ores?

7. What is meant by carbon reduction and electrolytic reduction with examples? What is the role of flux in the metallurgical operation? Name one mineral that can be used as a flux and describe its working.

8. Fill in the blanks and rewrite the whole statement.
   - (i) A metal, which can be, obtained as powder________.
   - (ii) A non-metal which shines like a metal and good conductor of electricity is _____.
   - (iii) Two metals used in alloy formation___________.
   - (iv) Two non-metals used in alloy formation__________.
   - (v) Two metals which occur in native state_________.
   - (vi) A metal which gives acidic oxide__________.

9. Discuss the various processes which are generally employed for concentration of the ore.

10. (a) What do you understand by the following tems?

    (i) Metallurgy (ii) Ore (iii) Mineral (iv) Gangue

    (b) How do metals occur in nature?

11. Write notes on -
    - (i) Aluminothermic process
    - (ii) Electrolytic reduction

12. What are the different methods of extracting a metal from its ore? Explain each method with one example.

13. Give the meaning of the following with example

    (a) Ore (b) Minerals

    (c) Refining (d) Smelting

14. Write notes on :
    - (i) Aluminothermic process
    - (ii) Carbon reduction process

15. Write down the reactions taking place at different zones of blast furnace during the extraction of Iron.

16. Write the chemical reactions taking place in the extraction of Zinc from Zinc blende. Write three uses of It.

17. What is Ellingham diagram ?

    With reference to this diagram explain the following:
    - (a) Mg is more reducing than Zn.
    - (b) Al acts as a better reducing agent than Fe.
    - (c) Extraction of metals like Ag and Hg from their oxides take place high temperature.

FILL IN THE BLANKS WITH ANSWERS

1. Sulphide ores, generally, concentrated by _______ process.
2. The process of heating ore in the absence or limited supply of air, is called____.
3. Roasting is heating of ore in presence of __________of air
4. Minerals, from which metal can be extracted economically, are called _________.
5. The art of extracting metals from their ores is called_______.
6. The process of removal of gangue or matrix from the ore is known as __________.
7. Coke used during smelting of iron acts as fuel as well as __________agent.
8. Substance used during smelting to remove gangue in the form of slag, is called_____.
9. The flux combines with the gangue to form fusible mass, called______.
10. The process of purification of metals to get extra-pure metals is known as _____.
11. A mineral used in the extraction of metal is called___________.
12. Highly electropositive metals such as alkaline earths are extracted by _________.
13. In electrolytic refining, the crude metal is made_____________.
14. Reduction of metal oxides by aluminium metal is called__________.
15. During carbon reduction process, an additional substance added to get rid of the impurities is called ____________.
16. _____________is the product obtained when flux combines with the impurities.
17. Calcination helps to remove ________and ________.
18. Na/Hg is prepared in order to decrease the ________. It is also used as a ________.

ANSWERS

1. Froth floatation
2. Calcination
3. Excess
4. Ores.
5. Metallurgy
6. Concentration
7. Reducing
8. Flux
9. Slag
10. Refining
11. Ore
12 Electrometallurgy
13 Anode
14 Aluminothermy
15 Flux
16 Slag
17 Moisture, volatile impurities
18 Activity of sodium, reducing agent

Multiple Choice questions with answers

1. The impurities associated with the ore after mining are collectively called:
   - (a) Flux ☐
   - (b) Slag ☐
   - (c) Minerals ☐
   - (d) Gangue ☐
2. An ore after levigation is found to have acidic impurities. Which of the following can be used as flux during smelting operation?
   - (a) H_2SO_4 ☐
   - (b) $CaCO_3$ ☐
   - (c) Both $CaCO_3$ and SiO_2 ☐
   - (d) SiO_2 ☐
3. The process in which metal oxide is reduced to metal is called:
   - (a) Smelting ☐
   - (b) Aluminothermy ☐
   - (c) Hydrothermy ☐
   - (d) No specific name ☐
4. Extraction of silver from Ag_2S by the use of sodium cyanide is an example of:
   - (a) Roasting ☐
   - (b) Hydrometallurgy ☐
   - (c) Electrometallurgy ☐
   - (d) Smelting ☐
5. Which of the following metals can be extracted by smelting?
   - (a) Aluminium ☐
   - (b) Magnesium ☐
   - (c) Iron ☐
   - (d) None of these ☐
6. The most abundant element in earth’s crust is :
   - (a) Nitrogen ☐
   - (b) Oxygen ☐
   - (c) Iron ☐
   - (d) Magnesium ☐

7. Which of the following barium salts is soluble in water?
   - (a) barium sulphate ☐
   - (b) barium cabonate ☐
   - (c) barium nitrate ☐
   - (d) barium phosphate ☐

8. The most abundant metal in the earth's crust is:
   - (a) Fe ☐
   - (b) Cu ☐
   - (c) Al ☐
   - (d) Ag ☐

9. Coper is extracted from
   - (a) Cuprite
   - (b) Copper glance
   - (c) Malachite
   - (d) Copper pyrite

10. The salt which least likely to be found in minerals is
    - (a) Sulphides
    - (b) Chlorides
    - (c) Nitrates
    - (d) Sulphates

ANSWERS

1. (d) 2. (b) 3. (b) 4. (b) 5. (c) 6. (b) 7. (c) 8. (c) 9. (d) 10. (c)

❑❑❑

UNIT - VII

p - BLOCK ELEMENTS

CHAPTER - 7

GROUP 15 ELEMENTS : NITROGEN FAMILY

The elements nitrogen, phosphorus, arsenic, antimony and bismuth occupy the group 15 of the periodic table. These elements are also known as the nitrogen family of elements as the first element is nitrogen. Nitrogen is present in the atmosphere in about 78% by volume. The family shows a change from nonmetallic and electronegative behaviour (N and P) to metallic and weakly electropositive behaviour (bismuth) through metalloids like arsenic and antimony.

7.1 OCCURRENCE :

Molecular nitrogen comprises about 78% by volume of our atmosphere. The chief ores of nitrogen found in earth's crust are sodium nitrate, $NaNO_3$ (chile salt petre) and potassium nitrate, KNO_3 (Indian salt petre). It is an important constituent of proteins in plants and animals.

Phosphorous is very reactive in nature. Therefore it does not occur in free state. It is found in minerals of the "apatite family", $Ca_9(PO_4)_6 \cdot CaX_2$ [X = F, Cl or OH].

e.g : (i) Fluorapatite, $Ca_9(PO_4)_6 \cdot CaF_2$

(ii) Chlorapatite, $Ca_9(PO_4)_6 \cdot CaCl_2$

(iii) Hydroxyapatite, $Ca_9(PO_4)_6 \cdot Ca(OH)_2$

These minerals are the major components of phosphate rocks.

Phosphoproteins are present in milk and eggs. It also occurs in ADP (Adenosine Di-Phosphate) and ATP (Adenosine Tri Phosphate) which have vital importance for production of energy in cells.

Arsenic, Antimony and Bismuth mainly occur as sulphide minerals.

e.g : (i) Stibnite, Sb_2S_3

(ii) Bismuth glance, Bi_2S_3.

7.2 TRENDS IN PHYSICAL PROPERTIES :

7.2.1 Electronic configuration :

The general outermost electronic configuration is given by ns^2np^3. In all these elements the completely filled s-orbital and half-filled p-orbitals make their electronic configuration extra stable.

Table 7.1 : Properties of elements of nitrogen family

Property	**N**	**P**	**As**	**Sb**	**Bi**
Atomic number	7	15	33	51	83
Atomic mass/g.mol^{-1}	14.01	30.97	74.92	121.75	208.98
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10}$ $4s^2 4p^3$	$[Kr]4d^{10}$ $5s^2 5p^3$	$[Xe]4f^{14}$ $5d^{10} 6s^2 56p^3$
First Ionisation Enthalpy (kJmol^{-1})	1403	1060	946	833	703
Electronegativity	3.0	2.1	2.0	1.9	1.9
Atomic radius (A°)	0.75	1.06	1.19	1.38	1.46
Melting point/K	63^a	317^b	1089^c	904	544
Boiling point/K	77.2^a	554^b	888^d	1860	1837

(^{a}Molecular N_2, ^{b}White phosphorus, ^{c}Grey $\propto$ – form at 38.6 atm, ^{d}Sublimation temperature)

7.2.2 Atomic Radii :

There is a considerable increase in atomic radii (covalent radii) from Nitrogen to Phosphorus. But from Arsenic to Bismuth only a small increase in covalent radius is observed (Table 7.1). This is becuase of the presence of completely filled 'd' and/or 'f' orbitals in those heavier elements.

7.2.3 Ionisation Enthalpy :

The ionisation enthalpy of Group 15 elements is much greater than that of the corresponding elements (present in the same period) of Group 14. This is because of the presence of extra-stable half-filled p-orbitals. On moving top to bottom along the group the Ionisation Enthalpy decreases (Table 7.1).

7.2.4 Electronegativity :

Nitrogen is the most electronegative element of the group. Though electronegativity of the elements decreases down the group, but the difference is not much pronounced for heavier elements.

7.2.5 Physical State :

Dinitrogen, the first member of this group exists in the gaseous state. But all other members are solids at room temperature and also exist in different allotropic forms.

7.3 TRENDS IN CHEMICAL PROPERTIES :

7.3.1 Oxidation States :

The outer ns^2np^3 electronic configuration of the elements of this group suggests the common oxidation states from –3 to +5. Nitrogen being the smallest and most electronegative element of the group shows –3 oxidation state. Ex.: Mg_3N_2, Ca_3N_2 etc.

Other elements of this group also form compounds with –3 oxidation state. Ex.: Ca_3P_2, Mg_3Bi_2, Zn_3Sb_2 etc.

As we move down the group this tendency to show –3 oxidation state decreases due to increase in size and metallic character.

Nitrogen also exhibits +1, +2, +4 oxidation states when it reacts with oxygen. Table 7.2 summarises the oxidation states shown by nitrogen in different compounds. It's oxidation states from +1 to +4 tend to disproportionate in an acid solution.

Table 7.2 : Oxidation states of nitrogen

Oxidation state	Compound
5	N_2O_5
4	N_2O_4
3	N_2O_3
2	NO
1	N_2O
0	N_2
–1	NH_2OH
–2	N_2H_4
–3	NH_3

For ex : $3H\overset{+3}{N}O_2 \rightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$

In case of phosphorus nearly all intermediate oxidation states disproportionate into '+5' and '–3' both in alkali and acid.

Ex : $4H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} 3H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$

The '+3' oxidation state of Arsenic, Antimony and Bismuth become increasingly stable with respect to disproportionation, because of inert pair effect.

Presence of four orbitals (one 's' and three 'p') of nitrogen in its valence shell restricts the covalency upto 4. So it can not form compounds like NF_5, NCl_5 etc. But the vacant d-orbitals present in the heavier elements of this group enable them to extend their covalency beyond 4. Ex : PCl_5, $[PF_6]^-$, AsF_5, $[SbF_6]^-$ etc.

7.3.2 Reaction with Hydrogen :

All the elements of this group form hydrides, MH_3. They are all covalent and pyramidal in shape. The basic character of the hydrides decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$

$$NH_3 + HCl \rightarrow NH_4Cl$$

$$PH_3 + HI \rightarrow PH_4I$$

Stability of the hydrides decreases and reducing character increases on moving down the group, BiH_3 being the strongest.

7.3.3 Reaction with Halogens :

All the elements of this family form trihalides. Trihalides of nitrogen except NF_3 are very unstable. They are readily hydrolysed by water.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

These halides are predominantly covalent. Ionic character increases on moving down the group. $BiCl_3$ is quite ionic.

Pentahalides are formed by phosphorus and other elements and are more covalent than trihalides. This is because, higher the possitive oxidation state of the central atom more will be its polarising power and more is the covalency. Nitrogen does not form pentahalides due to non-availability of d-orbitals. Bismuth does not form pentahalides because of inert pair effect of 6s-electrons.

7.3.4 Reaction with Oxygen :

All the elements of nitrogen family form oxides of type M_2O_3 and M_2O_5. N_2O_3, P_2O_3 and As_2O_3 are acidic with acidity decreasing down the group. Sb_2O_3 is amphoteric while Bi_2O_3 is basic. Nitrogen also forms N_2O, NO, NO_2, and N_2O_4. N_2O_5 is the strongest acidic oxide and Bi_2O_3 is the weakest.

7.3.5 Reaction with Sulphur :

Except nitrogen all other elements of the group react with sulphur to form sulphides. The stability of sulphides increases down the group due to increase in electo positive character.

7.3.6 Formation of Oxyacids :

Nitrous acid, HNO_2 and nitric acid, HNO_3 are the two common oxyacids of nitrogen. Phosphorus forms a large number of oxyacids like phosphorus acid, H_3PO_3, ortho- phosphoric acid, H_3PO_4, pyrophosphoric acid, $H_4P_2O_7$ and metaphosphoric acid, HPO_3. Arsenic forms oxyacids, arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4).

Antimony forms unstable H_3SbO_3 and bismuth, stable $HBiO_3$ (metabismuthic acid).

7.4 ANOMALOUS BEHAVIOUR OF NITROGEN :

Nitrogen differs from other members of the group in its behaviour because of

(i) Its very small size and high electronegativity

(ii) Nonavailability of vacant d-orbital.

(i) Effect of small size : Because of small size nitrogen can form $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity; ex: CN, NO etc. The small size of the atom leads to effective overlapping between atomic orbitals which is not possible in case of other members of the group. For the same reason nitrogen itself exists as diatomic molecule with triple bond. However, the repulsion of the non-bonding electrons make single N–N bond weaker which decreases its catenation tendency.

(ii) Effect of non-availability of vacant d-orbitals : Absence of vacant d-orbitals in nitrogen restricts (a) its covalency beyond 4 and (b) ability to fom $p\pi$ - $d\pi$ bond or $d\pi$ - $d\pi$ bond. The other members of the group can form compounds like $R_3P = 0$ or $R_3P = CH_2$ (R is an alkyl group) where $d\pi$ - $p\pi$ bond is present, which nitrogen can't. Compounds of 'P', 'As' etc. e.g. $(C_2H_5)_3P$, $(C_6H_5)_3$ As can act as ligands because of their ability to form $d\pi$ - $d\pi$ bond with transition metals.

7.5 DINITORGEN :

7.5.1 Preparation :

(1) Laboratory Method : Dinitrogen is prepared in the laboratory by treating an aqueous solution of NH_4Cl with $NaNO_2$.

$$NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq).$$

Small amount NO and HNO_3 are also formed in this reaction. These impurities are removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

(2) From Ammonium dichromate : Thermal decomposition of ammonium dichromate also produces dinitrogen gas.

$$(NH_4)_2\ Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3.$$

(3) **Thermal decomposition of Sodium or Barium Azide :** Very pure dinitrogen is obtained by the thermal decomposition of sodium or barium azide.

$$2NaN_3 \xrightarrow{\Delta} 2Na + 3N_2.$$

$$Ba\,(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2.$$

(4) **Commercial method of preparation :** Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. In this method the atmospheric air is first liquified and then subjected to fractional distillation. The fraction collected at 77.2K gives liquid nitrogen.

7.5.2 Properties :

Physical properties :

(1) Dinitrogen is a colourless, odourless, tasteless gas and is non-poisonous in nature.

(2) It has two stable isotopes ^{14}N and ^{15}N.

(3) It has very low solubility i.e. 23.2 cm^3 per litre of water at 273K and 1 bar pressure.

(4) It has boiling point 77.2K and freezing point 63.2K.

Chemical Properties :

(1) Dinitrogen is rather inert at room temperature because of high bond enthalpy (941.4 $kJmol^{-1}$) of $N \equiv N$ bond.

(2) Action with metals : With rise in temperature reactivity of dinitrogen increases. It combines with metals on heating to give the ionic nitrides.

$$6Li + N_2 \xrightarrow{Heat} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{Heat} Mg_3N_2$$

(3) **Action with non-metals :** With non-metals dinitrogen produces covalent nitrides.

(i) With dihydrogen : It combines with hydrogen at about 773K temp and 200 atmospheric pressure in presence of a catalyst to produce NH_3 and the process is commonly known as Haber's process.

$$N_2(g) + 3H_2(g) \underset{200\text{ atm}}{\overset{773K}{\rightleftharpoons}} 2NH_3(g).$$

(ii) With dioxygen : It combines with dioxygen at very high temperature (at about 2000K) to form nitric oxide.

$$N_2(g) + O_2(g) \overset{Heat}{\rightleftharpoons} 2NO(g)$$

(4) **Action with calcium carbide :** It reacts with calcium carbide at high temperature to give calcium cyanamide.

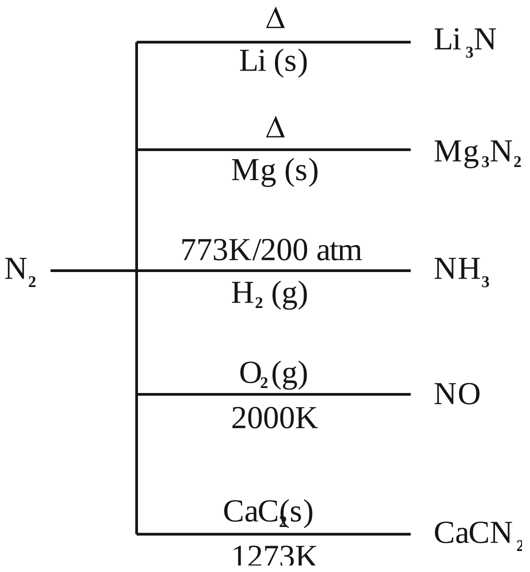
$$\underset{\text{Calcium carbide}}{CaC_2(s)} + N_2(g) \xrightarrow{1273K} \underset{\text{Calcium cyanamide}}{CaCN_2(s)} + C(s)$$

Calcium cyanamide reacts with water to form NH_3.

$$CaCN_2(s) + 3H_2O \rightarrow CaCO_3(s) + 2NH_3(g)$$

Therefore, it is used as a fertilizer under the name **nitrolim** ($CaCN_2$ + C).

Summary :



7.5.3 Uses :

(1) It is used in the manufacture of ammonia, nitric acid, calcium cyanamide etc.

(2) It produces an inert atmosphere in iron and steel industry.

(3) Dinitrogen acts as an inert diluent in reactive chemicals.

(4) Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

COMPOUNDS OF NITROGEN

7.6 PREPARATION, PROPERTIES AND USES OF AMMONIA :

7.6.1 Preparation :

(1) Haber's process : It is the cheapest method for producing ammonia in large scale. Nitrogen combines with hydrogen according to the equation, $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 93.6\ kJ$. Since the reaction is exothermic, according to Le-Chatelier's principle favourable conditions for maximum yield are high pressure, low temperature and high concentration of the reactants. Therefore, an optimum temperature of 500^0C and pressure of 200 atmosphere is used for maximum yield.

Further, to increase the rate of reaction, finely divided iron containing molybdenum as promoter is used as the catalyst.

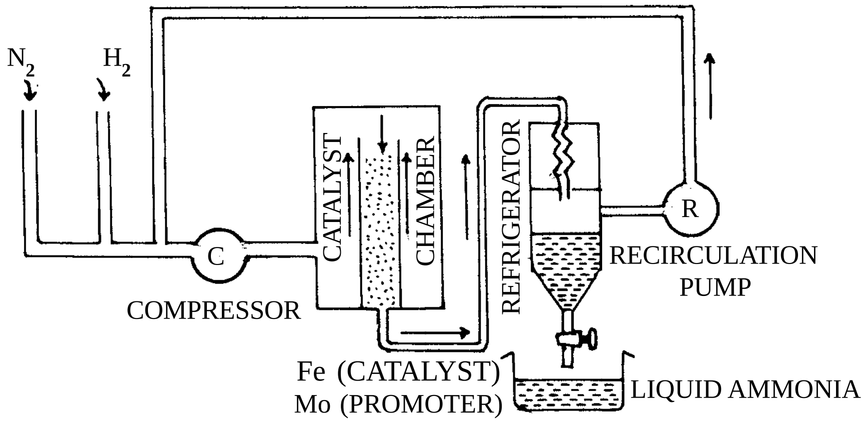


Fig. 7.1 : Haber's process of manufacture of ammonia

(2) **Laboratory Process :** The ammonia gas is prepared in the laboratory by heating ammonium chloride with slaked lime or quick lime.

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

$$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O$$

Ammoniun chloride and solid slaked or quick lime are mixed well in a mortar. The mixture is taken in a hard glass test tube half filled. The delivery tube is connected to a drying tower filled up with quick lime. On heating the test tube ammonia gas is produced.

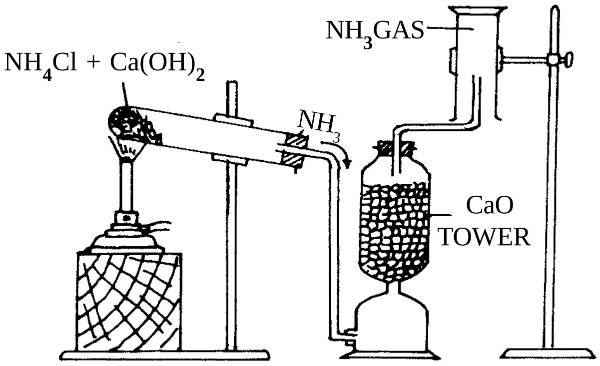


Fig. 7.2 : Laboratory process of preparing ammonia

Ammonia is lighter than air and highly soluble in water. Hence, it is collected by downward displacement of air. For pure ammonia, the gas is collected over mercury.

7.6.2 Properties :

Physical properties :

(1) Ammonia is a colourless gas with a characteristic smell.

(2) It is lighter than air.

(3) It is highly soluble in water.

(4) It has high M.Pt. and B.Pt. than expected on the basis of its molecular mass. This is because the molecules are associated with each other by intermolecular hydrogen bonding.

Chemical properties :

(1) **Basic properties :** The solution of ammonia in water is alkaline due to formation of ammonium hydroxide.

$$NH_3 + H_2O \rightarrow NH_4OH$$

It turns red litmus blue and reacts with acids to form salts.

$$NH_3 + HCl \rightarrow NH_4Cl \text{ (white fumes)}$$

(2) **Reducing properties :** Ammonia is a reducing agent. When passed over heated copper oxide, metallic copper, nitrogen and water vapour are produced.

$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

(3) **Oxidation :** Ammonia burns in atmospheric air or oxygen with a blue flame.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

In presence of platinum gauze at 500^0C, nitric oxide is formed.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

(4) **Reaction with halogens :** With insufficient amount of chlorine, ammonia produces nitrogen and hydrochloric acid. Hydrochloric acid reacts with ammonia producing ammonium chloride.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

$$6NH_3 + 6HCl \rightarrow 6NH_4Cl$$

$$8NH_3 + 3Cl_2 \rightarrow 6NH_4Cl + N_2$$

With excess of chlorine, NCl_3 is produced.

$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

Nitrogen tri-iodide is an explosive compound prepared by reacting NH_3 into excess of iodine.

(5) **Reaction with metals :** With alkalimetals metal amide and hydrogen are formed.

$$2Na + 2NH_3 \rightarrow \underset{\text{(Sodamide)}}{2NaNH_2} + H_2$$

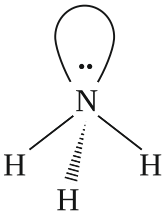
$$2K + 2NH_3 \rightarrow \underset{\text{(Potassamide)}}{2KNH_2} + H_2$$

(6) Reaction with salt solutions : With metal salt solutions, ammonia forms hydroxides.

$$FeCl_3 + 3NH_4OH \rightarrow \underset{\text{Brown}}{Fe(OH)_3} + 3NH_4Cl$$

$$ZnCl_2 + 2NH_4OH \rightarrow Zn\,(OH)_2 + 2NH_4Cl.$$

(7) Reaction with Lewis Base : Ammonia molecule has a distorted tetrahedral structure due to presence of a lone pair of electrons on the central nitrogen atom and this lone pair of electrons makes it to behave as a Lewis base. It forms dative bond with electron-deficient molecules (e.g. BF_3) and transition metal cations having vacant d-orbitals thus forming complex compounds. Many such reactions are used for the detection of metal ions such as $Cu^{2}+$, Ag^{+} etc.



$$AgCl(s) + 2NH_4OH(aq) \rightarrow [Ag(NH_3)_2]\ Cl(aq) + 2H_2O(l)$$

Diamminesilver (I) chloride

$$CuSO_4(aq) + 4NH_4OH(aq) \rightarrow [Cu(NH_3)_4]SO_4(aq) + 4H_2O(l)$$

Tetrammine copper(II)sulphate

(8) Reaction with Nessler's Reagent : Ammonia gives a brown precipitate with Nessler's reagent (an alkaline solution of K_2HgI_4) due to formation of iodide of Millon's base. This test is used for the identification of ammonium ion in qualitative analysis.

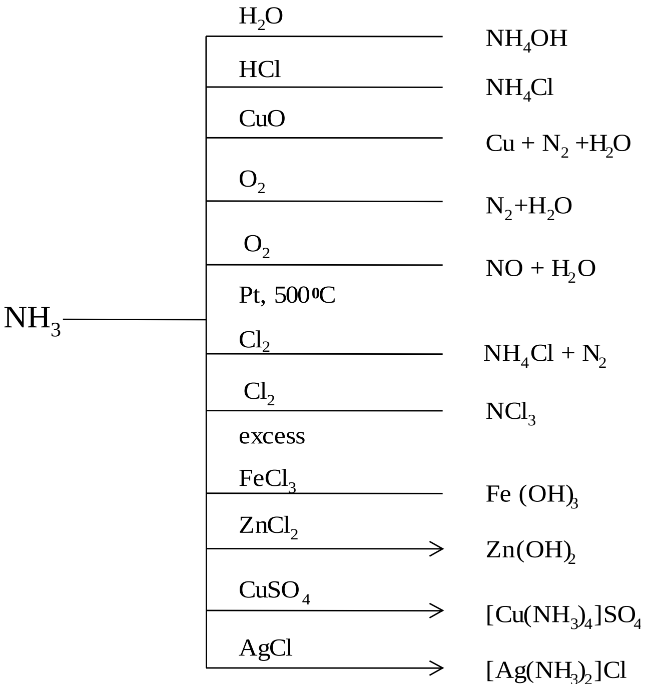
$$2K_2HgI_4 + NH_3 + 3KOH \rightarrow H_2N - Hg - O - Hg - I + 7KI + 2H_2O$$

Nessler's reagent Iodide of Millon's base (Brown ppt)

(9) Self Ionistion : Ammonia can undergo self-ionisation in liquid state due to which it acts as a good solvent for dissolving many polar compounds and hence helpful for carrying out many reactions in the non-aqueous medium.

$$2NH_3 \rightleftharpoons NH_4^{+} + NH_2^{-}$$

SUMMARY :



7.6.3 Uses :

(1) **Fertiliser :** Ammonia is used in the manufacture of fertilisers like urea, ammonium sulphate, ammonium nitrate and ammonium phosphate.

(2) **Preparation of various compounds :** It is used in the manufacture of nitric acid and sodium carbonate.

(3) **Refrigerant :** Liquid ammonia is used as a good refrigerant.

(4) **Laboratory reagent :** It is a valuable reagent in chemical laboratories.

7.7 PREPARATION, PROPERTIES AND USES OF NITRIC ACID :

7.7.1 Preparation :

Ostwald's process of manufacture of Nitric acid :

(i) **Principle :** A mixture of ammonia and oxygen or air is heated in presence of platinum catalyst to about 800°C.

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O + 21.5 \text{ kcal}$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

(ii) **Description :** A mixture of pure ammonia (1vol.) and dust free air (10 vols.) is passed through a converter containing platinum catalyst and heated to about 800°C (Fig.14.4) Ammonia and oxygen react to form nitric oxide and steam. These gases are cooled to about 50°C by passing through a tower. At this temperature conversion of nitric oxide to nitrogen peroxide is almost complete. Nitrogen peroxide is then passed through the absorbing tower where water is sprinkled from the top. It mixes with nitrogen peroxide to form nitric acid which is collected in the receiver.

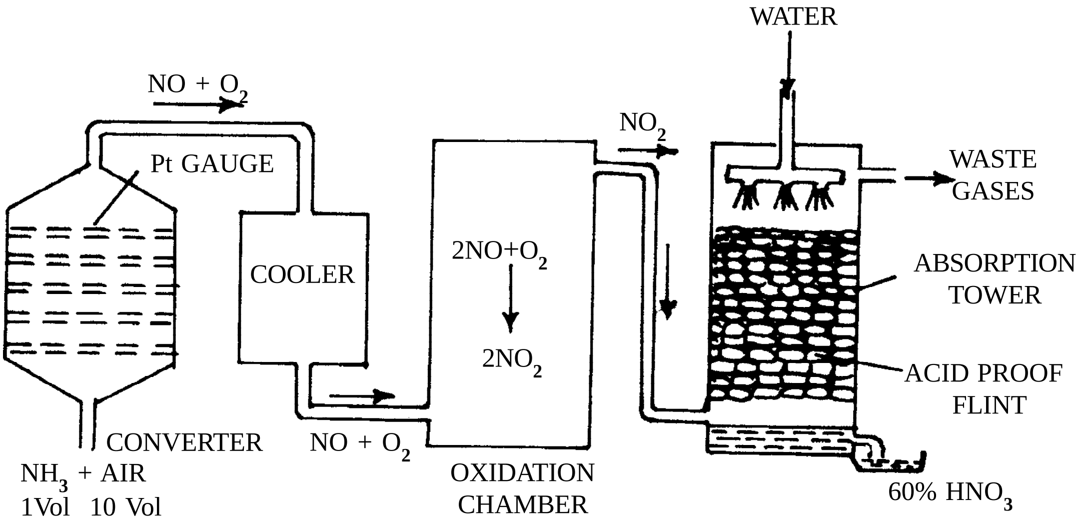


Fig. 7.3 : Ostwald's process of manufacture of HNO_3

7.7.2 Properties :

Physical : (1) Pure nitric acid is a colourless liquid. The impure acid is yellow due to dissolved NO_2 gas.

(2) The specific gravity of pure acid is 1.52.

(3) The acid is highly corrosive. It produces blisters on the skin which becomes yellow.

(4) It is hygroscopic and fumes in moist air.

(5) It is soluble in water in all proportions.

Chemical: (1) **Acidic properties :** It is a strong monobasic acid. It reacts with oxides, hydroxides and carbonates forming nitrates.

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$$

$$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O + CO_2$$

(i) Oxidising properties : Nitric acid is a powerful oxidising agent because it produces nascent (atomic) oxygen in the following manner.

$$2HNO_3 \rightarrow H_2O + 2NO + 3O$$

(a) **With H_2S :** Nitric acid oxidises hydrogen sulphide to sulphur.

$$2HNO_3 \rightarrow H_2O + 2NO + 3O$$

$$(H_2S + O \rightarrow H_2O + S) \times 3$$

$$2HNO_3 + 3H_2S \rightarrow 2NO + 4H_2O + 3S$$

(b) **With PbS :** Lead sulphide is oxidised to lead sulphate.

$$(2HNO_3 \rightarrow H_2O + 2NO + 3O) \times 4$$

$$(PbS + 4O \rightarrow PbSO_4) \times 3$$

$$8HNO_3 + 3PbS \rightarrow 3PbSO_4 + 4H_2O + 8NO$$

(c) **With KI :** Potassium iodide on treatment with nitric acid liberates iodine.

$$2HNO_3 \rightarrow H_2O + 2NO + 3O$$

$$(2KI + O \rightarrow K_2O + I_2) \times 3$$

$$(K_2O + 2HNO_3 \rightarrow 2KNO_3 + H_2O) \times 3$$

$$8HNO_3 + 6KI \rightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$$

3. **Action of nonmetals :** Nitric acid decomposes in presence of nonmetal to give NO_2.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O$$

(a) With carbon : Carbon gives carbon dioxide.

$$\begin{array}{l} (2HNO_3 \rightarrow H_2O + 2NO_2 + O) \times 2 \\ C + 2O \rightarrow CO_2 \\ \hline 4HNO_3 + C \rightarrow CO_2 + 4NO_2 + 2H_2O \end{array}$$

(b) With sulphur : Sulphur is oxidised to sulphur trioxide which reacts with water producing sulphuric acid.

$$\begin{array}{l} (2HNO_3 \rightarrow H_2O + 2NO_2 + O) \times 3 \\ S + 3O \rightarrow SO_3 \\ SO_3 + H_2O \rightarrow H_2SO_4 \\ \hline S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O \end{array}$$

(Nitric acid oxidises phosphorus to phosphoric acid (H_3PO_4), arsenic to H_3AsO_4 and iodine to iodic acid HIO_3)

(4) Action on metals : Except gold and platinum all metals react with nitric acid.

(a) **With Iron :**

Cold and dilute nitric acid produces ferrous nitrate and ammonium nitrate.

$$\begin{array}{l} (Fe + 2HNO_3 \rightarrow Fe(NO_3)_2 + 2H\ ) \times 4 \\ HNO_3 + 8H \rightarrow 3H_2O + NH_3 \\ NH_3 + HNO_3 \rightarrow NH_4NO_3 \\ \hline 4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O \end{array}$$

Concentrated nitric acid produces ferric nitrate and nitrogen dioxide.

$$\begin{array}{l} Fe + 3HNO_3 \rightarrow Fe(NO_3)_3 + 3H \\ (HNO_3 + H \rightarrow NO_2 + H_2O) \times 3 \\ \hline Fe + 6HNO_3 \rightarrow Fe(NO_3)_3 + 3NO_2 + 3H_2O \end{array}$$

Iron becomes passive when heated with very concentrated or fuming nitric acid.

(b) **With Copper :** Dilute nitric acid produces cupric nitrate and nitric oxide.

$$\begin{array}{l} 2HNO_3 \rightarrow H_2O + 2NO + 3O \\ (Cu + O \rightarrow CuO) \times 3 \\ CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O) \times 3 \\ \hline 3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \end{array}$$

Concentrated nitric acid produces nitrogen dioxide.

$$2HNO_3 \rightarrow H_2O + 2NO_2 + O$$
$$Cu + O \rightarrow CuO$$
$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

(5) Brown Ring Test for Nitrates (NO_3^-)

This is the confirmatory test for nitrates. About 1mL of the salt solution is taken in a clean test tube. It is treated with equal volume of Conc. H_2SO_4. The resulting solution is cooled under the tap. Freshly prepared $FeSO_4$ solution is added to it without disturbing the solution. A **brown ring** is formed at the junction of two liquids which disappears upon shaking but reappears upon further addition of $FeSO_4$. NO_3^- is confirmed. The formation of Brown ring is due to penta-aquanitroso iron (I) sulphate .

Reactions

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
$$FeSO_4 + NO + 5H_2O \rightarrow \left[Fe(H_2O)_5NO\right]SO_4$$

penta-aquanitroso iron (I) sulphate
(Brown).

SUMMARY :

HNO_3	CuO	$Cu(NO_3)_2$
	Na_2CO_3	$NaNO_3 + CO_2 + H_2O$
	H_2S	$NO + S + H_2O$
	PbS	$PbSO_4$
	KI	$KNO_3 + NO + I_2 + H_2O$
	C	$CO_2 + NO_2 + H_2O$
	S	$H_2SO_4 + NO_2 + H_2O$
	Fe dil. HNO_3	$Fe(NO_3)_2 + NH_4NO_3$
	Fe with Conc. HNO_3	$Fe(NO_3)_2 + NO_2 + H_2O$
	Cu dil.HNO_3	$Cu(NO_3)_2 + NO + H_2O$
	Cu Conc. HNO_3	$Cu(NO_3)_2 + NO_2 + H_2O$

7.7.3 Uses :

(1) Nitric acid is used in the preparation of aqua regia which is a mixture of conc. HCl and conc. HNO_3 (3:1). Aquaregia can dissolve metals like gold and silver.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl$$

$$Au + 3Cl \longrightarrow AuCl_3$$

(2) It is used in the manufacture of fertilisers, artificial silk and explosives like nitroglycerine, TNT, picric acid etc.

(3) It is used in the purification of gold and silver.

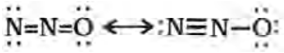
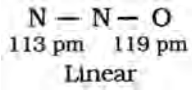
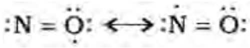
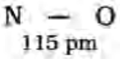
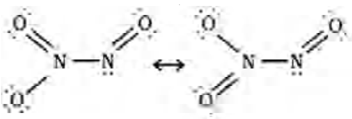
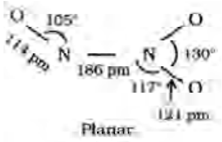
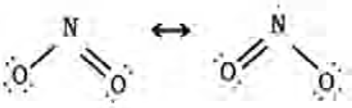
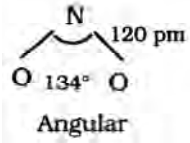
(4) It is extensively used as a laboratory reagent.

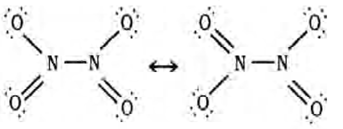
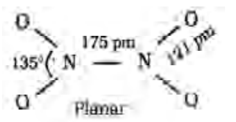
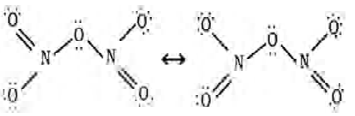
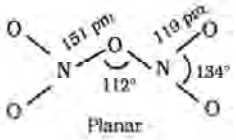
(5) It is used in the pickling of stainless steel, etching of metals and an oxidiser in rocket fuel.

7.8 OXIDES OF NITROGEN :

Nitrogen forms a number of oxides in different oxidation states. The names, formulae, oxidation states of nitrogen, Resonance structures and Bond parameters are summarised in Table 7.3.

Table 7.3 : Oxides of Nitrogen

Sl. No.	Name	Formula	Oxidation states of nitrogen	Resonance structures	Bond parameters
1.	Dinitrogen oxide [Nitrogen (I) oxide]	N_2O	+1		
2.	Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2		
3.	Dinitrogen trioxide [Nitorgen (III) oxide]	N_2O_3	+3		
4.	Nitrogen dioxide [Nitrogen (IV) oxide	NO_2	+4		

5. Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4		
6. Dinitrogen pentoxide [Nitrogen (V) oxide]	N_2O_5	+5		

7.9 PHOSPHORUS :

Allotropic forms of phosphorus :

Phosphorus is found in may allotropic forms, among which the white, black and red are important.

7.9.1 White phosphorus :

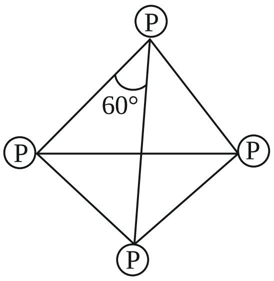


Fig. 7.4
White phosphorus

(1) It is a white waxy solid with garlic odour and translucent nature.

(2) It is poisonous.

(3) It is insoluble in water and soluble in organic solvents like carbon disulphide, alcohol, ether etc.

(4) White phosphorus is less stable and more reactive. Therefore it readily catches fire and gives a greenish glow, the phenomenon being, called as 'chemiluminescence' or 'phosphorescence'.

Reason : The P-P-P bond angle is 60°, which is much smaller than the normal tetrahedral angle. So the P_4 molecule is under strain.

$$P_4(s) + 5O_2(g) \xrightarrow{303K} P_4O_{10}(s).$$

Because of its low ignition temperature it is always kept under water.

(5) It dissolves in boiling NaOH solution in an inert atmosphere giving phosphine gas.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3(g)} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_4}$$

7.9.2 Red Phsophorus :

It is obtained by heating white phsphorus of 573K in an inert atmosphere for several days.

$$P_4(s) \xrightarrow[\text{CO}_2 \text{ or coal gas}]{573K} P_4(s)$$

Red phosphorus

(1) It is hard crystalline odourless solid with iron grey lustre.

(2) It is non-poisonous in nature.

(3) It is insoluble in water as well as in organic solvents.

(4) Red phosphorus is much less reactive than white phosphorus and does not show phosphorescence because of its polymeric structure. The chain of P_4 tetrahetrals are linked together to form the red allotrope which makes it comparatively more stable.

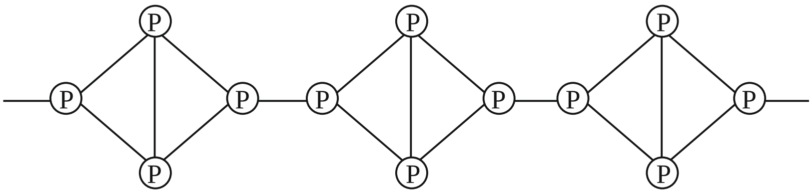


Fig. 7.5 : Red phosphorus

7.9.3 Black Phosphorus :

Black phosphorous has two forms : α - black phosphrus and β - black phosphorus.

α - Black phosphorus :

When red phsphorus is heated in a sealed tube at 803K, α - black phosphorus is obtained.

$$\text{Red phosphorus} \xrightarrow[\text{sealed tube}]{803K} \alpha \text{ - Black phosphorus.}$$

(1) Black phosphorus can be sublimed in air.

(2) It has opaque monoclinic or rhombohedral crystals.

(3) It does not oxidise in air.

(4) It does not conduct electricity.

β - Black phosphorus :

It is prepared by heating white phosphorus at 473K under a high pressure.

$$\text{White phosphorus} \xrightarrow[\text{High pressure}]{473K} \beta \text{ - Black phosphorus.}$$

(1) It is the most stable allotrope of phssphorus.

(2) It has a highly polymerised form of phosphorus and has black metallic lustre.

(3) It has sharp M.P. at 860K

(4) It as a layered graphite- like structure in which each phosphorus atom is covalently bonded to 3 neighbouring phosphorus atoms and is a good conductor of electricity.

7.10 PREPARATION, PROPERTIES AND USES OF PHOSPHINE (PH_3) :

Laboratory method of preparation of phosphine:

Yellow phosphorus reacts with sodium hydroxide on heating producing phosphine and sodium hypophosphite.

$$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

About 60 cc. of 30 - 40% NaOH solution is taken in a round bottomed flask. A few pieces of yellow or white phosphorus are added to the solution followed by 5 cc of ether. A cork fitted with a delivery tube is tightly fitted to the flask. Ether vapour removes air from the flask as phosphine explodes in air.

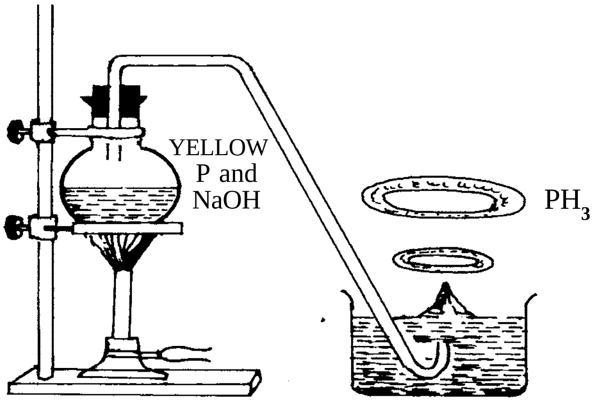


Fig. 7.6 : Preparation of Phosphine

The flask is placed on a tripod stand and heated. The gas is collected by the downward displacement of water. The gas contains diphosphine and hydrogen as impurities. Pure phosphine can be prepared by heating phosphorus acid.

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3 .$$

Properties :

Physical : (1) It is a colourless gas with a rotten fish smell.

(2) It is heavier than air.

(3) It is slightly soluble in water.

Chemical :

(1) Oxidation : Phosphine burns in air or oxygen producing a white smoke containing phosphorus pentoxide and metaphosphoric acid.

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

(2) With chlorine : Phosphine burns in chlorine producing phosphorus pentachloride.

$$PH_3 + 4Cl_2 \rightarrow PCl_5 + 3HCl$$

(3) **With halogen acids :** Phosphine reacts with HI and HBr producing phosphonium iodide and bromide respectively. With HCl, the reaction does not take place so easily.

$$PH_3 + HI \rightarrow PH_4I$$

$$PH_3 + HBr \rightarrow PH_4Br$$

(4) **Reducing property :** Just as ammonia, it is a reducing gas. It reacts with a solution of silver salt producing black phosphide and finally the metal.

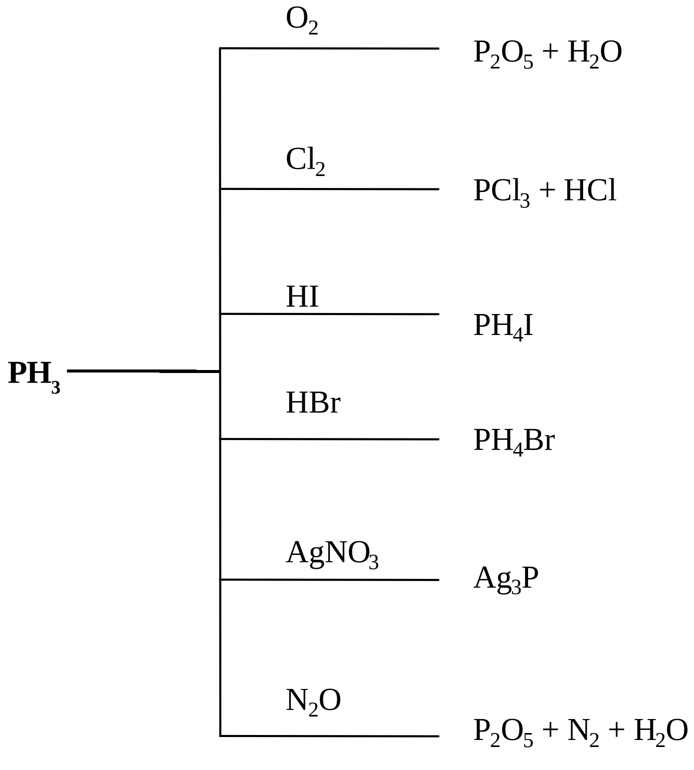
$$3AgNO_3 + PH_3 \rightarrow Ag_3P \text{ (black)} + 3HNO_3$$

$$Ag_3P + 3AgNO_3 + 3H_2O \rightarrow 6Ag + 3HNO_3 + H_3PO_3$$

(5) **With N_2O :** A mixture of phosphine and nitrous oxide in the ratio of 1:2 explodes when ignited.

$$2PH_3 + 8N_2O \rightarrow P_2O_5 + 3H_2O + 8N_2$$

SUMMARY :



USES :
(1) It is used for singnalling in the sea. It is called **Holme's signal.**
(2) It is used in naval warfare for locating enemy positions on the sea.

7.11 PHOSPHORUS HALIDES :

Phosprorus forms two types of halides, PX_3(X=F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

7.11.1 Phosphorus trichloride (PCl_3)

Preparation :

(1) By passing dry chlorine over heated white phosphorus phosphorus trichloride is obtained.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

(2) White phsophorus reacts with thionyl chloride yielding PCl_3

$$P_4(s) + 8SOCl_2 \rightarrow 4PCl_3(l) + 4SO_2(g) + \underset{\text{Sulphur monochloride}}{2S_2Cl_2}$$

Structure :

In PCl_3 the central 'P' atom is sp^3 hybridised and contains one lone pair of electrons. Thus the molecule has pyramidal structure with bond angle 100.4°.

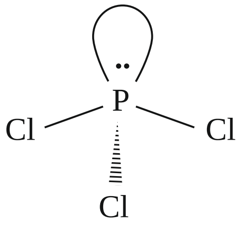


Fig. : 7.7

Properties :

Physical properties :

(1) It is a colourless liquid with pungent smell.

(2) It has boiling point 347K and freezing point 161K.

(3) It fumes in moist air.

Chemical properties :

(1) With water : It reacts violently with water to produce phosphorus acid (H_3PO_3) and hydrochloric acid.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

(2) **With acetic acid and ethyl alcohol :** It reacts with organic compounds like acetic acid, ethyl alcohol etc. and replaces the –OH group in them by –Cl atom, thus producing their chloroderivatives.

7.11.2 Phosphorus pentachloride (PCl_5) :

Preparation :

(1) PCl_5 is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4(s) + 10\ Cl_2(g) \rightarrow 4PCl_5(s).$$

(2) Thionyl chloride reacts with phosphorus producing PCl_5.

$$P_4 + 10\ SO_2Cl_2 \rightarrow 4\ PCl_5(s) + 10\ SO_2(g).$$

Structure :

In PCl_5, the central P-atom undergoes sp^3d–hybridisation and the molecule has trigonal bipyramidal structure in gaseous and liquid state. The axial bond lengths are 240 pm each being greater than equatorial bonds of length 202 pm each. This is because the two axial P–Cl bonds are repelled by 3 bond pairs while three equitorial bonds experience repulsion only by two bond pairs.

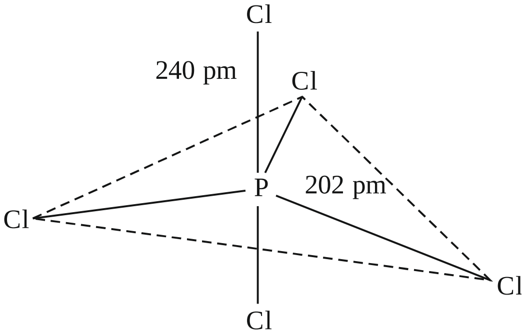


Fig.: 7.8 : Structure of PCl_5

In the solid state PCl_5 exists as ionic solid, $[PCl_4]^+ [PCl_6]^-$, in which the cation $[PCl_4]^+$ is tetrahedral and anion $[PCl_6]^-$ is octahedral.

Properties :

Physical properties :

(1) PCl_5 is a yellowish white solid.

(2) It has a characteristic pungent smell.

Chemical properties :

(1) Action of moist air : In moist air it hydrolyses to give $POCl_3$ and gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

(2) With acetic acid and ethyl alcohol : Like PCl_3 it also converts organic compounds containing –OH group to their chloro derivatives.

$$C_2H_5 + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

(3) With metals : Finely divided metals on heating with PCl_5 give corresponding chlorides.

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

$$Zn + PCl_5 \rightarrow ZnCl_2 + PCl_3$$

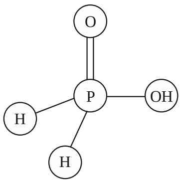
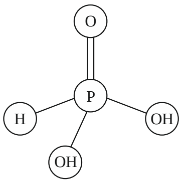
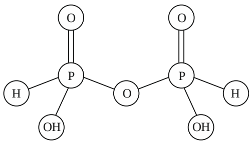
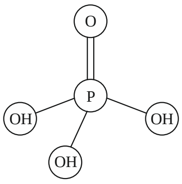
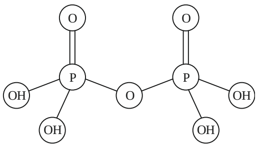
7.12 OXOACIDS OF PHOSPHORUS :

Phosphorus forms a number of oxo-acids. The important oxo-acids of phosphorus with their formula, oxidation state of phosphorus, characteristic bonds and structure are given in Table 7.4.

In oxoacids phosphorus is tetrahedrally surrounded by other atoms or groups. The P–H bonds are not ionisable to give H^+ ion. only the H atoms attached with oxygen in P–OH form are ionisable and cause the basicity. The P–H bond H–atoms help in reduction. Thus hypophosphorous acid reduces $AgNO_3$ to metallic silver.

$$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

Table 7.4 : Oxoacids of phosphorus

Sl. No.	Name	Formula	O.S. of Phosphorus	Characteristic bonds and their number	Structure
1.	Hypophosphorous acid (Phosphinic Acid)	H_3PO_2	+1	One P–OH Two P–H 1 One P=O	
2.	Orthophosphorous acid (Phosphonic Acid)	H_3PO_3	+3	Two P–OH One P–H 2 One P=O	
3.	Pyrophosphorous acid	$H_4P_2O_5$	+3	Two P–OH Two P–H 2 Two P=O	
4.	Orthophosphoric acid	H_3PO_4	+5	Three P–OH One P=O 3	
5.	Pyrophosphoric acid	$H_4P_2O_7$	+5	Four P–OH Two P=O 4 One P–O–P	

CHAPTER (7) AT A GLANCE

1. The elements belonging to Group 15 are nitrogen, phosphorus, arsenic, antimony and bismuth.
2. The general outermost electronic configuration is ns^2np^3.
3. Oxidation State : Elements show oxidation states from –3 to +5. +3 oxidation state is found to be more common in the group due to inert pair effect.
4. Nitrogen differs from other members of the group in behaviour due to its small size, high electronegativity, non availalility of vacant d-orbitals and capacity to form stable multiple bond.
5. Pure dinitrogen is obtained by the thermal decomposition of sodium azide NaN_3 or Barium azide, $Ba(N_3)_2$.
6. Dinitrogen is used in the manufacture of ammonia, nitric acid, calcium cyanamide etc.
7. Calcium cyanamide reacts with water to form ammonia. Therefore, it is used as a fertilizer under the name nitrolim ($CaCN_2$ + C)
8. Dinitrogen forms oxides in various oxidation states as N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5.
9. Ammonia, a colourless gas, lighter than air, soluble in water, used in preparation of fertilisers like urea and ammonium sulphate. Liquid NH_3 is a good refrigerant.
10. Haber's process : $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 93.6$ kJ mole

    An optimum temperature of 500^0 C and 200 atmospheric pressure is used for maximum yield. Finely divided iron containing molybdenum as promoter is used as catalyst.
11. Ammonia is prepared in the laboratory by heating $NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3 + H_2O$.
12. The brown precipitate formed by ammonia with Nessler's reagent (alkaline solution of $K_2Hg\ I_4$) is due to formation of iodide of Millon's base.
13. Nitric acid is a colourless liquid, highly corrosive, hygroscopic, soluble in water, used in the purification of gold and silver, extensively used as laboratory reagent.
14. Ostwald's Process for manufacture of HNO_3.

    $$4NH_3 + 5O_2 \xrightarrow[800^0C]{Pt} 4NO + 6H_2O + 21.5 \text{ kcal.}$$

    $$2NO + O_2 \longrightarrow 2NO_2$$

    $$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3.$$
15. In the brown ring test for the detection of NO_3^- group, Fe^{2+} acts as a reducing agent and forms $[Fe(H_2O)_5NO]^{2+}$, the brown coloured complex.

16. White phosphorus catches fire readily and burns with a greenish glow. This phenomenon is called as 'Chemiluminescence' or 'Phosphorescence'. Therefore, white phosphorus is kept under water.

17. β - Black phosphorus is good conductor of electricity.

18. Phosphine is a colourless gas with rotten fish small, heavier than air, slightly soluble in water used for signalling in the sea. (Holme's signal)

19. Phosphine (PH_3) is prepared in the laboratory by heating yellow phosphorus with NaOH.

    $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

20. Collection of gases

    NH_3 - downward displacement of air.

    PH_3 - downward displacement of water.

21. Phsophorus forms halides having common formula PX_3 or PX_5 (where X = halogen).

22. In PCl_5, the central P - atom is sp^3d - hybridised and the molecule is trigonal bipyramidal in gaseous and liquid state. In solid state it exists as an ionic solid $[PCl_4]^+ [PCl_6]^-$.

23. Phsophorus forms a number of oxo-acids. The basicity of those oxo-acids depends upon the number of P–OH groups present.

24. The oxo-acids which have P–H bonds are good reducing agents.

QUESTIONS

A. Very short answer type questions : (1 mark each)

1. Which is the anhydride of nitric acid ?
2. Balance the equation.

   $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + H_2O + NO$
3. What happens when ammonium chloride is heated with quick lime ?
4. Name two elements of group VA of periodic table.
5. How can you get nitric acid from potassium nitrate ?
6. Which catalyst is used in the manufacture of ammonia in Haber's process ?
7. Which of the following gas is evolved when NH_4NO_3 is strongly heated ?

   (a) NO (b) N_2O (c) NH_3 (d) N_2
8. What substance is used for drying ammonia gas ?
9. Write the formula of nitric anhydride.

10. Phosphine catches fire because of the presence of ——— as impurity in it ?
11. What is producer gas ?
12. Name the catalyst used in the manufacture of nitric acid by Ostwald process.
13. Write the reaction of thermal decomposition of sodium azide.
14. What is the basicity of H_3PO_4?

B. Short answer type questions (2 marks each) :

1. What happens when ammonia reacts with chlorine ?
2. What happens when ammonia gas is passed through copper sulphate solution ? Give equations.
3. How ammonia is prepared in the laboratory ?
4. What is the action of conc. HNO_3 on copper ? Give equation.
5. Why ammonia is not dried by cocentrated H_2SO_4 ?
6. Why ammonia gas is not collected by the displacement of water ?
7. What happens when ammonium chloride is heated with slaked lime ?
8. What is the best substance for drying ammonia and why ?
9. What happens when ammonia is passed over red hot copper oxide.
10. State the reaction of conc. HNO_3 with sulphur. Give equation.
11. In the ring test for nitrate, which complex compound is formed ?
12. Why ammonia gas is not dried by conc. H_2SO_4 ?
13. How ammonia gas is tested with Nessler's reagent ?
14. What happens when very dilute nitric acid reacts with zinc ?
15. Write the equation for the preparation of phosphine.
16. How does magnesium react with very dilute nitric acid ?
17. What happens when phosphine is passed through silver nitrate solution, give equation.
18. Why does NH_3 forms hydrogen bond but PH_3 does not ?
19. Give the reasonating structures of NO_2 and N_2O_5.
20. Explain why NH_3 is basic while BiH_3 is only feebly basic.
21. Nitrogen exists as a diatomic molecule and phosphorus as P_4. Why ?
22. The HNH bond angle is higher than HPH, HAsH and HSbH angles. Why?

    (Hint : The decrease in electronegativity down the group leads the bond pairs to lie close to each other as repulsion is less)
23. Why does the reactivity of nitrogen differs from that of phosphorus?

24. Why nitrogen does not form pentahalide, but phosphorus pentahalide exists?
25. Explain why Bismuth is a strong oxidising agent in the pentavalent state.
26. Explain why stability of +5 oxidation state decreases down the group 15 of the periodic table.
27. Why does nitrogen shown catenation property less than phosphorus.
28. Why is N_2 less reactive at room temperature?
29. Explain why ammonia acts as a ligand?

C. Short answer type questions (3 marks each) :

1. Why is BiH_3 the strongest reducing agent among all hydrides of Group-15 elements?
2. Give resonating structure of NO_2, N_2O_5 and N_2O.
3. Why does $R_3P = O$ exists but $R_3N = O$ does not. (R = alkyl group)
4. Give the disproportionation reaction of H_3PO_3.
5. Arrange the following in the order of increasing bond strength : NH_3, PH_3, AsH_3, SbH_3, BiH_3. Give suitable explanation for your answer.
6. Write the difference between the properties of red phosphorus and white phosphorus?

D. Long answer type questions (7 marks each) :

1. How is ammonia prepared in the laboratroy? Write with equation what happens when it reacts with (a) cupric oxide (b) insufficient quantity of chlorine (c) $CuSO_4Sol^n$ (d) Excess of chlorine.
2. Discuss briefly the principle involved in the Ostwald's process of manufacture of HNO_3. How does conc. HNO_3 reacts with iodine and copper?
3. Describe the laboratary method of preparation of phosphine. State three of its properties with equations.
4. Name important oxides and oxyacids of nitrogen and phosphorus and write their formulae.

MULTIPLE CHOICE TYPE QUESTIONS

1. Elements of Gr 15 belong to

(a) s - block (b) p - block

(c) d - block (d) f - block

2. The outer electronic configuration of 15 group elements is :

(a) $ns^2\ np^1$ (b) $ns^2\ np^2$

(c) $ns^2\ np^3$ (d) $ns^2\ np^4$

3. In the reduction of HNO_3 to N_2O, the number of moles of electrons involved per mole of HNO_3 is

(a) 8	(b) 4
(c) 2	(d) 3

4. Which of the following oxides combines with Fe(II) ions to form a brown complex ?

(a) N_2O	(b) NO
(c) N_2O_5	(d) N_2O_3

5. Which of the following is neutral.

(a) N_2O_3	(b) N_2O_4
(c) N_2O_5	(d) N_2O

6. Conc. HNO_3 oxidises phosphorus to

(a) H_3PO_4	(b) P_2O_5
(c) H_2PO_3	(d) $H_4P_2O_7$.

7. Which of the following liberates H_2 with nitric acid ?

(a) Zn	(b) Cu
(c) Mg	(d) Hg

8. Which of the following is least basic ?

(a) NF_3	(b) NCl_3
(c) NI_3	(d) NBr_3

9. Which of the following is most explosive ?

(a) NCl_3	(b) PCl_3
(c) $AsCl_3$	(d) All

10. In the manufacture of safety match sticks we use

(a) White P	(b) Black P
(c) Violet P	(d) Red P.

11. Which is oxidised in air ? (AFMC 1987)

(a) White P	(b) CH_4
(c) H_2O	(d) SO_2

12. When Conc H_2SO_4 in added to dry KNO_3, brown fumes are evolved. These fumes are

(a) SO_2	(b) SO_3
(c) N_2O	(d) NO_2

13. Which of the following has tetrahedral structure ?

(a) NH_3 (b) NH_4^+

(c) $[K_4[Fe(CN)_6]$ (d) $[Ni(CN)_4]^{2-}$

14. Phosphine is prepared by the reaction of

(a) P and H_2SO_4 (b) P and NaOH

(c) P and H_2S (d) P and HNO_3

15. Aquaregia is a mixture of

(a) 3 HCl + 1 HNO_3 (b) 3 HNO_3 + 1 HCl

(c) $H_3PO_4 + H_2SO_4$ (d) HCl + CH_3COOH.

16. With excess of Cl_2, ammonia gives

(a) NCl_3 (b) HCl

(c) NH_4Cl (d) N_2O

17. NH_3 is a lewis base. It forms complexes with cations. Which one of the following cations does not form complex with NH_3 ?

(a) Ag^+ (b) Cu^{2+}

(c) Cd^{2+} (d) Pb^{2+}

18. Which of the following forms of phosphorus is most stable ?

(a) Red P (b) White P

(c) Black P (d) all are stable

19. $FeSO_4$ forms brown ring with

(a) NO_3 (b) NO_2

(c) NO (d) N_2O_3

20. In Birkland and Eyde process, the temperature of electric arc is about ?

(a) 1500^0 C (b) 4000^0 C

(c) 3000^0 C (d) 2000^0 C

21. The anhydride of HNO_2 is

(a) NO (b) N_2O_3

(c) N_2O (d) N_2O_5

22. Which of the following does not exist

(a) NCl_5 (b) AsF_5

(c) PF_5 (d) $SbCl_5$

23. The gas obtained on heating ammonium nitrite is

(a) N_2O (b) N_2

(c) N_2O_3 (d) N_2O_4

24. The gas not having oxidising and bleaching property is

(a) Chlorine (b) Ozone

(c) SO_2 (d) N_2O

25. Sequence of acidic character is

(a) $SO_2 > CO_2 > CO > N_2O_5$ (b) $SO_2 > N_2O_5 > CO > CO_2$

(c) $N_2O_5 > SO_2 > CO > CO_2$ (d) $N_2O_5 > SO_2 > CO_2 > CO$

26. Extra pure N_2 can be obtained by heating

(a) NH_3 and CuO (b) NH_4NO_3

(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

27. An inorganic salt (A) is decomposed on heating to give two products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus while compound (B) is a colourless neutral gas. Compounds (A), (B) and (C) are

(a) NH_4NO_3, N_2O, H_2O (b) NH_4NO_2, NO, H_2O

(c) CaO, H_2O, $CaCl_2$ (d) $Ba(NO_3)_2$, H_2O, NO_2

28. With excess Cl_2, ammonia forms

(a) nitrogen (b) nitrosyl chloride

(c) ammonium chloride (d) nitrogen trichloride

29. Which statement is wrong for NO ?

(a) It is anhydride of HNO_2 (b) Its dipole moment is 0.22D

(c) It forms dimer (d) It is paramagnetic

30. The brown ring test for nitrates depends upon

(a) the reduction of nitrate to nitric oxide

(b) oxidation of nitric oxide to nitrogen dioxide

(c) reduction of ferrous sulphate to iron.

(d) oxidising action of sulphuric acid.

ANSWERS TO MULTIPLE CHOICE QUESTIONS

1. b	2. c	3. b	4. b	5. d	6. a
7. c	8. a	9. a	10. d	11. a	12. d
13. b	14. b	15. a	16. a	17. d	18. a
19. c	20. c	21. b	22. a	23. b	24. d
25. d	26. d	27. a	28. d	29. a	30. a

* * *

CHAPTER - 8

GROUP 16 ELEMENTS : OXYGEN FAMILY

Group 16 of the periodic table consists of the normal elements oxygen, sulphur, selenium, tellurium and polonium. Oxygen and sulphur are the typical non-metals, selenium and tellurium are metalloids and polonium is a radioactive metal. These are also called 'chalcogens' (pronounced as kal' - ke - jens) or ore forming elements because many metal ores occur as oxides and sulphides.

8.1 OCCURRENCE :

Dioxygen, the most vital component of our atmosphere comprises of about 21% of dry air by volume. It is also the most abundant element in the earth's crust because most of the elements are available in the form of their oxides, carbonates, sulphates, nitrates etc.

Sulphur comprises of only 0.03 – 0.1% of earth's crust in the form of ores like

(a)	Gypsum $CaSO_4 \cdot 2H_2O$	(b)	Epsom $MgSO_4 \cdot 7H_2O$
(c)	Galena PbS	(d)	Baryte $BaSO_4$
(e)	Zinc blende ZnS	(f)	Copper pyrite $CuFeS_2$
(g)	Cinnabar HgS etc.		

In volcanoes sulphur is present in the form of hydrogen sulphide gas. Organic materials like garlic, onion, mustard, wooll, eggs etc. also contain sulphur.

Selenium and Tellurium are present as metal selenides and tellurides in sulphide ores. In Thorium and Uranium minerals Polonium is present as a decay product.

8.2 TRENDS IN PHYSICAL PROPERTIES :

8.2.1 Electronic configuration :

The general outermost electronic configuration of Group 16 elements is given by $ns^2\ np^4$ (Table 8.1).

Table 8.1 : Properties of elements of oxygen family

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/gmol^{-1}	16	32	78.2	127.6	210
Electronic configuration	[He]$2s^2$ $2p^4$	[Ne]$3s^2$ $3p^4$	[Ar]$3d^{10}$ $4s^2 4p^4$	[Kr]$4d^{10}$ $5s^2 5p^4$	[Xe]$4f^{14}$ $5d^{10} 6s^2 6p^4$
Ionisation Enthalpy (kJ mol^{-1})	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Atomic radius (Ä)	0.73	1.02	1.16	1.35	1.52
Melting point / K	55	392 [a]	490 [b]	723	527
Boiling point / K	90	718	958	1263	1235

[a] monoclinic form, [a] grey form.

8.2.2 Atomic Radii :

Atomic radius or size increases from oxygen to polonium. This is due to addition of electronic shells with increase in atomic numbers.

8.2.3 Ionisation Enthalpy :

Ionisation enthalpy decreases down the group (Table 8.1) due to increase in size. The elements of this group possess lower ionisation enthalpy values as compared to the Group 15 elements of the same period because of their extra stability due to half filled p-orbitals.

8.2.4 Electronegativity :

Oxygen is the most electronegative element in the group. Next to fluorine it has the highest electronegative value among the elements. The electronegativity decreases, hence metallic character increases from oxygen to polonium.

8.2.5 Physical State :

Oxygen exists as a diatomic gas at room temperature. Sulphur, Selenium, Tellurium exist as octa atomic solids and polonium is a radioactive metal with a very short half-life.

8.3 TRENDS IN CHEMICAL PROPERTIES :

8.3.1 Oxidation States :

The four p-electrons in the last orbit are arranged in the three 'p' orbitals as $np_x^2\ np_y^1\ np_z^1$. Thus, there are two half-filled 'p' orbitals which are responsible for chemical bonding with other elements. Thus, they show the properties of normal elements with usual valency of 2 and maximum valency 6. For oxygen, the –2 oxidation state is predominant. The stability of –2 oxidation state decreases down the group. Thus polonium hardly show –2 oxidation state. As oxygen is less electronegative than fluorine in OF_2, it has +2 oxidation state. Other elements show +2, +4, +6 oxidation states, +4, +6 being more common. Stability of +6 oxidation state decreases down the group while that of +4 oxidation state increases due to inert pair effect. However, bonding in both +4 and +6 oxidation states is covalent in nature.

8.3.2 Reaction with Hydrogen :

All elements of this group form volatile hydrides of the type H_2R. The stability of the hydrides diminishes from oxygen to polonium. While water is an odourless liquid, the other hydrides are offensive smelling gases at ordinary temperature. The liquid character of H_2O is due to hydrogen bonding in molecules of water. Their acidic character increases from H_2O to H_2Te due to decrease in bond enthalpy.

8.3.3 Reaction with Oxygen :

S, Se and Te form oxides of MO_2 and MO_3 type.

Ex : SO_2, SeO_2, TeO_2, PoO_2, SO_3, SeO_3 and TeO_3

The trioxides are more acidic than dioxides.

8.3.4 Reaction with Halogens :

The elements of this group form a number of halides, a few examples being mentioned below.

Examples :

O	F_2O, Cl_2O, ClO_2, Cl_2O_7, Br_2O, I_3O_5 etc.
S	S_2F_2, S_2F_4, SF_6, S_2Cl_2, SCl_2, S_2Br_2
Se	Se_2F_2, Se_2F_4, SeF_6, Se_2Cl_2, $SeCl_4$, $SeBr_2$, $SeBr_4$
Te	TeF_4, TeF_6, $TeCl_2$, $TeCl_4$, $TeBr_2$, $TeBr_4$, TeI_4
Po	$PoCl_2$, $PoCl_4$, $PoBr_2$, $PoBr_4$, PoI_4

The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$

All the elements of the group except oxygen form dichlorides and dibromides. Here the dihalides are formed by sp^3 hybridisation and have tetrahederal structure. The monohalides are dimeric in nature.

Ex : S_2F_2, S_2Cl_2, Se_2Cl_2, Se_2Br_2 etc. They undergo disproportionation as given below.

$$2\,\overset{+1}{Se_2}\,Cl_2 \rightarrow \overset{+4}{Se}Cl_4 + 3\,\overset{0}{Se}$$

The tetrafluorides like SF_4, SeF_4, TeF_4 etc. have sp^3d hybridisation and have trigonal bipyramidal structure where one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also called as "see-saw" geometry.

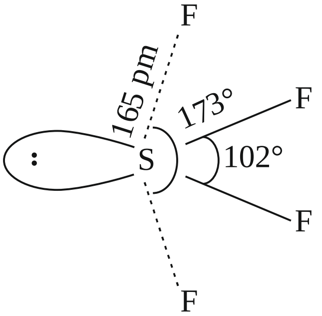


Fig. 8.1(a) : Structure of SF_4

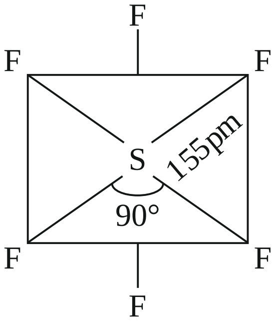


Fig. 8.1(b) : Structure of SF_6

All hexafluorides have octahedral structures. For example : S in SF_6 is sp^3d^2 hybridized and hence has octahedral structure.

8.3.5 Formation of Oxyacids :

S, Se and Te form similar oxyacids. These are formed by the reaction of dioxide or trioxide with water.

H_2SO_3 H_2SeO_3 H_2TeO_3

H_2SO_4 H_2SeO_4 H_2TeO_4

Thus we see that there is close resemblance among oxygen, sulphur, selenium, tellurium and polonium. Hence, their position in the same group of the periodic table is justified.

8.4 ANOMALOUS BEHAVIOUR OF OXYGEN :

Anomalous behaviour of oxygen is due to

(i) its small size, high electronegativity.

(ii) non-availability of vacant d-orbitals.

(i) **Effect of small size :** Because of small size and high electronegativity O-atom carries partial –ve charge in water molecule which leads to hydrogen bonding. Thus H_2O is a liquid, whereas H_2S is a gas.

(ii) **Absence of d-orbitals :** The absence of d-orbitals limits its covalency to four, whereas other elements may show covalency beyond four.

8.5 DIOXYGEN :

8.5.1 Preparation :

(1) **Laboratory Method :** Dioxygen can be prepared in the laboratory by the following methods.

(a) **From chlorates, nitrates and permanganates :** By heating oxygen containing salts like chlorates, nitrates and permanganates dioxygen gas is obtained.

$$2KClO_3\ (s) \xrightarrow[MnO_2]{Heat} 2KCl\ (s) + 3O_2(g)$$

Potassium chlorate

$$2KMnO_4(s) \xrightarrow{Heat} K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

Potassium permanganate Potassium manganate

$$2KNO_3\ (s) \xrightarrow{Heat} 2KNO_2(s) + O_2(g)$$

Potassium nitrate Potassium nitrate

(b) **The oxides of some heavy metals** like Hg, Pb, Ag etc. on heating decompose to liberate dioxygen.

$$2\ HgO\ (s) \xrightarrow{\Delta} 2\ Hg\ (l) + O_2(g)$$

$$2\ Pb_3O_4\ (s) \xrightarrow{\Delta} 6\ PbO_{(s)} + O_2(g)$$

$$2\ Ag_2O\ (s) \xrightarrow{\Delta} 4\ Ag(s) + O_2(g)$$

(c) **From Hydrogen peroxide :** Hydrogen peroxide decomposes in presence of catalysts such as finely divided Nickel and Manganese dioxide to give dioxygen.

$$2H_2O_2\ (aq) \xrightarrow{MnO_2(s)/Ni} 2H_2O\ (l) + O_2(g)$$

(d) **Electrolysis of water :** Electrolysis of acidulated water leads to release of dihydrogen gas at cathode and dioxygen gas at anode.

$$2H_2O \xrightarrow{Electrolysis} 2H_2(g) + O_2(g)$$

(2) **Commercial method of preparation :** Dioxygen is obtained from liquid air by the method of fractional distillation. Air free from CO_2 and water vapour is subjected to liquefaction, followed by fractional distillation. The fraction collected at 77K is liquid nitrogen. The liquid left over (Boiling point 90K) is dioxygen.

8.5.2 Properties :

Physical properties :

(1) Dioxygen is a colourless, odourless and tasteless gas.

(2) Its solubility is about 3.08 cm^3 in 100 cm^3 of water at 298K, which is responsible for sustainability of marine and aquatic life.

(3) It liquifies at 90K and freezes at 55K.

(4) Dioxygen has three stable isotopes ^{16}O, ^{17}O and ^{18}O.

(5) Dioxygen is paramagnetic in nature in spite of having even number of electrons (which can be explained on the basis of Molecular Orbital Theory).

Chemical properties :

The bond dissociation energy of dioxygen molecule is high (493.4 kJ mol^{-1}) due to presence of double bond between the atoms. As the reactions with dioxygen are exothermic in nature which provide sufficient energy to carry out the reaction, oxygenation process is most common.

(1) **Reaction with metals :** Dioxygen directly combines with most of the metals (except noble metals such as gold and platinum) to form their respective oxides.

$4\,Na\,(s) + O_2\,(g) \rightarrow 2\,Na_2O\,(s).$

$4\,Al\,(s) + 3O_2\,(g) \rightarrow 2\,Al_2O_3\,(s).$

Sodium also reacts with dioxygen at 575K to form sodium peroxide.

$$2\,Na\,(s) + O_2(g) \xrightarrow{575K} Na_2O_2(s).$$

Magnesium burns in dioxygen to form magnesium oxide.

$$2\,Mg\,(s) + O_2(g) \xrightarrow{Heat} 2\,MgO\,(s).$$

(2) **Reaction with Non-metals :** Dioxygen combines with non-metals (except the noble gases) and produce the corresponding oxides.

$$C\,(s) + O_2(g) \xrightarrow{\Delta} CO_2\,(g)$$

$$P_4(s) + 5O_2(g) \xrightarrow{\Delta} 2\,P_2O_5\,(g)$$

$$S(s) + O_2(g) \xrightarrow{\Delta} SO_2(g)$$

(3) **Reaction with compounds :** Some compounds are catalytically oxidised by dioxygen.

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

720K, 2atm. pressure

$$4\ HCl\ (g) + O_2(g) \xrightarrow{700K,\ CaCl_2} 2\ H_2O(g) + Cl_2(g)$$

Uses : (1) Dioxygen is an essentail component for the process of respiration and combustion.

(2) Oxygen cylinders are used in hospitals, high altitude flying and in mountaneering.

(3) Liquid dioxygen with hydrazine is used as a rocket fuel.

(4) It is used in oxy-acetylene torches which provide high temperaure for cutting and welding purposes.

8.6 CLASSIFICATION OF OXIDES :

As discussed earlier, oxygen reacts with most of the elements of the periodic table and form binary compounds known as **oxides**.

These oxides may be classified as :

(I) Simple oxides (e.g.MgO, Al_2O_3 etc.)

(II) Mixed Oxides (e.g.Pb_3O_4, Fe_3O_4 etc.)

(I) Simple Oxides : The oxides in which the element other than oxygen present in the compound exhibit a single valency are known as simple oxides. Depending on their nature they may be further classified as :

(a) Acidic oxides, (b) Basic oxides, (c) Amphoteric oxides and (d) Neutral oxides.

(a) Acidic Oxides : The oxide which dissolves in water to give an acid is termed as acidic oxide.

(e.g. SO_2, Cl_2O_7, CO_2, N_2O_5 etc.)

$$SO_2\,(g) + H_2O\ (l) \rightarrow H_2SO_3\,(aq)$$

Sulphurous acid.

$$Cl_2O_7\,(g) + H_2O\ (l) \rightarrow 2\ HClO_4\,(aq)$$

Perchloric acid

$$CO_2\,(g) + H_2O\ (l) \rightarrow H_2CO_3(aq)$$

Carbonic acid

$$N_2O_5\,(s) + H_2O\ (l) \rightarrow 2\ HNO_3(aq)$$

Nitric acid

Generally the oxides of non-metals are acidic in nature. In addition to these, the oxides of some metals in higher oxidation state also have acidic character. Ex. Mn_2O_7, CrO_3, V_2O_5 etc.

$$Mn_2O_7 + H_2O \rightarrow \underset{\text{Permanganic acid}}{2HMnO_4}$$

$$CrO_3 + H_2O \rightarrow \underset{\text{Chromic acid}}{H_2CrO_4}$$

(b) **Basic Oxides :** The oxides which combine with water to give a base are known as basic oxides (e.g. Na_2O, CaO, BaO etc.)

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

$$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(aq)$$

Usually the metallic oxides are basic in nature.

(c) **Amphoteric Oxides :** Some metal oxides exhibit the characteristics of both acidic as well as basic oxides. They are known as amphoteric oxides. (e.g. Al_2O_3, ZnO, PbO etc.)

$$\underset{\text{Basic}}{Al_2O_3(s)} + 6\ HCl\ (aq) + 9\ H_2O(l) \rightarrow \underset{\text{Hexaaquaaluminium (III) ion.}}{2\ [Al\ (H_2O)_6]^{3+}} + 6\ Cl^-$$

$$\underset{\text{Acidic}}{Al_2O_3(s)} + 6NaOH(aq) + 3H_2O(l) \rightarrow \underset{\text{Sodium hexahydroxoaluminate (III)}}{2Na_3\ [Al(OH)_6]\ (aq)}$$

(d) **Neutral Oxides :** There are some oxides which are neither acidic nor basic in nature. Such oxides are known as neutral oxides (e.g. H_2O, CO, NO and N_2O)

(II) **Mixed Oxides :** These oxides consist of two simple metal oxides where the metal is present in different oxidation state. These oxides exhibit the properties of both the oxides simultaneously. (e.g. Pb_3O_4, Fe_3O_4, Mn_3O_4 etc.)

Ex :

$$\begin{array}{c} Pb_3O_4 \\ \text{or} \\ PbO_2 \cdot 2PbO \end{array} + 4\ HNO_3 \rightarrow PbO_2 + 2\ Pb(NO_3)_2 + 2H_2O$$

$$\begin{array}{c} Fe_3O_4 \\ \text{or} \\ Fe_2O_3 \cdot FeO \end{array} + 8\ HCl \rightarrow 2\ FeCl_3 + FeCl_2 + 4\ H_2O$$

8.7 OZONE :

Molecular formula : O_3 **Molecular mass : 48**

Ozone is the active allotrope of oxygen.

8.7.1 Occurrence :

Ozone occurs in minute traces (about 1 part per ten million) in air, especially in sea air and in some what larger quantities in the upper atmosphere.

8.7.2 Preparation :

Pure ozone is very difficult to prepare. A mixture of ozone with air or oxygen is generally prepared by the action of **silent electric discharge** on oxygen

$$3O_2 \rightleftharpoons 2O_3 \qquad \Delta H = +142 \text{ kJ mol}^{-1}$$

Ozone is unstable at ordinary temperature. Hence, ozone should be removed from the reaction medium immediately to avoid decomposition. Low temperature is used in order to slow down the rate of decomposition.

Two types of apparatus, viz. the Siemen's ozoniser or Brodie's ozoniser are generally used for the preparation of ozone in the laboratory.

(i) **Siemen's ozoniser :** The apparatus in made up of two co-axial glass tubes fused with each other at one end as shown in the Fig 8.2. The inside of the inner tube and the outside of the outer tube are covered with tin foils.

A current of dry and pure oxygen is passed through the space between the two tubes and is subjected to **silent electric discharge** by connecting the tin-foils to an induction coil. About 10 percent of oxygen is converted to ozone and the mixture coming out of the apparatus is ozonised oxygen.

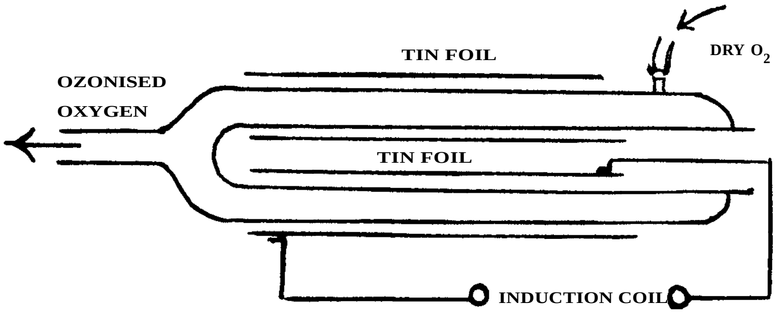


Fig. 8.2 Siemen's ozoniser

(ii) **Brodie's ozoniser :** The apparatus consists of U-shaped glass tube one limb of which is wider than the other. A narrow glass tube, closed at one end is introduced into the wide limb and the two are fused together at the open ends, so that an annular space is left between the two tubes.

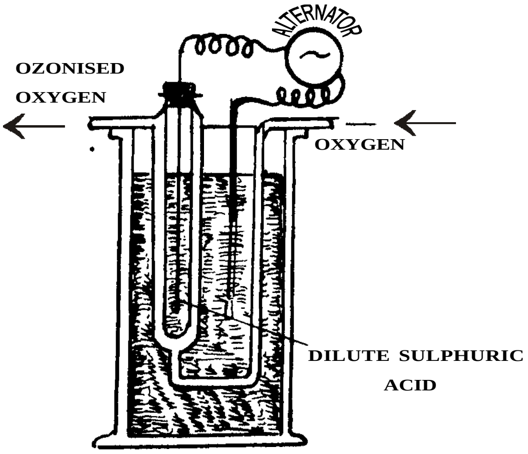


Fig. 8.3 Brodie's Ozoniser

The wide limb is also provided with a side tube. Dilute sulphuric acid is taken in the inner tube and the whole apparatus is kept immersed in a glass jar containing the same dilute sulphuric acid as in the inner tube. Two platinum electrodes are introduced, one in the inner tube and the other in the glass jar.

The two platinum electrodes are connected with terminals of an induction coil, and a **slow** stream of **pure** oxygen is passed through the side tube, thus subjecting the gas to a series of silent electric discharge. Ozonised oxygen is formed and collected at the outlet.

N.B.: By (i) Cooling the apparatus to 273K, (ii) Using powerful coil and (iii) avoiding sparks, 25% of oxygen by weight may be converted into ozone.

Pure ozone : Pure ozone may be obtained by cooling ozonised oxygen in liquid air and subjecting the condensed deep blue liquid to fractional evaporation. Liquid oxygen evaporates first (90K), leaving behind less volatile liquid ozone, which may be evaporated (161.1K) and collected subsequently.

8.7.3 Properties of ozone :

(a) Physical :

1. Ozone is a pale blue gas with a fishy odour.
2. It is heavier than air.
3. It can be condensed at 161.1K to a deep blue explosive liquid.
4. It is slightly soluble in water, but the solubility is more than oxygen. It readily dissolves in oil of turpentine, which is used as an adsorbent for the gas.
5. Unlike oxygen which is paramagnetic, ozone is diamagnetic.
6. Its concentration above 100 ppm makes breathing uncomfortable resulting headache and nausea.

(b) Chemical :

1. **Stability :** Ozone is an unstable gas. Its decomposition to oxygen is a thermodynamically favourable process as ΔH = –ve and ΔS +ve for it thus making ΔG = –ve. Hence the high concentration of ozone is dangerously explosive.

2. **Oxidising agent :** Ozone is a powerful oxidising agent because it readily undergoes decomposition to produce atomic oxygen.

$$O_3 \rightarrow O_2 + O$$

(i) **With metals :** Ozone reacts with all the metals except gold and platinum producing oxides. Mercury loses its mobility and forms mercurous oxide which sticks to glass. This is called **tailing of mercury**.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2Hg + O & \rightarrow & Hg_2O \\ \hline 2Hg + O_3 & \rightarrow & Hg_2O + O_2 \end{array}$$

Silver is oxidised to silver oxide.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2Ag + O & \rightarrow & Ag_2O \\ \hline 2Ag + O_3 & \rightarrow & Ag_2O + O_2 \end{array}$$

(ii) **With lead sulphide :** Lead sulphide (black) is oxidised to lead sulphate (white).

$$\begin{array}{lcl} [O_3 & \rightarrow & O_2 + O\ ] \times 4 \\ PbS + 4O & \rightarrow & PbSO_4 \\ \hline PbS + 4O_3 & \rightarrow & PbSO_4 + 4O_2 \end{array}$$

(iii) **With potassium iodide :** It oxidises potassium iodide to iodine.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ [KI + H_2O & \rightarrow & KOH + HI] \times 2 \\ 2HI + O & \rightarrow & H_2O + I_2 \\ \hline 2KI + H_2O + O_3 & \rightarrow & 2KOH + I_2 + O_2 \end{array}$$

When ozone reacts with an excess of KI solution buffered with a borate buffer (pH 9.2) iodine is liberated quantitatively which can be titrated against a standard solution of sodium thiosulphate ($Na_2S_2O_3$). This reaction is used for quantitative estimation of ozone.

(iv) **With halogen acids :** It oxidises halogen acids to halogens.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2HCl + O & \rightarrow & H_2O + Cl_2 \\ \hline 2HCl + O_3 & \rightarrow & Cl_2 + H_2O + O_2 \end{array}$$

(v) **With sulphur dioxide :** It oxidises sulphur dioxide to sulphur trioxide.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ SO_2 + O & \rightarrow & SO_3 \\ \hline SO_2 + O_3 & \rightarrow & SO_3 + O_2 \end{array}$$

(vi) **With stannous chloride :** It oxidises acidified stannous chloride to stannic chloride.

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ [SnCl_2 + 2HCl + O & \rightarrow & SnCl_4 + H_2O] \times 3 \\ \hline 3SnCl_2 + 6HCl + O_3 & \rightarrow & 3\,SnCl_4 + 3H_2O \end{array}$$

(vii) **With potassium ferrocyanide :** It oxidises potassium ferrocyanide to potassium ferricyanide

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2K_4[Fe(CN)_6] + H_2O + O & \rightarrow & 2K_3[Fe(CN)_6] + 2KOH \\ \hline 2K_4[Fe(CN)_6] + H_2O + O_3 & \longrightarrow & 2K_3[Fe(CN)_6] + 2KOH + O_2 \end{array}$$

(ix) **With ferrous sulphate :** It oxidises acidified ferrous sulphate to ferric sulphate

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2FeSO_4 + H_2SO_4 + O & \rightarrow & Fe_2(SO_4)_3 + H_2O \\ \hline 2FeSO_4 + H_2SO_4 + O_3 & \rightarrow & Fe_2(SO_4)_3 + H_2O + O_2 \end{array}$$

(x) **With potassium manganate :** It oxidises a solution of potassium manganate (green) to potassium permanganate (pink).

$$\begin{array}{lcl} O_3 & \rightarrow & O_2 + O \\ 2K_2MnO_4 + H_2O + O & \rightarrow & 2KMnO_4 + 2KOH \\ \hline 2K_2MnO_4 + H_2O + O_3 & \rightarrow & 2KMnO_4 + 2KOH + O_2 \end{array}$$

(xi) **With moist iodine :** It oxidises moist iodine to iodic acid.

$$\begin{array}{lcl} [\,O_3 & \rightarrow & O_2 + O\,] \times 5 \\ I_2 + 5O & \rightarrow & I_2O_5 \\ I_2O_5 + H_2O & \rightarrow & 2HIO_3 \\ \hline I_2 + 5O_3 + H_2O & \rightarrow & 2HIO_3 + 5O_2 \end{array}$$

3. **Reducing agent :** When ozone reacts with peroxides such as hydrogen peroxide and barium peroxide, both the reactions undergo reduction with the liberation of oxygen.

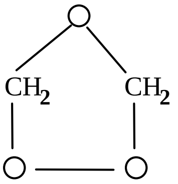
$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

$$BaO_2 + O_3 \rightarrow BaO + 2O_2$$

4. **Formation of ozonised compounds :** It reacts with unsaturated organic compounds containing double bonds, such as ethylene, to form addition products called ozonides.

$CH_2= CH_2 + O_3 \rightarrow$

Ethylene



Ethylene ozonide

5. **Bleaching agent :** Ozone acts as a bleaching agent. The atomic oxygen that it liberates on decomposition, oxidises colouring matter to colourless compounds. Thus, it can bleach vegetable matter, silk, starch, wax and oils.

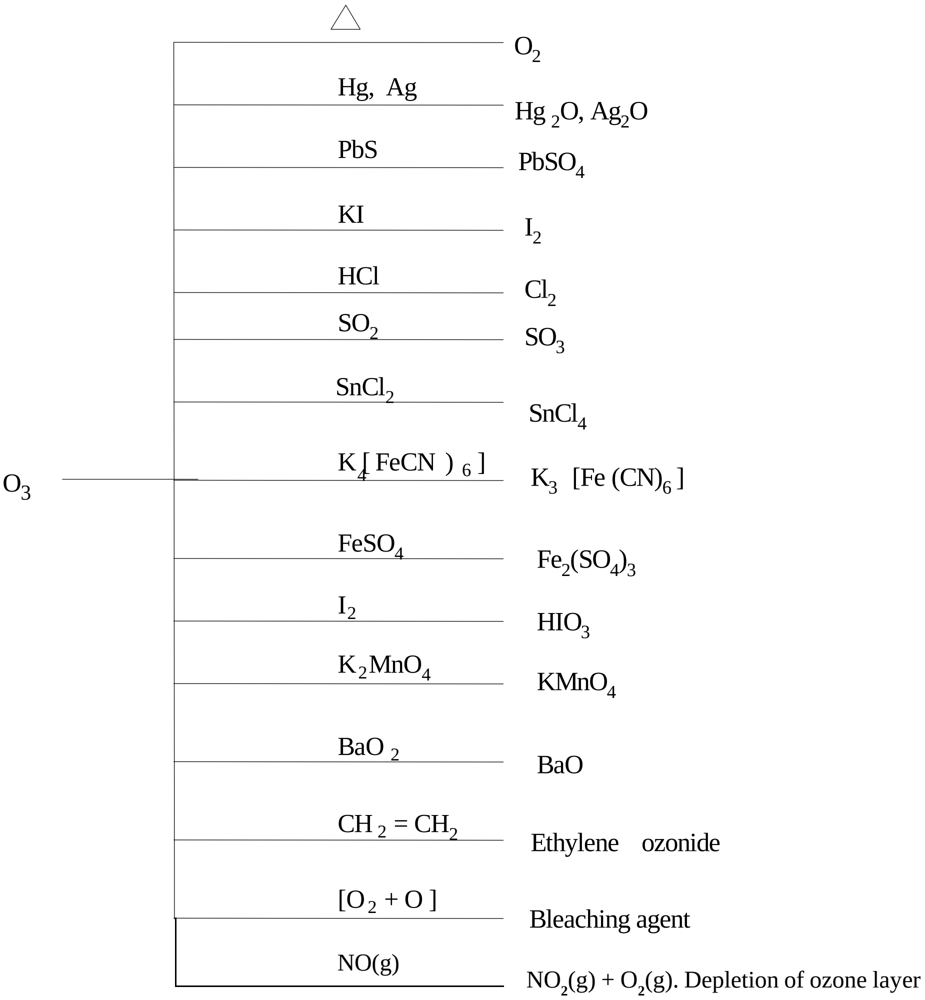
6. **Depletion of ozone layer :** The oxides of nitrogen (nitric oxide in particular) combine rapidly with ozone and destroy the molecules of ozone.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

The nigrogen oxides emitted from supersonic jet aeroplanes might be slowly depleting the protective ozone layer in the upper atmosphere because of this reaction.

Freons present in aerosol sprays and used as refrigerants also cause depletion of ozone layer.

Summary :



Tests :

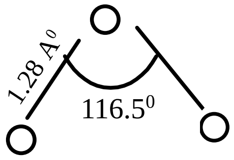
1. Ozone can be detected by its sharp characteristic odour (fishy odour).
2. It turns starch iodide paper blue.
3. It turns benzidine paper brown and tetramethyl base paper violet.
4. It produces tailing of mercury.
5. It blackens metallic silver.
6. It cannot decolourise acidified potassium permanganate solution.

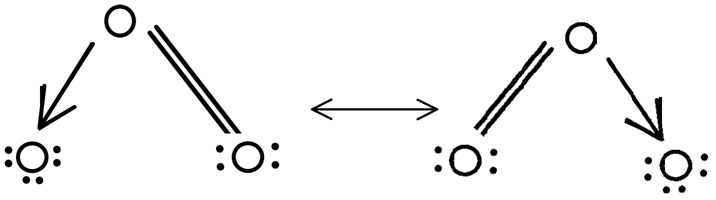
8.7.4 Uses : Ozone is used :

1. As a germicide for sterilisation of drinking water.
2. For bleaching silk, ivory, wax and oils.
3. As an oxidising agent.
4. For purifying air especially in under-ground railways, mines, crowded places such as cinema halls.
5. In the manufacture of synthetic camphor and artiticial silk.

8.7.5 Structure of ozone :

Ozone is not para-magnetic. Hence, all the electrons are paired. The three atoms are at the apices of an equilateral triangle. It has got sp^2 hybridisation. The bond angle between O-O-O is 116.5^{-0} and O-O bond length is 1.28A^{O} . The structure is a resonance hybrid of two main forms.





8.8 SULPHUR :

Allotropic forms of sulphur : Sulphur exists in a number of allotropic forms. Also a number of allotropic forms of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the past two decades. Two important allotropic forms of sulphur are :

(a) Rhombic sulphur ($\propto$ - Sulphur)

(b) Monoclinic sulphur (β - Sulphur)

(a) Rhombic sulphur ($\propto$ - Sulphur) is prepared by dissolving roll sulphur in carbon disulphide solvent and then evaporating the solution. The octahedral crystals separated out in this process are **rhombic sulphur**. It is the most stable allotrope at room temperature.

It is yellow in colour

Its M.P. is 385.8K and has specific gravity 2.06

It is insoluble in water. But dissolves to some extent in alcohol, benzene and ether.

It is readily soluble in carbondisulphide.

(b) **Monoclinic sulphur (β - Sulphur)** is parepared by melting rhombic sulphur in a china dish and then cooling it till crust is formed. Two holes are made in crust and the remaining liquid is poured out. On removing the crust, colourless needle shaped crystals of monoclinic sulphur are found.

The melting point of β - Sulphur is 393K. At 369K ∝ - Sulphur changes to β - Sulphur. Below 369K β - Sulphur changes to ∝ - Sulphur. This particular 369K temperature is called transition temperature because both Rhombic and Monoclinic sulphur co-exist at that temperature.

$$\text{Rhombic Sulphur} \underset{\text{Below 369K}}{\overset{\text{Above 369K}}{\rightleftharpoons}} \text{Monoclinic sulphur.}$$

Both these allotropes have S_8 molecules packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape (Fig. 8.4)

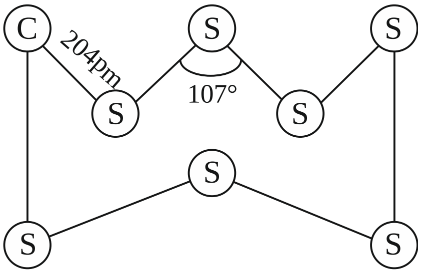


Fig. 8.4

Cyclo-S_6 is another allotropic form of sulphur where six no. of sulphur atoms are arranged in chair form.

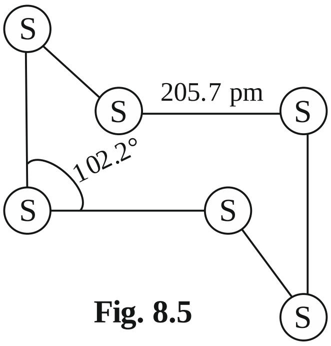


Fig. 8.5

Above 1000K sulphur exists as S_2 molecule in its vapour state and is paramagnetic in nature. This is because two unpaired electrons are present in two antibonding π* orbitals like that of O_2 molecule (MO Theory).

8.9 SULPHUR DIOXIDE :

Molecular formula : SO_2 **Mol. mass : 64**

Occurrence : Sulphur dioxide is present in volcanic gases, in the springs of volcanic districts and in the air of urban and industrial area, where it is produced when coal containing sulphur compounds is burnt.

Preparation :

1. **Synthesis :** Sulphur dioxide may be prepared synthetically by burning sulphur in oxygen or air.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

2. **Laboratory method :**

(i) **Principle :** Sulphur dioxide is prepared by heating conc. sulphuric acid with copper turnings.

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2$$

Description : Copper turnings are taken in a round bottomed flask fitted with a thistle funnel and a delivery tube bent twice at right angles (Fig.8.6).The flask is clamped to a stand and placed on a wire gauze.

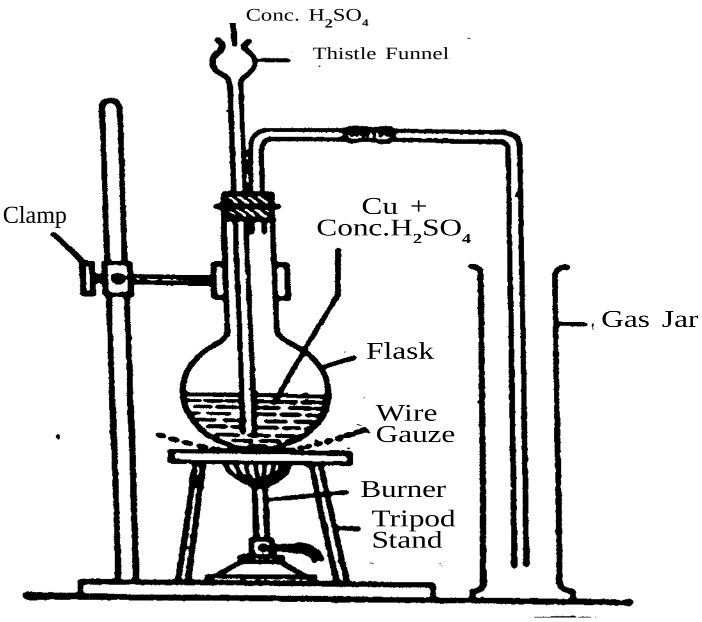


Fig. 8.6 Preparation of SO_2

Concentrated sulphuric acid is poured through the thistle funnel so that the end of the funnel dips in the acid. On heating the flask sulphur dioxide is evolved.

(iii) **Collection :** The gas is heavier than air and soluble in water, so it is collected in gas jars by the upward displacement of air.

(iv) **Purification :** The gas is dried by passing through concentrated sulphuric acid.

3. **Other methods :** SO_2 can be prepared :

(i) **From sulphites and bisulphites :** It can be prepared by the action of dil. HCl or dil. H_2SO_4 on metallic sulphite or bisulphite at ordinary temperature.

$$CaSO_3 + 2HCl \rightarrow CaCl_2 + H_2O + SO_2$$

(ii) **From sulphuric acid :** It may be prepared by heating metals like copper, mercury, silver etc. and non-metals like carbon, sulphur etc. with conc. sulphuric acid.

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + 2H_2O + SO_2$$

$$C + 2H_2SO_4 \rightarrow 2H_2O + CO_2 + 2SO_2$$

$$S + 2H_2SO_4 \rightarrow 2H_2O + 3SO_2$$

(iii) **Manufacture :** On a large scale, sulphur dioxide is prepared.

(a) By burning crude sulphur in air.

$$S + O_2 \rightarrow SO_2$$

(b) By roasting iron pyrites in air.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

Properties of SO_2 :

(a) Physical

1. It is a colourless gas with suffocating smell of burning sulphur and is poisonous.
2. It is readily soluble in water. About 80 litres of the gas dissolve in one litre of water at ordinary temperature.
3. It may be easily liquified to a colourless liquid which boils at 263K and freezes at 198K.

(b) Chemical :

1. **Stability :** Sulphur dioxide is thermally very stable. It dissociates into sulphur trioxide and sulphur by electric spark (1473K) or on strong heating.

$$3SO_2 \rightarrow 2SO_3 + S$$

2. **Combustibility :** The gas neither burns nor ordinarilly supports combustion.
3. **Acidic nature.**

(i) It is highly soluble in water and its solution is acidic due to the formation of unstable sulphurous acid.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

(ii) **Reaction with basic oxides and alkalis :**

It reacts with basic oxides and alkalis forming sulphites.

$$CaO + SO_2 \rightarrow CaSO_3$$

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + SO_2 \text{ (excess)} + H_2O \rightarrow 2NaHSO_3$$

(iii) **Reaction with lime water :** It turns lime water milky. With excess of gas, milkiness disappears. Insoluble calcium sulphite is converted to soluble calcium bisulphite.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$$
$$CaSO_3 + H_2O + SO_2 \rightarrow Ca\,(HSO_3)_2$$

4. **As reducing agent :** In presence of moisture, it acts as a strong reducing agent. This is due to liberation of **nascent hydrogen** as per the following potential equation.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$

Similarly, it absorbs oxygen in presence of an oxidising agent :

$$SO_2 + H_2O + O \rightarrow H_2SO_4$$

Since SO_2 loses electrons during a chemical reaction, hence it is a reducing agent.

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e$$

Hence, under all the conditions it acts as a powerful reducing agent.

(i) **With ferric salts**

(a) SO_2 reduces ferric chloride solution to ferrous chloride.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$
$$2FeCl_3 + 2H \rightarrow 2FeCl_2 + 2HCl$$

(b) Ferric sulphate is reduced to ferrous sulphate in solution.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$
$$Fe_2(SO_4)_3 + 2H \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$Fe_2\,(SO_4)_3 + SO_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

(ii) **With potassium permanganate :** It decolourises the pink colour of acidified potassium permanganate solution in cold.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5SO_2 + 5O + 5H_2O \rightarrow 5H_2SO_4$$

$$\underset{\text{(pink)}}{2KMnO_4} + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + \underset{\text{(colourless)}}{2MnSO_4} + 2H_2SO_4$$

(iii) **With potassium dichromate :** It reduces acidified solution of potassium dichromate (orange) giving a green solution due to the formation of chromic sulphate.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2\,(SO_4)_3 + 4H_2O + 3O$$
$$3SO_2 + 3O + 3H_2O \rightarrow 3H_2SO_4$$

$$\underset{\text{(orange)}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + H_2O$$

(iv) **With halogens :** It reduces halogens to halogen acids in presence of moisture

$X_2 + SO_2 + 2H_2O$ u $2HX + H_2SO_4$ (X = Cl, Br, I)

(v) **With potassium iodate :** It reduces potassium iodate to iodine.

$2KIO_3 + 5SO_2 + 4H_2O \rightarrow 2KHSO_4 + 3H_2SO_4 + I_2$

5. **As oxidising agent :** It acts as an oxidising agent because it is reduced to sulphur with some reducing agents. It can also be explained on the basis of ion - electron method since it gains electrons during a chemical reaction. $SO_2 + 4H^+ + 4e \rightarrow S + 2H_2O$

(i) **With magnesium :** When a piece of burning magnesium wire is introduced to a jar of sulphur dioxide it forms magnesium oxide and fine particles of sulphur are deposited on the walls of the jar.

$2Mg + SO_2 \rightarrow 2MgO + S$

(ii) **With hydrogen sulphide :** It reacts with H_2S to give sulphur

$2H_2S + SO_2 \rightarrow 3S + 2H_2O$

(iii) **With hydrogen iodide :** It reacts with HI to give iodine.

$4HI + SO_2 \rightarrow 2H_2O + S + 2I_2$

6. **As an antichlor :** It is known as antichlor since it destroys the properties of chlorine.

$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$

7. **As an unsaturated compound (addition reactions)**

Sulphur is hexavalent but only four valencies of sulphur are satisfied in SO_2 and the remaining two valencies of sulphur remains unsatisfied. This makes SO_2 an unsaturated compound.

(i) It reacts with chlorine in presence of sunlight forming sulphuryl chloride.

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$

(ii) It forms an addition product with sodium peroxide.

$Na_2O_2 + SO_2 \rightarrow Na_2SO_4$

(iii) In presence of platinum, vanadium pentoxide or manganese sulphate as catalyst, it combines with oxygen to form sulphur trioxide.

$2SO_2 + O_2 \rightarrow 2SO_3$

8. **As bleaching agent :** In the presence of moisture it possesses strong bleaching properties. It decolourises vegetable colouring matters to colourless reduction products. On standing in air, the colourless reduced product is re-oxidised by atmospheric oxygen to regain its original colour. It bleaches due to reduction and the **bleaching is temporary**.

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$

Coloured substance + H → Colourless (reduction product)
air ↓
Coloured

Summary

$SO_2 \xrightarrow{\text{Electric spark}} SO_3 + S$

$SO_2 \xrightarrow{H_2O} H_2SO_3$

$SO_2 \xrightarrow{CaO} CaSO_3$

$SO_2 \xrightarrow{NaOH} Na_2SO_3$

$SO_2 \xrightarrow{Ca(OH)_2} CaSO_3, \text{(excess) } Ca(HSO_3)_2$

$SO_2 \xrightarrow{FeCl_3} FeCl_2$

$SO_2 \xrightarrow{KMnO_4\ (H_2SO_4)} MnSO_4$

$SO_2 \xrightarrow{K_2Cr_2O_7\ (H_2SO_4)} Cr_2(SO_4)_3$

$SO_2 \xrightarrow{X_2} HX$

$SO_2 \xrightarrow{KIO_3} I_2$

$SO_2 \xrightarrow{Mg} MgO$

$SO_2 \xrightarrow{H_2S} S$

$SO_2 \xrightarrow{HI} I_2$

$SO_2 \xrightarrow{Cl_2} SO_2Cl_2$

$SO_2 \xrightarrow{Na_2O_2} Na_2SO_4$

$SO_2 \xrightarrow[\text{(Catalyst)}]{O_2} SO_3$

$SO_2 \xrightarrow{\text{Bleaching action}} \text{Bleaches by reduction}$

Tests : I. It can be detected by its characteristic suffocating smell of burning sulphur.

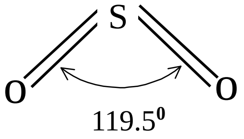
2. It turns acdified potassium dichromate solution green.
3. It decolourises acidified potassium permanganate solution.
4. It turns lime water milky.

Uses : 1. In the manufacture of sulphuric acid.

2. As bleaching agent.
3. As a disinfectant and germicide.
4. As a refrigerent.
5. As an antichlor.

Structure :

The sulphur dioxide molecule is inverted V-shaped with bond angle of 119.5^0.



8.10 SULPHURIC ACID (H_2SO_4) :

Molecular formula : H_2SO_4 **Molecular mass : 98**

Occurrence : Free sulphuric acid occurs in traces in rain water. Some mineral springs also contain this acid.

Methods for the preparation :

1. **By the action of water on sulphur trioxide.** It is formed by dissolving sulphur trioxide in water.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

2. **By the action of H_2O_2 on SO_2.** It is formed by the action of sulphur dioxide on hydrogen peroxide

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

3. **Laboratory method :**

(i) Chemicals required :

(a) Sulphur dioxide	(c) Air
(b) Nitric oxide	(d) Steam or water

(ii) Principle : Since sulphur trioxide is the anhydride of sulphuric acid, the latter can be prepared by the action of water on suphur trioxide.

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

When sulphur dioxide and oxygen (or air) are mixed with nitrogen peroxide in presence of steam or water, a series of reactions takes place at the end of which sulphuric acid is produced.

Nitrogen peroxide oxidises sulphur dioxide to sulphur trioxide and gets itself reduced to nitric oxide. Sulphur trioxide reacts with water to produce sulphuric acid.

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Nitric Oxide, thus formed, again combines with oxygen of the air producing NO_2. This NO_2 oxidises further quantity of SO_2 into SO_3, which reacts with water to produce more of H_2SO_4.

$$2NO + O_2 \rightarrow 2NO_2$$

Thus, there is no loss of nitric oxide, and the reactions go on in a cycle. A small amount of oxide of nitrogen can convert a relatively large quantity of SO_2 into H_2SO_4. Nitric oxide acts here as a 'carrier', for it carries oxygen from the air to sulphur dioxide.

(iii) Description : A large flask fitted with a rubber cork through which five glass tubes are inserted is taken. Four of these tubes reach near the bottom of the flask, while the fifth is a short one and acts as an exit tube. (Fig.8.7) Air is introduced through the first tube into the flask and then nitric oxide is passed through the second tube by connecting it with a Woulfe's bottle in which the gas is generated by the action of moderate concentrated nitric acid on copper till red fumes are formed. Sulphur dioxide is prepared in another flask by the action of conc. H_2SO_4 on copper and the gas is passed through the third tube. The red fumes, first formed (NO_2) disappears. At this stage steam is passed through the fourth tube. Steam reacts with SO_3 producing sulphuric acid which collects at the bottom of the flask as an oily liquid.

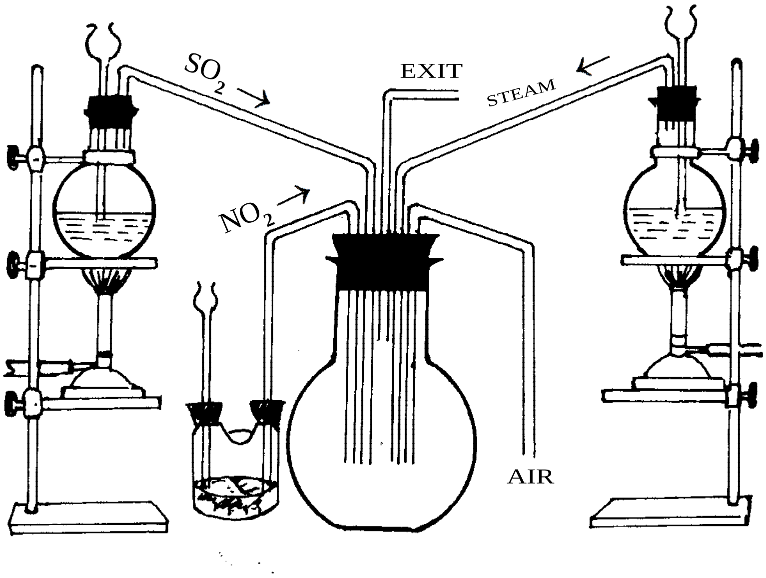


Fig. 8.7 Preparation of H_2SO_4

Manufacture of sulphuric acid The two common methods are

(a) Chamber process

(b) Contact process

The principle of manufacture of sulphuric acid by Chamber's process is same as that of the laboratory mehod.

Principle of manufacture of H_2SO_4 by Contact process

Materials required :

(a) Sulphur dioxide

(b) Air

(c) Platinised asbestos or finely divided platinum or vanadium pentoxide.

Plantinised asbestos :

It is asbestos dipped into platini chloride solution and then taken out and strongly heated, when a deposit of finely divided platinum on asbestos is obtained.

Principle :

When a mixture of pure and dry sulphur dioxide and oxygen (1:7) is passed over platinised asbestos or finely divided platinum or vanadium pentoxide (V_2O_5) the gases combine to form sulphur trioxide.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45, 200 \text{ Cal.}$$

The reaction is reversible and exothermic.

Conditions of the process :

1. The mixture of SO_2 and air must be free from (i) dust, (ii) sulphur particles, (iii) arsenious oxide, etc for they **poison** the catalyst.
2. According to Le-Chatelier's prinicple, the favourable conditions for the formation of sulphur trioxide is :
   - (i) Excess of oxygen or air
   - (ii) High pressure
   - (iii) Low temperature

The **optimum** temperature and pressure condition is $450^0 - 500^0$C and 1.5 – 1.7 atmospheric pressure.

Sulphur trioxide dissolved in H_2SO_4 to obtain **oleum or fuming sulphuric acid.** This gives on dilution with water sulphuric acid of desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4.$$

Properties of sulphuric acid :

Physical :

1. It is a colourless, odourless, syrupy liquid.
2. The concentrated acid fumes in the moist air.
3. The acid boils at 339^0C and freezes at 10.5^0C.
4. Its specific gravity is 1.85.
5. It is miscible in water in all proportions with evolution of heat.
6. It is a good conductor of electricity.
7. It is highly hygroscopic and absorbs water vapour.

Chemical :

The chemical properties of sulphuric acid may be discussed under the following headings.

(1) As an acid, (2) As a dibasic acid, (3) As an oxidising agent, (4) Action on metals, (5) As a desiccating agent, (6) As a dehydrating agent, (7) As a sulphonating agent, (8) As less volatile than nitric or hydrochloric acids and (9) Action of heat.

1. **As an acid :** It turns blue litmus red. On adding water it dissociates as follows :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

It reacts with bases like oxides, hydroxide and carbonates of metals to form salts.

$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + CO_2 + H_2O$$

2. **As dibasic acid :** It is a strong dibasic acid and it forms two series of salts i.e. normal salt (Na_2SO_4) and acid salt ($NaHSO_4$) with NaOH.

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

3. **As an oxidising agent :** It acts as an oxidising agent because it takes up electrons.

$$H_2SO_4 \longrightarrow 2H^+ + 2SO_4^{2-}$$

$$SO_4^{2-} + 4H^+ + 2e \longrightarrow SO_2 + 2H_2O$$

$$H_2SO_4 + 2H^+ + 2e \longrightarrow SO_2 + 2H_2O$$

The oxidising action can also be explained by the potential equation as it evolves atomic oxygen.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + O$$

(i) It oxidises carbon and sulphur to their oxides.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(ii) Hydrogen sulphide is oxidised to sulphur.

$$H_2S + H_2SO_4 \longrightarrow 2H_2O + SO_2 + S$$

(iii) Iodides and bromides are oxidised to iodine and bromine respectively.

$$KI + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + 2H_2O + I_2$$

$$2KBr + 2H_2SO_4 \longrightarrow K_2SO_4 + SO_2 + 2H_2O + Br_2$$

Hydrobromic and hydriodic acids are also oxidised to the corresponding halogens.

$$2HX + H_2SO_4 \longrightarrow SO_2 + 2H_2O + X_2 \ (X = Br, I)$$

4. **Action on metals :**

(i) Dilute acid reacts with Zn, Fe etc (metals which are above hydrogen in the electrochemical series) liberating hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

(ii) Metals like copper, lead etc react with conc. H_2SO_4 producing sulphur dioxide.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

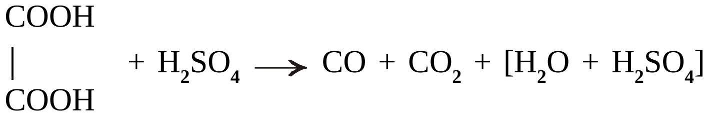
5. **As a desiccating agent :** Conc. H_2SO_4 is used as a desiccating agent for acidic gases (chlorine, carbon dioxide) because it has strong affinity for water.

6. **As dehydrating agent :** The concentrated acid acts as a dehydrating agent and it removes water from compounds. It brings about chemical change.

(i) Charring of cane sugar.

$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + [\ 11H_2O + H_2SO_4]$$

(ii) Reaction with oxalic acid :



$$\begin{array}{l} COOH \\ | \\ COOH \end{array} + H_2SO_4 \longrightarrow CO + CO_2 + [H_2O + H_2SO_4]$$

(iii) Reaction with formic acid :

$$HCOOH + H_2SO_4 \longrightarrow CO + [H_2O + H_2SO_4]$$

(iv) Reaction with ethyl alcohol :

$$C_2H_5OH + H_2SO_4 \xrightarrow{160^0C} CH_2 = CH_2 + [H_2O + H_2SO_4]$$

7. **As sulphonating agent :** Concentrated H_2SO_4 is used in the sulphonation of benzene.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Sulphuric acid}}{HOSO_3H} \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + H_2O$$

8. **As less volatile than HNO_3 and HCl :**

Conc. H_2SO_4 is less volatile than HNO_3 or HCl and hence used in the preparation of these acids from metal nitrates and chlorides.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$$

9. **Action of heat :** When heated, gives sulphur dioxide and oxygen.

$$2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + O_2$$

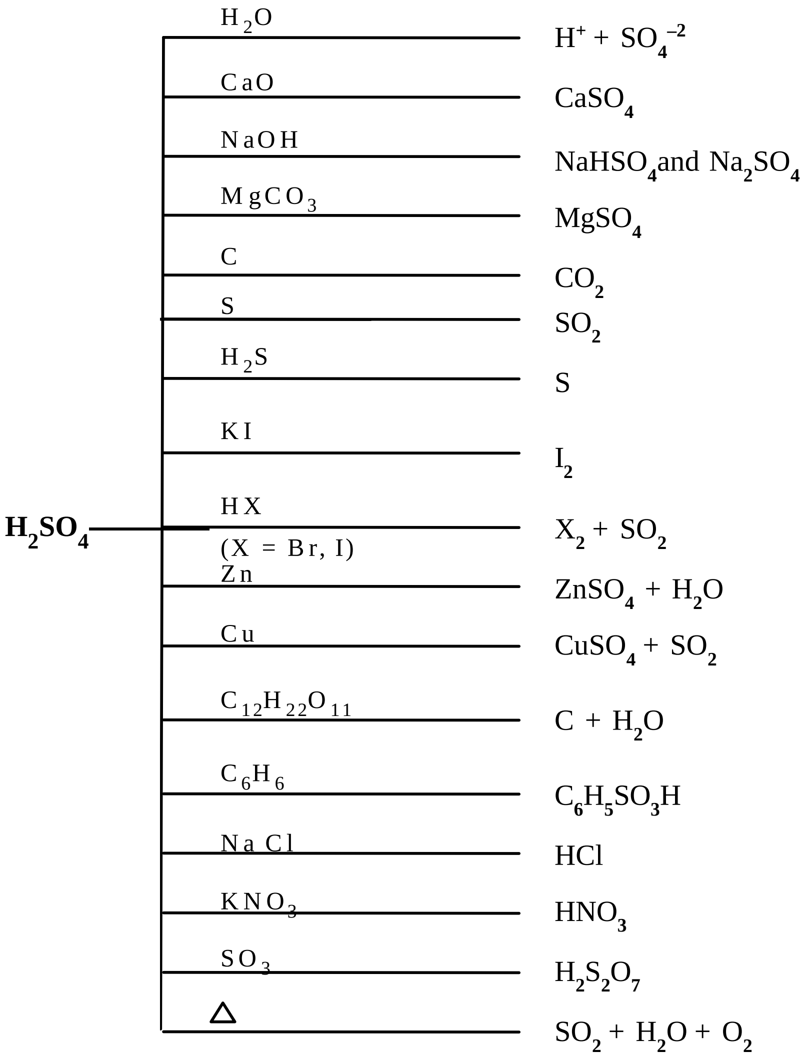
Fuming sulphuric acid : When sulphur trioxide is dissolved in conc H_2SO_4, Pyro-sulphuric acid is formed. This is known as **fuming sulphuric acid**.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

Precipitation of insoluble salts of sulphates : Calcium, strontium, barium and lead salt solutions gives insoluble sulphates with dilute sulphuric acid.

$$M\,(NO_3)_2 + H_2SO_4 \longrightarrow MSO_4 \downarrow + 2HNO_3.$$

Summary :



Tests : 1. Conc. H_2SO_4 gives SO_2 when heated with copper. The gas turns acidified dichromate paper green.

2. Sulphuric acid gives white precipitate with barium chloride solution which is insoluble in mineral acids.

3. It gives white precipitate with lead nitrate solution.

Uses : 1. For the manufacture of calcium superphosphate and ammonium sulphate which are important fertilisers.

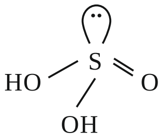
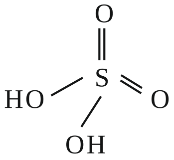
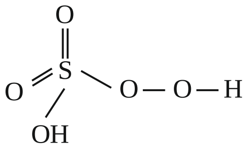
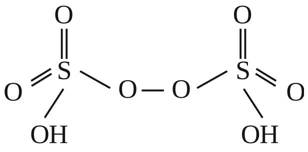
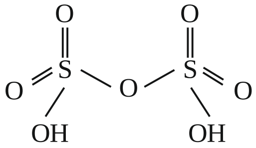
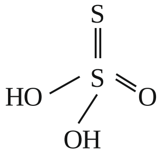
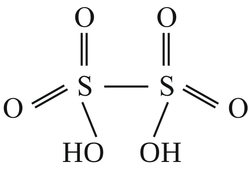
2. In the refining of petroleum.

3. In the manufacture of HNO_3, HCl, etc.
4. In the manufacture of paints, dyes, drugs, disinfectants, explosives, textiles and rayon.
5. In the lead storage batteries.
6. As a dehydrating and desiccating agent. It is also an important laboratory reagent.

8.11 OXO-ACIDS OF SULPHUR :

Sulphur forms a number of oxoacids. The molecular formula and structure of important oxoacids are given below.

Table - 8.2

Sl.No.	Name	Molecular formula	Structure
1.	Sulphurous acid	H_2SO_3	
2.	Sulphuric acid	H_2SO_4	
3.	Peroxomonosulphuric acid or Caro's acid	H_2SO_5	
4.	Peroxodisulphuric acid	$H_2S_2O_5$	
5.	Pyrosulphuric acid (Oleum)	$H_2S_2O_7$	
6.	Thiosulphuric acid	$H_2S_2O_3$	
7.	Dithionic acid	$H_2S_2O_6$	

CHAPTER (8) AT A GLANCE

1. **Elements of oxygen family :** Oxygen, sulphur, selenium, tellurium and polonium.
2. **Electronic configuration :** The general electronic configuration in the outer most orbit is ns^2np^4.
3. **Dioxygen** can be prepared in the laboratory by heating $KClO_3$ in presence of MnO_2.
4. Liquid dioxygen with hydrazine is used as a rocket fuel.
5. Dioxygen combines with elements to gives oxides, classified as simple and mixed oxides. In mixed oxides the metal is present in different oxidation states and also exhibit the properties of both the oxidation states simultaneously.
6. **Ozone (O_3)** is the active allotrope of oxygen. It is pale-blue unstable gas, powerful oxidising agent, reducing agent, bleaching agent and diamagnetic in nature. The bleaching action is due to its oxidising property.
7. **Ozone** is prepared in the laboratory in Siemen's Ozoniser or Brodie's Ozoniser. Pure ozone may be obtained by cooling ozonised oxygen in liquid air and subjecting the condensed deep blue liquid to fractional evaporation.
8. **Structure of Ozone :** The three atoms are at the apices of an equilateral triangle. It has sp^2 hybridisation. O – O – O bond angle is 116.50^0 and O – O bond length in 1.28 A^0.
9. Ozone reacts with mercury forming mercurous oxide which sticks to the glass surface and it is called 'tailing of mercury'.
10. Sulphur exists in a number of allotropic forms of which $\propto$ - and β - forms are most important. At 369 K (transition temperature) both these forms co-exist.
11. Above 1000K sulphur exists as S_2 molecule which is paramagnetic in nature.
12. **Sulphur dioxide (SO_2)** is a colourless gas having smell of burning sulphur, acidic, acts both as reducing and oxidising agent. It acts as a bleaching agent only in presence of moisture. The bleaching is due to reduction and temporary.
13. **Sulphur dioxide (SO_2)** is prepared in the laboratory by the action of conc H_2SO_4 on copper turnings.

    $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$.

    The gas is collected by upward displacement of air, purified by passing through conc H_2SO_4.
14. **Sulphur dioxide** is inverted V–shaped with bond angle of 119.5^0.

15. **Sulphuric acid** (H_2SO_4) is a colourless, odourless syrupy liquid, highly hygroscopic in nature. It acts as an oxidising agent, dehydrating agent and sulphonating agent.

16. **Sulphuric acid** **(H_2SO_4)** is prepared in the laboratory by the action of water on sulphur trioxide.

    $H_2O + SO_3 \longrightarrow H_2SO_4.$

    SO_3 is the anhydride of sulphuric acid. It is prepared by the action of nitrogen peroxide on sulphur dioxide.

    $$NO_2 + SO_2 \longrightarrow SO_3 + NO.$$

17. **Sulphuric acid** is **manufactured** by Contact process.

    $$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}200 \text{ Cals.}$$

    $$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

    $$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4.$$

    Platinised asbestos or finely divided Pt or V_2O_5 acts as catalyst. The optimum temperature and pressure condition is 450^0–500^0C and 1.5–1.7 atmospheric pressure.

18. **Fuming sulphuric acid :** SO_3 is dissolved in conc. H_2SO_4 to form fuming sulphuric acid.

    $$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_{7.}$$

QUESTIONS

A. Very short answer type questions (1 mark each) :

1. Complete the following reactions :

   $C_2H_4 + O_2 \rightarrow$ ——— + ———

   $4\ Al + 30_2 \rightarrow$ ———

2. Give one reaction in which SO_2 behaves as a reducing agent.
3. What is the basicity of sulphuretted hydrogen ?
4. What happens when a paper soaked in lead acetate solution is shown in H_2S gas ?
5. Name one catalyst which is used in the manufacture of sulphuric acid by contact process.
6. What is the action of SO_2 with H_2S ?
7. Name two elements of Group 16 of periodic table.
8. Write the electronic configuration of second element of group 16 of the periodic table.
9. Name two allotropic modifications of sulphur.
10. What is the bond angle in the molecule of sulphur dioxide ?

11. Why SO_2 gas cannot be collected over water ?
12. What is the colour change observed when SO_2 is passed through acidified $K_2Cr_2O_7$ solution ?
13. Name the catalyst used in the manufacture of Sulphuric acid by contact process.
14. Which form of sulphur shows paramagnetic behaviour ? What happens when SO_3 is passed through water ?
15. Conc. H_2SO_4 chars paper, wood and sugar because it removes ——— from them.
16. Which oxide of oxygen family is amphoteric in nature ?
17. Whether Sulphur dioxide is a lewis base or acid ?
18. What is the shape of Ozone molecule.

B. Short answer type questions (2 marks each) :

1. What happens when SO_2 is passed through lime water ? Give equations.
2. Why oxygen is a gas, whereas sulphur is a solid ?
3. Water is a liquid while hydrogen sulphide is a gas at room temperature. Give reasons.
4. What is the action of ozone on lead sulphide ? Give equation.
5. What happens when hydrogen peroxide reacts with ozone ? Give equation.
6. What happens when H_2S is passed through aqueous solution of $ZnCl_2$. Give equation.
7. What is allotropy ? Give example.
8. Write with equation what happens when dilute sulphuric acid is added to sodium carbonate.
9. Why is hydrogen sulphide not dried by concentrated sulphuric acid ?
10. Why does sulphur dioxide exhibit bleaching action only in presence of water ?
11. What is the action of ozone on acidified ferrous sulphate ? Give equation.
12. (a) What gas is produced when conc. H_2SO_4 reacts with common salt at room temperature ? Write equation.
    (b) Write the eqn. for the reaction that takes place in stages when soild NaCl is heated with conc H_2SO_4
13. Give one reaction in which SO_2 behaves as a reducing agent. Give equation.
14. Why is ozone not collected over mercury ?
15. What happens when conc. H_2SO_4 is added to formic acid ? Give equation.
16. What happens when sulphuretted hydrogen is passed through chlorine water ? Give equation.
17. What is the action of conc. H_2SO_4 on Potassium bromide ? Give equation.
18. Complete the equation given below and make it a balanced one.

$$SnCl_2 + HCl + O_3 \longrightarrow$$

19. What happens when SO_2 is passed through sulphuretted hydrogen dissolved in water ? Give equation.
20. Explain the bleaching action of Sulphur dioxide.
21. Why does ozone acts as a powerful oxidising agent?
22. How is the presence of SO_2 detected ?
23. List the important sources of sulphur.
24. H_2S is less acidic than H_2Te. Why ?
25. How is SO_2 an air pollutant ?
26. What happens when SO_2 is passed through sulphuretted hydrogen dissolved in water ? Give equation.
27. Write the Lewis structure of sulphuric acid molecule.
28. Write the structure and formula of Caro's acid.

C. Short answer type (3 marks each) :

1. Write the conditions to maximize the yield of H_2SO_4 by Contact process. What happens when sulphur dioxide is passed through an aqueous solution of Fe (III) salt ?
2. Arrange the hydrides of oxygen family in decreasing order of their bond angle? Explain.
3. SF_6 exists while OF_6 does not. Explain.
4. What happens when SO_2 gas is passed through lime water first slowly and then in excess?
5. Explain why bleaching action of SO_2 is temporary?
6. What are amphoteric oxides ? Explain their amphoteric behaviour with suitable examples.
7. What happens when ozone is passed through KI solution?

D. Long Questions (7 marks each) :

1. Write notes on preparation and any two properties and uses of SO_2.
2. How ozone is prepared ? State three chemical properties.
3. Give a comparative account of Group 16 elements (Oxygen family) of periodic table.
4. How is ozone prepared ? Show with equation how does it react with - (i) Lead sulphide, (ii) Hydrogen peroxide and (iii) Potassium iodide solution.
5. How is sulphur dioxide prepared in the laboratory ? State its two physical and three chemical properties with equations.
6. Describe any one method of preparation of ozone. Discuss its reaction with I_2, $KMnO_4$ and ethylene.

7. Give the laboratory method of preparation of SO_2. How does it react with acidified $KMnO_4$ and $K_2Cr_2O_7$ solution ? What is the cause of bleaching action of SO_2 ?

8. How are the following prepared in the laboratory ?

   (a) O_3 (b) SO_2

9. What happens when ? Write equations.

   (a) Copper reacts with conc. H_2SO_4

   (b) Na_2CO_3 solution is evaporated with excess of SO_2.

10. How Ozone is prepared ? How does it react with

    (a) Potassium iodide solution,

    (b) $SnCl_2$ solution (acidified). Why the presence of Ozone in the atmosphere is essential ?

11. How is Ozone prepared ? Show with equation how does it react with

    (a) KI solution (b) hydrogen peroxide and (c) lead sulphide.

MULTIPLE CHOICE TYPE QUESTIONS

1. Group 16 elements are

   (a) s - block elements (b) p - block elements

   (c) d- block elements (d) f - block elements

2. Which of the following has the maximum catenation property.

   (a) S (b) Se

   (c) Po (d) Te

3. Most abundant element in earth crust is

   (a) O (b) Se

   (c) Po (d) Te

4. Sulphur molecule is

   (a) S_2 (b) S_4

   (c) S_6 (d) S_8

5. Bleaching action of SO_2 is due to

   (a) Oxidation (b) Reduction

   (c) Hydrolysis (d) Its acidic nature

6. SO_2 oxidises

   (a) Mg (b) $K_2Cr_2O_7$

   (c) $KMnO_4$ (d) All

7. Which is not correct in case of H_2SO_4

(a) Reducing agent
(b) Oxidising agent
(c) Sulphonating agent
(d) Highly viscous

8. Which dissolves in H_2SO_4 to give oleum

(a) SO_2
(b) SO_3
(c) S_2O
(d) H_2S

9. Oil of Vitriol is

(a) H_2SO_4
(b) H_2SO_3
(c) $H_2S_2O_7$
(d) $H_2S_2O_8$

10. Which of the following would quickly absorb oxygen

(a) Alkaline solution of Pyrogallic acid
(b) Conc. H_2SO_4
(c) Lime water
(d) Alkaline solution of $CuSO_4$

11. Oxygen will react with each of the following elements readily, except

(a) P
(b) Na
(c) S
(d) Cl

12. O_3 reacts with KI solution to produce

(a) Cl_2
(b) I_2
(c) IO_3
(d) HI

13. A gas which cannot be collected over water is

(a) N_2
(b) O_2
(c) SO_2
(d) PH_3

14. When SO_2 is passed over which of the solution, it turns green

(a) $K_2Cr_2O_7$
(b) H_2SO_4
(c) P_2O_5
(d) SO_3

15. Anhydride of H_2SO_4 is

(a) HSO_4
(b) SO_2
(c) SO_3
(d) $H_2S_2O_3$

16. How many unpaired electrons are present in an atom of configuration $Is^2 2s^2 2p^4$

(a) 2
(b) 3
(c) 1
(d) 6

17. SO_2 is dehydrated by

(a) CaO
(b) Conc H_2SO_4
(c) P_2O_5
(d) Anly $CaCl_2$

18. In Which of the following reactions does SO_2 act as an oxidising agent.
    (a) Acidified $KMnO_4$ (b) Acidified $K_2Cr_2O_7$
    (c) Acidified C_2H_5OH (d) H_2S

19. Which will liberate H_2 gas from dilute H_2SO_4
    (a) Cu (b) Al
    (c) ZnO (d) Ag

20. The Hybridisation of sulphur in H_2SO_4 is
    (a) Sp (b) Sp^2
    (c) Sp^3 (d) Sp^3d^2

21. Ozone reacts with
    (a) C_2H_4 (b) C_2H_2
    (c) C_6H_6 (d) All

22. There is no S-S bond in
    (a) $S_2O_4^{2-}$ (b) $S_2O_5^{2-}$
    (c) $S_2O_7^{2-}$ (d) $S_2O_3^{2-}$

23. Formula of rhombic sulphur is
    (a) S_2 (b) S
    (c) S_4 (d) S_8

24. Which oxide on heating gives oxygen
    (a) HgO (b) Na_2O
    (c) BaO (d) MgO

25. Ozone is manufactured by
    (a) Siemen's Ozoniser (b) Brodie's Ozoniser
    (c) Siemen's and Malkes Ozoniser (d) All

26. The values of oxidation number of S in S_8, S_2F_2 and H_2S are respectively:
    (a) –2, +1 and –2 (b) 0, +1, –2
    (c) –2, –1 and +2 (d) 0, +1, +2

27. Ozone is tested by
    (a) Ag (b) Hg
    (c) Zn (d) Au

28. When SO_2 is passed through a solution of H_2S in water.
    (a) H_2SO_5 is produced (b) H_2SO_3 is produced
    (c) Sulphur percipitates is produced (d) None of the above

29. Which of the following is known as king of chemicals.

(a) H_2SO_4 (b) HNO_3

(c) NaOH (d) NH_4OH

30. Which of the following hydrides of oxygen family shows the lowest boiling point ?

(a) H_2O (b) H_2S

(c) H_2Se (d) H_2Te

ANSWERS TO MULTIPLE TYPE QUESTIONS

1. b	6. a	11. d	16. a	21. d
2. a	7. a	12. b	17. b	22. c
3. a	8. b	13. c	18. d	23. d
4. d	9. a	14. a	19. b	24. a
5. b	10. a	15. c	20. c	25. d
26. b	27. b	28. c	29. a	30. b

* * *

CHAPTER - 9

GROUP 17 ELEMENTS : HALOGEN FAMILY

Group 17 of the periodic table consists of the normal elements fluorine, chlorine, bromine, iodine and astatine. Among these astatine is radioactive. Fluorine, chlorine, bromine and iodine are very reactive and closely related family of elements, known as ***halogens.*** *All of these are p-block elements. There are seven electrons in the outermost shell and are arranged in group 17 of the periodic table. Since they are reactive, they do not occur free in nature. The word 'halogen' has come from two greek words (i) halos (sea salt), (ii) genes (to produce). These elements show a marked resemblance and possess a regular gradation in their properties. It justifies their inclusion in the same group of the periodic table.*

9.1 OCCURRENCE :

Fluorine is extremely reactive and hence does not occur in free state. It is widely found in the combined state as fluorides. The important minerals are : (i) Fluorspar, CaF_2. (ii) Cryolite, Na_3AlF_6 (iii) Fluorapatite, $CaF_2.3Ca_3(PO_4)_2$

It is also present in small amounts as fluoride in plant ash, soil, sea water, bones and teeth of animals.

Chlorine does not occur in the free state. It is largely found in combination with various metals. Common salt or rocksalt (NaCl) is the most important chloride which occurs in sea water, lakes and in rocks. Other minerals like Sylvine (KCl), Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), Chlorapatite [$3Ca_3(PO_4)_2.\ CaCl_2$], Horn silver (AgCl) etc. are also good sources of chlorine. In combination with hydrogen, it forms an important constituent of the gastric juice.

Bromides and Iodides of sodium, potassium, magnesium and calcium are also present in sea water. Seaweeds contain iodine upto 0.5%. Chile salt petre contains iodine in the form of sodium iodate upto 0.2%.

1. **Electronic configuration :** The general electronic configuration in the outermost orbit (n) is $ns^2\ np^5$. Each element has seven electrons in its outermost or valence shell.

Element	At. No.	Electronic configuration
F	9	$Is^2\ 2s^2\ 2p^5$
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Br	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$
I	53	$Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$
At	85	$Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^5$

2. **Molecular state :** Halogens form diatomic molecules.
3. **Mono electrovalency :** Being short of one electron of the stable octet, they readily react with alkali metals which possess an easily detachable single electron in the outermost orbit (ns^1) and are thus monovalent in electrovalent compounds.

9.2 TRENDS IN PHYSICAL PROPERTIES :

Size of the atom, atomic mass, density, melting point and boiling point, atomic radius, atomic volume and vander Waals' forces of attraction increase regularly with rise in atomic number. Fluorine and chlorine are gases at ordinary temperature. Bromine is reddish brown fuming liquid and iodine, violet solid.

9.2.1 Electronic configuration :

The Group 17 elements have seven electrons in their valence shell. Their outermost electronic configuration is given by $ns^2\ np^5$ which is one electron short of the next noble gas.

Table 9.1 Physical properties of the Halogens

Property	**Fluorine**	**Chlorine**	**Bromine**	**Iodine**
Atomic number/ g.mol^{-1}	9	17	35	53
Atomic mass	19	35.5	80	127
Electronic configuration	$[He]2s^2\ 2p^5$	$[Ne]3s^2\ 3p^5$	$[Ar]\ 3d^{10}\ 4s^2 4p^5$	$[Kr]4d^{10}\ 5s^2 5p^5$
Physical state	Gas	Gas	Liquid	solid
M.P (^{0}C)	– 218.5	– 101	– 7.2	114
B.P (^{0}C)	– 188	– 34.6	59.5	185.2
Density (in liquid state) (gm per c.c)	1.1	1.16	2.95	3.76
Colour of vapour	Pale yellow	Greenish yellow	Orange-red	Violet
Colour of liquid	Yellow	Amber Yellow	Reddish brown	Shining dark solid
Atomic radius (A^0)	0.72	0.99	1.14	1.33

Ionic radius (X^-) (A^0)	1.33	1.84	1.96	2.20
Atomic volume (c.c.)	17.1	18.7	23.5	25.7
Electronegativity	4.0	3.0	2.8	2.5
Electron affinity (kcal / mole)	81	83	77	71
Ionisation potential (kcal / mole)	401	300	273	241
Oxidation states	– 1	–1, + 1, + 3 + 4, + 5, + 6, +7	–1, +1, + 3, + 4, + 5, + 6,	–1, +1, + 3, + 4, + 5, + 6, +7

9.2.2 Atomic Radii :

The halogens have the smallest atomic radii in their respective periods because the effective nuclear charge is maximum. Atomic radius increases from fluorine to iodine, as new quantum shells are added to each element when we move gradually from top to bottom along the group.

9.2.3 Ionisation enthalpy :

Ionisation enthalpy of the halogens are very high indicating that they have very small tendency to lose electrons. The value decreases from fluorine to iodine, as expected. In case of iodine, the value is comparatively low. This enables the iodine atom to lose an electron and form I^+ ion.

9.2.4 Electronegativity :

The halogens have very high values of electronegativity. Fluorine is the most electronegative element in the periodic table. The values decrease as we move down the group from fluorine to iodine indicating a gradual decline in the non-metallic character. The last element iodine shows some metallic character also. For example, it forms in a few cases a positive ion and has a metallic lustres.

9.2.5 Stability :

The stability of their molecules X_2 decreases with increase of atomic mass. Thus, at 1200^0 C while fluorine is not dissociated at all, chlorine is slightly dissociated, bromine is dissociated to the extent of 6%, iodine is highly dissociated.

9.2.6 Colour :

Halogen molecules are coloured (due to absorption of visible light). Fluorine absorbs violet (high energy) and iodine absorbs yellow light (lower energy). Thus, they are yellow and violet respectively. Similarly we can account for the greenish yellow colour of chlorine and orange red colour of bromine. The colour deepens with the increase in atomic number (with the change in the state of aggregation).

9.2.7 Non-metallic character :

On account of high electronegativities, all the halogens are non-metallic in character. The non-metallic character, however, decreases as we move down the group.

9.2.8 Electron affinity :

All the elements have high electron affinities. Therefore, they have a strong tendency to gain an electron to acquire noble gas configuration (ns^2np^6). Chlorine has the highest electron affinity which decreases gradually as we move down the group from chlorine to iodine. The electron affinity of fluorine is lower than that of chlorine. This lower value is due to the small size of the fluorine atom. The addition of an extra electron in fluorine atom produces a high electron density in a relatively compact 2p–subshell and, therefore, there is strong electron electron repulsion. Hence, fluorine has lesser tendency to accept extra electron, that is, electron affinity is low.

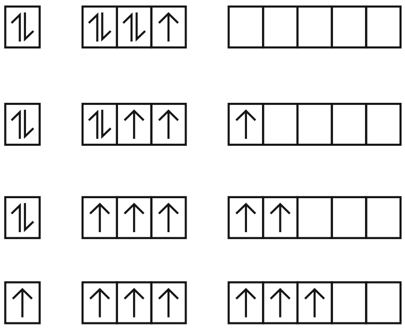
9.3 TRENDS IN CHEMICAL PROPERTIES :

9.3.1 Oxidation states :

All the halogens have the configuration ns^2np^5 in the valency shell, in the ground state. These elements, therefore, tend to gain or share one electron to acquire noble gas configuration. Hence, they show an oxidation state of –1 or +1, depending upon whether the element with which they combine is less electronegative or more electronegative than the halogen. Thus, in hydrogen halides (HF, HCl, HBr and HI) all the halogens are in oxidation state of –1 and in fluoro compounds (ClF, BrF, and IF) and also in the oxy compounds (HClO, HBrO and HIO), chlorine, bromine and iodine are in oxidation state of +1.

Since fluorine is the most electronegative element, **it always exhibits an oxidation state of –1. It does not exhibit any positive oxidation state.** Also, fluorine has no d - orbitals in its valency shell and hence it cannot have any excited states. Consequently, **it does not exhibit any higher oxidation states.**

The other halogens exhibit higher positive oxidation states of +3, +4, +5, +6 and +7 as well because they have vacant d-orbitals in their valency shell which allow for early excitation of d-as well as p- and s- electrons which is explained below :



Halogen atom in ground state (Other than fluorine)	One unpaired electron account for –1 or +1 oxidation state.
First excited state	Three unpaired electrons account for +3 oxidation states.
Second excited state	Five unpaired electrons account for +5 oxidation state.
Third excited state	Seven unpaired electrons account for +7 oxidation state

9.3.2 Reactivity :

Halogens are very reactive. Fluorine is the most reactive. The reactivity decreases as we move down the group. Fluorine is highly reactive because of low energy of F - F bond, small size of atom or ions, high electronegativity and also due to very powerful oxidising power.

9.3.3 Combination with hydrogen :

All combine with hydrogen to form their hydracids. The reactivity decreases from fluorine to iodine. Fluorine reacts in dark, chlorine reacts in sunlight, bromine reacts on heating, while iodine reacts only in the presence of catalyst .

$$H_2 + X_2 \rightarrow 2HX \ (X = F, Cl, Br, I)$$

The acidic strength of these acids varies in the order : HI > HBr > HCl > HF. This is due to increase in bond (H – X) dissociation enthalpy in the order HI < HBr < HCl < HF.

9.3.4 Reaction with water :

The reactivity with water decreases from fluorine to iodine. Fluorine reacts with water violently in dark forming O_2 and O_3. Chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is non-spontaneous.

$$X_2 + H_2O \xrightarrow{\text{Sunlight}} HX + HXO$$

$$(X_2 = Cl_2 \text{ or } Br_2)$$

$$2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$$

9.3.5 Oxidising action :

On account of electron affinites, the halogens have a strong tendency to gain electrons and thus they act as strong oxidising agents. It decreases from fluorine to iodine. Fluorine is the strongest oxidising halogen which oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

$$\frac{1}{2} X_2 + e^- \rightarrow X^-$$

9.3.6 Reaction with oxygen :

Halogens combine with oxygen to form oxides. But most of these oxides are unstable in nature. Fluorine forms two compounds OF_2 and O_2F_2 with oxygen out of which only OF_2 is thermally stable at 298K. These oxides are called oxygen fluorides rather than oxides of fluorine because fluorine is more electronegative than oxygen. O_2F_2 is a strong fluorinating agent and oxidises plutonium to PuF_6. This reaction of O_2F_2 is employed for removing plutonium in the form of PuF_6 from spent nuclear fuel.

Chlorine with oxygen forms oxides like Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. These compounds are highly reactive and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles.

Bromine forms oxides bearing formula Br_2O, BrO_2 and BrO_3. These oxides exist only at low temperature being unstable at higher temperatures. They are very powerful oxidising agents.

I_2O_4, I_2O_5, I_2O_7 are the oxides of iodine available in the form of solids. I_2O_5 is a good oxidising agent and is used for estimation of CO.

9.3.7 Displacement reactions :

It decreases with rise in atomic number. Fluorine displaces all other halogens from their salts while iodine cannot do so at all.

$$2NaCl + F_2 \longrightarrow 2NaF + Cl_2$$

$$2\ KBr + F_2 \longrightarrow 2KF + Br_2$$

$$2\ KI + F_2 \longrightarrow 2KF + I_2$$

9.3.8 Reaction with metals :

As halogens are highly electronegative elements and metals are highly electropositive elements, they react to form electrovalent compounds. Their ionic character decreases in the order MF > MCl > MBr > MI

$$2Na + X_2 \longrightarrow 2NaX \quad (X = F, Cl, Br, I)$$

9.3.9 Formation of interhalogen compounds :

The halogens combine with each other to form interhalogen compounds.

9.3.10 Reaction with nonmetals :

Halogens also combine with a number of non-metals like S, P, etc. The reactivity decreases from fluorine to iodine. For example, sulphur forms hexafluoride (SF_6) with fluorine, tetrachloride (SCl_4) with chlorine, dibromide (SBr_2) with bromine and there is no reaction between sulphur and iodine.

The similarity and gradation in their properties justifies the inclusion of all the four halogens in the same group of the periodic table.

9.4 ANOMALOUS BEHAVIOUR OF FLUORINE :

Fluorine because of its small size and high electronegativity shows anomality in its behaviour in comparison to other halogens. The low F–F bond dissociation enthalpy and non-availability of d-orbitals in valence shell are also reasons for its anomalous behaviour. Some of the consequences of its anomalous behaviour are as follows :

(1) Fluorine is most reactive of all the halogens and has a much higher electrode potential than those of other halogens. Most of the reactions of fluorine are exothermic as it forms strong bond with other elements.

(2) Fluorine does not show higher oxidation states (positive or negative) because of the absence of d-orbitals in its valence shell.

(3) Due to small atomic size and high electronagativity hydrogen bonding is observed in some fluorine compounds. HF is a liquid with boiling point 293K and is a weak acid because of hydrogen bonding.

(4) Fluorine has the highest electrode potential. So it is the strongest oxidising agent among all the halogens. It can act as oxidising agent among all the halogens. It can oxidise most of the other elements, including some of the noble gases (Kr, Xe).

Due to such special properties of fluorine, it is usually called as **super halogen**.

9.5 CHLORINE :

Symbol : Cl **At.No. 17** **At.mass : 35.5**

Mol.formula : Cl_2 **Mol.mass : 71**

Preparation :

All the methods for the preparation of chlorine involve the oxidation of chloride ion either by chemical or electrolytic method.

1. **By oxidation of hydrochloric acid :** The oxidising agents which can be used are MnO_2, PbO_2, $KMnO_4$, $K_2Cr_2O_7$, NaClO, O_3 etc.

(i) MnO_2 oxidises HCl producing $MnCl_2$, H_2O and chlorine.

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$4\ NaCl + MnO_2 + 4\ H_2SO_4 \longrightarrow MnCl_2 + 4\ NaHSO_4 + 2\ H_2O + Cl_2$

(ii) PbO_2 oxidises HCl forming $PbCl_2$, H_2O and Cl_2

$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

(iii) $KMnO_4$ oxidises HCl producing $MnCl_2$, KCl, H_2O and Cl_2 in cold.

$2KMnO_4 + 16HCl \longrightarrow 2\ MnCl_2 + 2KCl + 8H_2O + 5Cl_2$

(iv) $K_2Cr_2O_7$ also oxidises HCl producing $CrCl_3$, KCl, H_2O and Cl_2.

$K_2Cr_2O_7 + 14HCl \longrightarrow 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2$

(v) Sodium hypochlorite (NaClO) and Ozone (O_3) can also oxidise HCl producing chlorine gas.

$NaClO + 2HCl \rightarrow NaCl + H_2O + Cl_2$

$O_3 + 2HCl \rightarrow O_2 + H_2O + Cl_2$

In the laboratory, chlorine can be prepared adopting the methods (i), (iii) and (iv).

2. **By heating any chloride with Conc. H_2SO_4 in presence of MnO_2**

When a mixture of NaCl and MnO_2 in heated with Conc. H_2SO_4, chlorine is formed. Conc. H_2SO_4 produces HCl from the chloride which is subsequently oxidised by MnO_2 to chlorine.

$2NaCl + 3H_2SO_4 + MnO_2 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$

This method is also employed for the preparation of chlorine in the laboratory.

3. **Electrolytic Method :** Commercially, Chlorine is produced by the electrolysis of concertrated solution of sodium chloride (brine). Chlorine is obtained as a by-product in the manufacture of NaOH and sodium from sodium chloride.

$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} H_2 + Cl_2 + 2NaOH$

At the anode : $2Cl^- \rightarrow Cl_2 + 2e$ (oxidation)

At the cathode : $2H_2O + 2e \rightarrow H_2 + 2OH^-$(reduction)

$2NaCl \text{ (fused)} \xrightarrow{\text{Electrolysis}} 2Na + Cl_2$

Laboratory methods of preparation : The following methods are usually followed in the laboratory for the preparation of chlorine.

(i) **By the action of HCl on $KMnO_4$**

This is a convenient method for the preparation of chlorine in the laboratory. It consists of the addition of cold concentrated HCl to solid potassium permanganate.

$2KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 2KCl + 8H_2O + 3Cl_2$

The apparatus is shown in Fig. 9.1

A small quantity of $KMnO_4$ in taken in a flat bottom flask fitted with a dropping funnel and a delivery tube. HCl is added drop by drop from this funnel when greenish yellow gas is evolved. Chlorine, prepared by this method may contain HCl gas. Therefore, it is passed through water to remove HCl gas and then through Conc. H_2SO_4 to remove water vapour

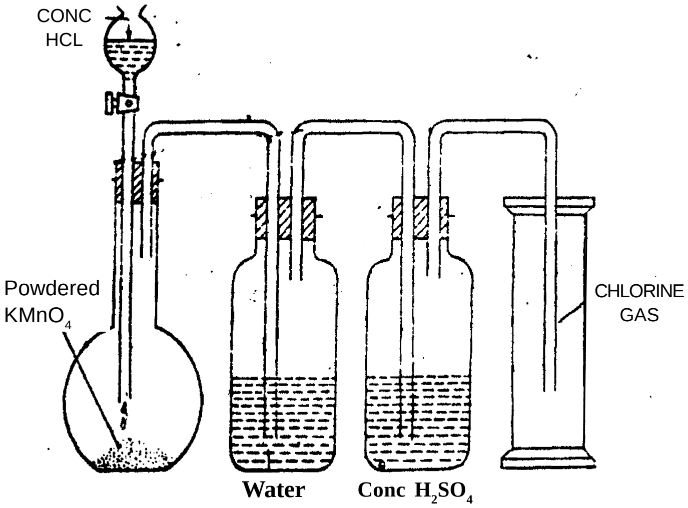


Fig 9.1 Laboratory preparation of chlorine

Finally, dry and pure chlorine is collected in a jar by upward displacement of air. This method yields chlorine *without heating*.

(ii) By heating a mixture of NaCl and MnO_2 with Conc. H_2SO_4

This method is commonly adopted in the laboratory for the preparation of chlorine. A mixture of NaCl and MnO_2 in taken in a round bottom flask fitted with a thistle funnel and a delivery tube. The flask is clamped to a stand (Fig 9.2) Concentrated H_2SO_4 is added through the thistle funnel and the flask is heated gently. Chlorine is evolved. To purify the gas, it is passed through water to remove HCl gas and then through Conc. H_2SO_4 to remove water vapour. Finally, the gas is collected by the upward displacement of air.

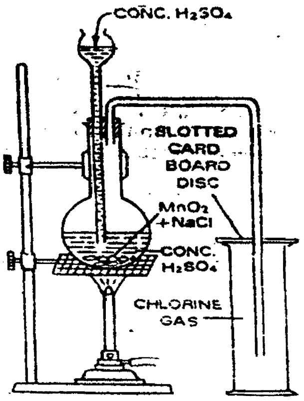


Fig 9.2 Laboratory preparation of chlorine

$$2NaCl + 3H_2SO_4 + MnO_2 \xrightarrow{\text{heat}} 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

Pure Chlorine : Pure chlorine can be obtained by heating dry platinic chloride ($PtCl_4$) or gold chloride ($AuCl_3$) in a hard glass tube.

$$PtCl_4 \xrightarrow{374^0C} PtCl_2 + Cl_2 \xrightarrow{582^0C} Pt + 2Cl_2$$

$$2AuCl_3 \xrightarrow{175^0C} 2AuCl + 2Cl_2 \xrightarrow{185^0C} 2Au + 3Cl_2$$

Manufacture of chlorine :

Chlorine gas is manufactured in large scale by the following process.

(1) **Deacon's process :** In this process, hydrogen chloride gas is oxidised by atmospheric oxygen in the presence of $CuCl_2$ as catalyst at 723K.

$$4\,HCl + O_2 \xrightarrow{CuCl_2,\,723K} 2Cl_2 + 2\,H_2O$$

(ii) Chlorine gas is also obtained by the electrolysis of concentrated solution of NaCl (brine). In this method chlorine gas is liberated at the anode and sodium metal is liberated at cathode.

During the manufacture of sodium metal by electrolysis of fused NaCl in Down's process, Cl_2 gas is also obtained as a by-product.

At anode : $Cl^- \rightarrow Cl + e-$

$2\,Cl \rightarrow Cl_2$

At cathode : $Na^+ + e^- \rightarrow Na$

PROPERTIES

Physical Properties :

1. Chlorine is a greenish-yellow gas with pungent suffocating smell.
2. It is heavier than air.
3. It can be liquefied by cooling under pressure (b.p. 239K). On further cooling, it solidifies to a pale yellow solid.
4. It is poisonous and affects mucous membrane if inhaled.
5. It is fairly soluble in water and the aqueous solution is called **chlorine water**, which looks yellow.

Chemical properties : Chlorine is neither combustible nor a supporter of combustion.

1. Reaction with water and alkalies

(a) Chlorine is fairly soluble in water. The aqueous solution, known as **chlorine water** contains a mixture of hydrochloric and hypochlorous acid.

$Cl_2 + H_2O \rightleftharpoons HCl + HClO$

The solubility of chlorine increases in presence of OH^- ions. In alkaline solution, H_3O+ ions are removed by OH^- ions as water molecules and the hydrolysis goes to completion.

(b) When passed through cold dilute alkali solution, it forms chlorides and hypochlorites.

$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$

$2KOH + Cl_2 \rightarrow KCl + KClO + H_2O$

When the alkali solutions are hot and concentrated, chlorates are formed.

$6\ NaOH + 3Cl_2 \rightarrow 5\ NaCl + \underset{\text{(Sod.chlorate)}}{NaClO_3} + 3H_2O$

$6\ KOH + 3Cl_2 \rightarrow 5KCl + \underset{\text{(Pot.chlorate)}}{KClO_3} + 3H_2O$

When chlorine is passed over dry slaked lime, **bleaching powder** is obtained.

$\underset{\text{(Slaked lime)}}{2\ Ca(OH)_2} + 2\ Cl_2 \rightarrow \underset{\text{(Bleaching Powder)}}{Ca(OCl)_2} + CaCl_2 + 2H_2O$

The composition of bleaching power is $Ca(OCl)_2{\cdot}CaCl_2{\cdot}Ca(OH)_2{\cdot}2H_2O$.

Red hot quicklime (CaO) reacts with dry chlorine forming calcium chloride and oxygen.

$2CaO + 2Cl_2 \rightarrow 2CaCl_2 + O_2$

2. Reaction with other elements : It combines with all nonmetals except nitrogen, oxygen, carbon and inert gases.

(a) **Reaction with hydrogen :** Chlorine combines with hydrogen in presence of light (not in dark) with explosion forming HCl.

$H_2 + Cl_2 \longrightarrow 2HCl$

Turpentine ($C_{10}H_{16}$) burns in chlorine forming HCl and carbon.

$C_{10}H_{16} + 8Cl_2 \longrightarrow 10\,C + 16HCl$

(b) **Reaction with other non-metals :** Boron, sulphur, phosphorus (red) etc. combine with chlorine when heated forming their respective chlorides.

$2B + 3Cl_2 \longrightarrow 2BCl_3$
(Boron trichloride)

$S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$
(Disulphur dichloride)

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$
(Phosphorus trichloride)

Yellow phosphorus immediately catches fire in chlorine.

(c) **Reaction with metals :** Alkali metals burn brilliantly in chlorine. Iron, copper, aluminium, zinc, magnesium etc form their respective chlorides when heated in chlorine.

$2Na + Cl_2 \longrightarrow 2NaCl$

$2\,Fe + 3Cl_2 \longrightarrow 2FeCl_3$

$Cu + Cl_2 \longrightarrow CuCl_2$

$2Al + 3Cl_2 \longrightarrow Al_2Cl_6$

$Zn + Cl_2 \longrightarrow ZnCl_2$

$Mg + Cl_2 \longrightarrow MgCl_2$

3. **Reaction with ammonia :** Chlorine reacts with ammonia under two different conditions.

(i) **When ammonia is in excess,** the products are nitrogen and ammonium chloride.

$$\begin{array}{l} 2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl \\ 6NH_3 + 6HCl \longrightarrow 6NH_4Cl \\ \hline 8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl \end{array}$$

(ii) **When chlorine is in excess,** the products are nitrogen trichloride and HCl.

$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$

4. **Oxidising property :** Chlorine, in presence of moisture is a good oxidising agent. As discussed earlier, chlorine oxidises many metals to their respective chlorides.

(i) It oxidises H_2S to S. either as such or in aqueous solution.

$H_2S + Cl_2 \longrightarrow 2HCl + S$

In aq. soln.,
$$\begin{array}{l} Cl_2 + H_2O \longrightarrow HCl + HClO \\ HClO \longrightarrow HCl + O \\ H_2S + O \longrightarrow H_2O + S \\ \hline Cl_2 + H_2S \longrightarrow 2HCl + S \end{array}$$

(ii) In presence of water, chlorine oxidises sulphur dioxide to sulphuric acid.

$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$

(iii) It also oxidises sulphites to sulphates and precipitates sulphur from sodium thiosulphate.

$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl$

$Na_2S_2O_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl + S$

(iv) Chlorine oxidises ferrous chloride to ferric chloride and ferrous sulphate to ferric sulphate in presence of H_2SO_4.

$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$

$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$

(v) Chlorine oxidises HBr to Br_2, HI to I_2 and itself reduced to hydrogen chloride. It liberates iodine from an aqueous solution of KI.

$2HBr + Cl_2 \rightarrow 2HCl + Br_2$

$2HI + Cl_2 \rightarrow 2HCl + I_2$

$2KI + Cl_2 \rightarrow 2KCl + I_2$

5. **Bleaching property :** In presence of moisture, chlorine acts as a bleaching agent. Chlorine reacts with water forming HCl and HClO (hypochlorous acid). HClO being unstable decomposes giving nascent oxygen which is responsible for its bleaching properties. The bleaching action takes place by oxidation. Dry chlorine does not bleach.

$Cl_2 + H_2O \rightarrow HCl + HClO$

$HClO \rightarrow HCl + O$

$Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured matter + Nascent oxygen → Colourless matter.

The bleaching action of chlorine is permanent. The delicate articles should **not** be bleached with chlorine though wood pulp and cotton fibres are bleached by chlorine.

6. **Addition reactions :** Chlorine forms addition products with SO_2, CO and unsaturated hydrocarbons.

$SO_2 + Cl_2$	$\rightarrow$	SO_2Cl_2 (Sulphuryl chloride)
$CO + Cl_2$	$\rightarrow$	$COCl_2$ (Carbonyl chloride or phosgene)
$C_2H_4 + Cl_2$ (Ethylene)	$\rightarrow$	$C_2H_4Cl_2$ (Ethylene chloride)

7. **Substitution reaction :** With saturated hydrocarbons, chlorine forms a number of substitution products in presence of sunlight. Thus, methane, CH_4 reacts with Cl_2 in presence of sunlight giving a number of products.

$CH_4 + Cl_2 \longrightarrow HCl + CH_3Cl$
(methyl chloride)

$CH_3Cl + Cl_2 \longrightarrow HCl + CH_2Cl_2$
(methylene chloride)

$CH_2Cl_2 + Cl_2 \longrightarrow HCl + CHCl_3$
(chloroform)

$CHCl_3 + Cl_2 \longrightarrow HCl + CCl_4$
(carbon tetrachloride)

Summary :

$Cl_2 \xrightarrow{H_2} HCl$

$Cl_2 \xrightarrow{B} BCl_3$

$Cl_2 \xrightarrow{S} S_2Cl_2$

$Cl_2 \xrightarrow{P} PCl_3$

$Cl_2 \xrightarrow{Metal}$ Metal chloride

$Cl_2 \xrightarrow{H_2O} HCl + HClO, 2HCl + [O]$

$Cl_2 \xrightarrow[(Cold)]{NaOH} NaClO + NaCl + H_2O$

$Cl_2 \xrightarrow[hot.conc]{NaOH} NaClO_3 + NaCl + H_2O$

$Cl_2 \xrightarrow[dry]{Ca(OH)_2} CaOCl_2.H_2O$ (bleaching power)

$Cl_2 \xrightarrow[(Excess)]{NH_3} N_2 + NH_4Cl$

$Cl_2 \xrightarrow[(less)]{NH_3} NCl_3 + HCl$

$Cl_2 \xrightarrow{H_2S} HCl + S$

$Cl_2 \xrightarrow{SO_2+H_2O} H_2SO_4$

$Cl_2 \xrightarrow{HX} HCl + X_2$ (X=Br,I)

$Cl_2 \xrightarrow{SO_2} SO_2Cl_2$

$Cl_2 \xrightarrow{CO} COCl_2$

$Cl_2 \xrightarrow{C_2H_4} C_2H_4Cl_2$

$Cl_2 \xrightarrow{SO_3^{2-}} SO_4^{2-}$

$Cl_2 \xrightarrow{S_2O_3^{2-}} SO_4^{2-} + S$

$Cl_2 \xrightarrow{FeCl_2} FeCl_3$

$Cl_2 \xrightarrow{FeSO_4+H_2SO_4} Fe_2(SO_4)_3 + HCl$

$Cl_2 \xrightarrow{CH_4} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

$Cl_2 \xrightarrow{aq.KI} KCl + I_2$

Uses of chlorine : It is used

(i) in the manufacture of bleaching powder.

(ii) as a bleaching agent for cotton fabrics, paper, and rayon.

(iii) in the purification of drinking water.

(iv) as a germicide and disinfectant.

(v) as an oxidising agent.

(vi) in the manufacture of chlorates, hypochlorites, chloroform, carbon tetrachloride and a number of synthetic organic compounds.

(vii) for the manufacture of poisonous gases like phosgene ($COCl_2$), tear gas ($CCl_3 . NO_2$) and mustard gas ($Cl\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}Cl$).

(viii) In the extraction of platinum and gold.

9.6 HYDROGEN CHLORIDE (HYDROCHLORIC ACID) :

Mol. formula : HCl **Mol. mass : 36.5**

Occurrence : Hydrogen chloride is occasionally found in the gases emitted from volcanoes. It is also present in the gastric juices. The salts of the acid occur plentifully in nature. Hydrochloric acid is obtained by dissolving hydrogen chloride gas in water.

Preparation :

1. **Synthesis :** HCl can be prepared from its elements by exposing a mixture of equal volumes of hydrogen and chlorine to sunlight.

$$H_2 + Cl_2 \rightarrow 2HCl$$

2. **From metal chlorides :** When metal chlorides react with conc. H_2SO_4, hydrogen chloride gas is obtained.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

3. **Laboratory method :** Hydrogen chloride gas is prepared in the laboratory by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \xrightarrow{823K} Na_2SO_4 + HCl$$

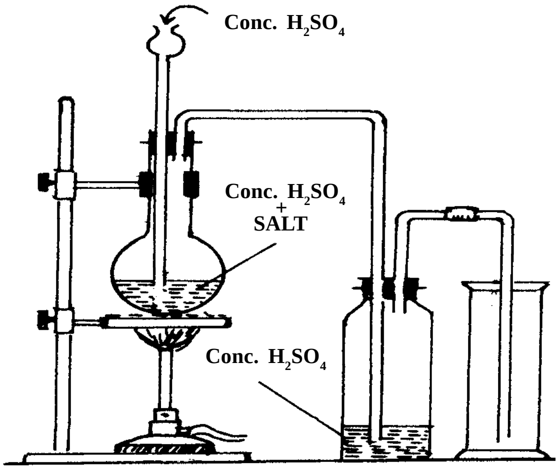


Fig. 9.3 Lab. preparation of hydrogen chloride

Sodium chloride is taken in a round-bottomed flask which is fitted with thistle funnel and a delivery tube. Conc. sulphuric acid is added through the thistle funnel so that the end of the thistle funnel dips under the liquid. Hydrogen chloride gas is evolved (more on heating) and is collected in gas jars by upward displacement of air. The gas can be dried by bubbling it through conc. sulphuric acid before it is collected. It cannot be dried by using phosphorus pentoxide or quick lime since it reacts with these compounds.

$$2P_2O_5 + 3HCl \rightarrow \underset{\text{Metaphosphoric acid}}{3\ HPO_3} + \underset{\text{phosphorus oxychloride}}{POCl_3}$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

Hydrochloric acid : Hydrogen chloride gas is highly soluble in water and the resulting solution is called hydrochloric acid. A saturated solution of hydrogen chloride in water is the concentrated hydrochloric acid.

Properties :

A. Physical :

1. It is a colourless gas with pungent suffocating odour. The gas fumes in moist air.
2. It is heavier than air and on cooling liquifies to a colourless liquid (B.P 189K) and on further cooling it is converted to solid (Freezing point 159K).
3. It is highly soluble in water and the solution is a strong acid, hydrochloric acid. It forms constant boiling (azeotropic) mixture containing 22.2% of the acid and boiling at 383K. A solution of hydrochloric acid cannot, therefore, be concentrated beyond 22.2% by boiling.
4. When inhaled it attacks mucous membrane.

B. Chemical :

Hydrogen chloride in the gaseous state is essentially covalent. In aqueous solution, it ionises and acts as acid, hydrochloric acid ($K_a = 7 \times 10^{8}$)

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

The solution is strongly acidic and turns blue litmus red. The gas neither is combustible nor supports combustion.

1. Acidic Properties :

(i) Hydrochloric acid reacts with most of metals, such as zinc, magnesium, iron, tin and sodium forming metal chlorides and hydrogen gas.

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$, $Fe + 2HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

(ii) It reacts with bases i.e. metal oxides, hydroxides, carbonates etc. to form metal chlorides.

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

$NaOH + HCl \longrightarrow NaCl + H_2O$

$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$

2. **Action of salts :** HCl decomposes the salts of weaker acids like sulphides, sulphites, thiosulphates, and nitrites. The corresponding chlorides are formed with the evolution of different gases.

$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$

$ZnSO_3 + 2HCl \longrightarrow ZnCl_2 + H_2O + SO_2$

$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + S + SO_2$

$2NaNO_2 + 2HCl \longrightarrow 2NaCl + H_2O + NO + NO_2$

3. **Precipitation reactions :** HCl forms insoluble chlorides with soluble salts of Ag, Pb, Hg (Ous).

$AgNO_3 + HCl \longrightarrow \underset{\text{(white)}}{AgCl} + HNO_3$

$Pb\,(NO_3)_2 + 2HCl \longrightarrow \underset{\text{(white)}}{PbCl_2} + 2HNO_3$

$Hg_2\,(NO_3)_2 + 2HCl \longrightarrow \underset{\text{(white)}}{Hg_2Cl_2} + 2HNO_3$

4. **Reaction with fluorine :** Since fluorine is more electronegative than chlorine, it displaces chlorine from hydrochloric acid.

$2HCl + F_2 \longrightarrow 2HF + Cl_2$

5. **Reaction with ammonia :** It produces dense white fumes of ammonium chloride with ammonia.

$NH_3 + HCl \longrightarrow NH_4Cl$

6. **Reactions as reducing agent :** It acts as a reducing agent in presence of strong oxidising agents such as MnO_2, PbO_2, Pb_3O_4 (red lead), $KMnO_4$, $K_2Cr_2O_7$, NaClO, O_3 etc. In all the reactions chlorine is the product.

(i) $MnO_2 + 2HCl \longrightarrow MnCl_2 + H_2O + O$

$2HCl + O \longrightarrow H_2O + Cl_2$

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(ii) $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$

(iii) $Pb_3O_4 + 6HCl \longrightarrow 3PbCl_2 + 3H_2O + O$

$2HCl + O \longrightarrow H_2O + Cl_2$

$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$

(iv) $2KMnO_4 + 6HCl \longrightarrow 2KCl + 2MnCl_2 + 3H_2O + 5O$

$10HCl + 5O \longrightarrow 5H_2O + 5Cl_2$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

(v) $K_2Cr_2O_7 + 8HCl \longrightarrow 2KCl + 2CrCl_3 + 4H_2O + 3O$

$6HCl + 3O \longrightarrow 3H_2O + 3Cl_2$

$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

(vi) $NaClO \longrightarrow NaCl + O$

$2HCl + O \longrightarrow H_2O + Cl_2$

$NaClO + 2HCl \longrightarrow NaCl + H_2O + Cl_2$

(vii) $O_3 \longrightarrow O_2 + O$

$2HCl + O \longrightarrow H_2O + Cl_2$

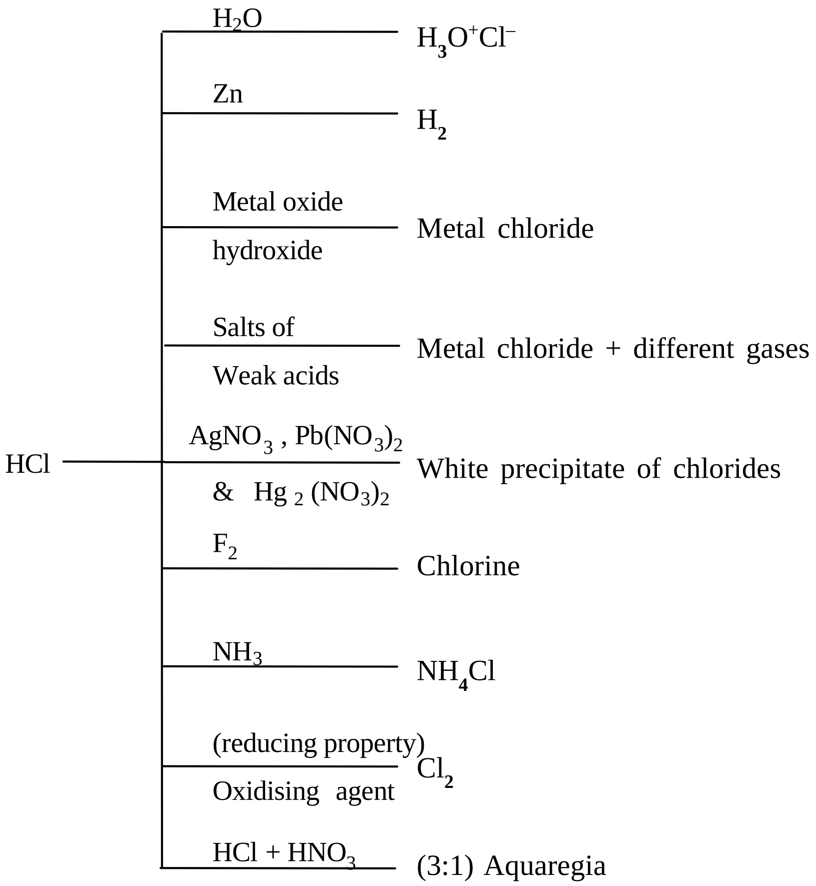
$2HCl + O_3 \longrightarrow H_2O + O_2 + Cl_2$

7. Formation of aquaregia : A mixture of concentrated hydrochloric acid and concentrated nitric acid in the ratio 3:1 is called aquaregia, It dissolves even noble metals like gold and platinum.

$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$

$3Pt + 16H^+ + 4NO_3^- + 18\ Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

Summary :



Uses : Hydrochloric acid is used :

1. As a laboratory reagent.
2. In the preparation of chlorine, chlorides and aquaregia.
3. For cleaning iron sheets during tin plating and galvanisation.
4. In the manufacture of dyes and in textile industry.
5. For extraction of glue from animal tissue and bones.
6. In medicine.
7. In the manufacture of glucose. (from corn starch)

Tests :

1. HCl gas fumes in moist air and forms dense white fumes of NH_4Cl with ammonia.
2. Chlorine is evolved when HCl gas is passed through a heated tube containing MnO_2.
3. Solution of HCl in water

(i) Turns blue litmus red and

(ii) Gives a white precipitate with $AgNO_3$ solution. The precipitate, AgCl, is insoluble in nitric acid, but readily dissolves in dilute ammonium hydroxide.

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

$$AgCl + 2NH_4OH \longrightarrow [AgNH_3)_2]\ Cl + 2H_2O$$

9.7 OXOACIDS OF HALOGENS :

Halogenes form different oxo-acids commonly known as

(a) Hypohalous acid (b) Halous acid

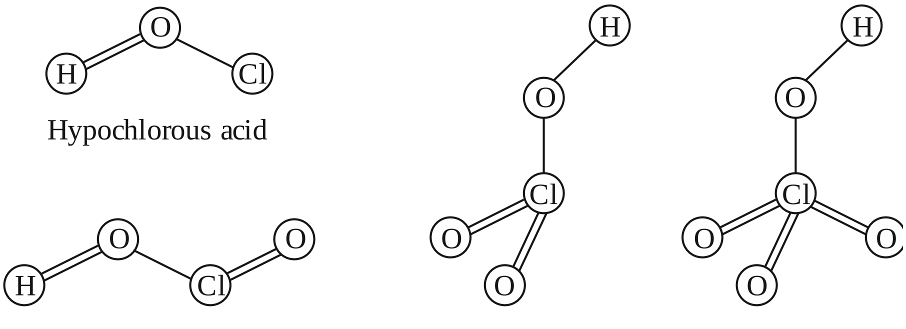
(c) Halic acid and (d) Perhalic acid (Table 9.2)

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of these oxoacids can not be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are given in Table 9.2 and their structures are given in Fig. 9.3.

Table 9.2 : Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous) acid)	HOBr (Hypobromous acid)	HOI (Hypolodous acid)
Halic (III) acid (Halous acid)	– –	HOCIO (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOCIO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	– –	HOCIO3 (perchloric acid)	HOBrO3 (perbromic acid)	HOIO3 (periodic acid)

Fig. 9.4 : The structure of oxoacids of chlorine



Hypochlorous acid

Chlorous acid Chloric acid Perchloric acid

9.8 INTERHALOGEN COMPOUNDS OR INTERHALOGENS :

9.8.1 Each halogen combines with every other halogen to form compounds amongst themselves. These are known as **interhalogens** or **interhalogen compounds.** In naming the compounds, the less electronegative element is mentioned first. These are generally covalent compounds.

1. Interhalogens of the type XY (Diatomic interhalogens)

Preparation : These are prepared by the direct combination of the halogens.

$$I_2 + F_2 \xrightarrow{228K} 2IF$$

$$I_2 + X_2 \rightarrow 2IX \ (X = Cl, Br)$$

$$Cl_2 + F_2 \xrightarrow{523K} 2ClF$$

Properties : The properties of these interhalogens lie between those of the parent halogens. However, they are more reactive than the halogens concerned. Because, the bond energy of X – Y bond is less than the bond energy of X – X or Y – Y bond.

(i) These compounds readily convert metals into metal halides.

$$XY + 2M \rightarrow MX + MY$$

$$ClF + 2Na \rightarrow NaCl + NaF$$

(ii) On hydrolysis, they give oxy-halides and hydrides of the more electronegative halogen.

$$XY + H_2O \rightarrow HOX + HY \quad \text{(Y is more electronegative)}$$

(iii) They add to double bond forming dihalocompounds.

$$-CH = CH- + XY \rightarrow -CHX-CHY-$$

2. Interhalogens of the type XY_3 (Tetra-atomic interhalogens)

Three atoms of one halogen combine with one atom of another halogen to form these type of compounds. Some of the known compounds of this type are ClF_3, BrF_3 and ICl_3.

These compounds are generally prepared by the direct combination of the elements under suitable conditions. Among these, ClF_3 is most reactive.

$$Cl_2 + 3F_2 \xrightarrow{473\text{–}573K} 2ClF_3$$

$$Br_2 + 3F_2 \xrightarrow{N_2} 2BrF_3$$

$$I_2 + 3Cl \xrightarrow{373K} 2ICl_3$$

3. Interhalogens of the type XY_5 (Hexa–atomic interhalogens)

Five atoms of one halogen combine with one atom of another halogen to form these type of interhalogens. The stable compounds are ClF_5, IF_5 and BrF_5.

These are generally prepared by the direct fluorination of the element or the lower fluorides.

$$Cl_2 + 5F_2 \xrightarrow[250\ \text{atm.}]{623K} 2\ ClF_5$$

$$Br_2 + 5F_2 \xrightarrow[> 423K]{\text{excess F}} 2\ BrF_5$$

$$I_2 + 5F_2 \xrightarrow{\text{excess } F_2} 2IF_5$$

4. Interhalogens of the type XY_7 (Octa-atomic interhalogens)

Seven atoms of one halogen combine with one atom of another halogen to form this type of interhalogen. Only one compound, IF_7 of this type is formed. The reason for the formation of this compound lies in the large size of iodine atom and very small size of fluorine atom.

Iodine haptafluoride, IF_7, is formed by heating iodine pentafluoride with fluorine at 623K – 673K

$$IF_5 + F_2 \longrightarrow IF_7$$

9.8.2 Properties of Interhalogen Compounds :

Some properties of interhalogen compounds are summarised in the Table 9.3

Table 9.3 : Some properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XY	CIF	Colourless gas	–
	BrF	pale brown gas	–
	IF[a]	detected spectroscopically	–
	BrCl[b]	Gas	
	ICl	Ruby red solid (α-form) Brown red solid (β-form)	
	IBr	black solid	
XY_3	CIF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped (?)
	ICl_3[C]	orange solid	Bent T-shaped (?)
XY_5	IF_5	colourless gas but solid below 77K	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	CIF_5	colourless liquid	Square pyramidal
XY_7	IF_7	colourless gas	Pentagonal bipyramidal

[a] Very unstable; [b] The pure solid is known at room temperature; [C] Dimerises as Cl-bridged dimer (I_2Cl_6)

(1) As halogen atoms have small electronegativity difference between each other, the interhalogen compounds are covalent in nature.

(2) They are volatile solids or liquids at 298K except ClF, BrF, ClF_3, IF_5 and IF_7 which are gases at room temperature (Table 9.3)

(3) Due to absence of unpaired electrons these compounds are diamagnetic in nature.

(4) Their physical properties are intermediate between those of constituent halogens. However, their melting points and boiling points are a little higher than expected due to some polarity associated with these molecules.

(5) Interhalogen compounds are more reactive than halogens (except fluorine), because X–X' bond in interhalogens is weaker than X–X bond in halogens except F–F bond. The sequence of reactivity of various interhalogen compounds decrease in the order:

$$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF > IF_3 > IF$$

(6) (a) The compounds of the type XY on hydrolysis give halide ion of smaller halogen and a hypohalite derived from the larger halogen.

$$XY + H_2O \longrightarrow HY + HOX$$

$$ICl + H_2O \longrightarrow HCl + HOI \text{ (Hypoiodous acid)}$$

(b) The interhalogen compounds of the type XY_3 also yield halide ion of smaller halogen on hydrolysis and a halate is formed, where as XY_7 type compounds yield perhalate anion derived from larger halogen along with halide ion of the smaller halogen.

9.8.3 Structure of Interhalogen Compounds :

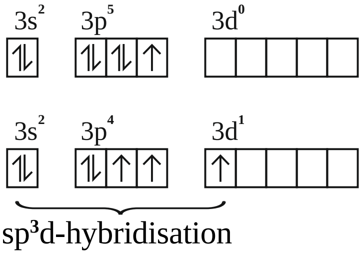
The molecular structure of Interhalogen compounds can be explained on the basis of VSEPR theory.

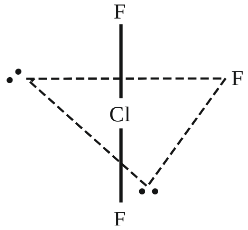
(a) XY_3 type : These compounds involve sp^3d hybridization of central atom X and hence have trigonal bipyramidal geometries or are T-shaped. (Fig. 9.4)

Ex : Structure of ClF_3

Cl (Ground state)

Cl (Second Excited state)





(Fig. 9.4 : Bent T-shaped structure of ClF_3

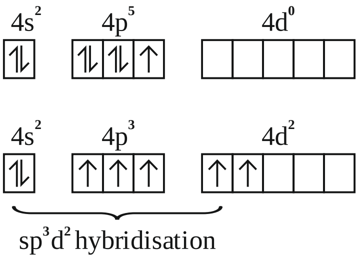
The central Cl atom is surrounded by three bond pairs and two lone pairs of electrons. These electron pairs occupy the corners of a trigonal bipyramid. The two lone pairs occupy the equatorial positions to minimise lonepair-lonepair and the bond pair-lonepair repulsions which are greater than the bond-pair-bond pair repulsions. The axial fluorine atoms bend towards the equatorial fluorine in order to minimise the lone pair-lone pair repulsions. So the molecule has a bent T-shape.

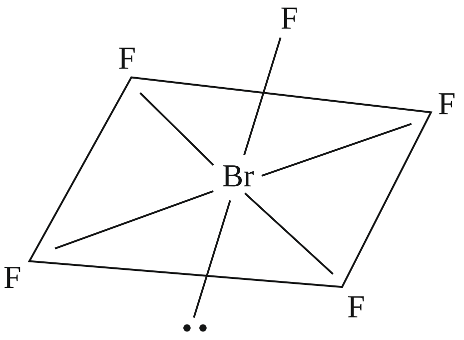
(b) **XY_5 type :** All interhalogen compounds of the type XY_5 involve sp^3d^2 hybridization of the central halogen atom X and hence have distorted octahedral (square pyramidal) geometry due to single lone pair electrons around the central atom.

Ex : Structure of BrF_5

Br (Ground State)

Br (Excited state)





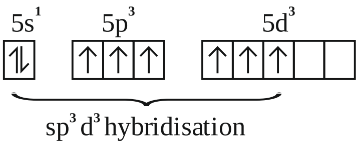
The molecule has square-pyramidal geometry

(Fig. 9.5 : Structure of BrF_5)

(c) **XY_7 type :** The interhalogen compounds of this type involve sp^3d^3 hybridization of the central halogen atom X and have pentagonal bipyramidal geometry.

Ex : Structure of IF_7 :

Electronic structure of I
(in the third excited state)



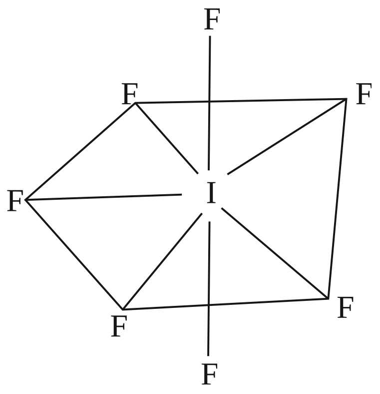


Fig. 9.6 : Pentagonal bipyramidal structure of IF_7

9.8.4 Uses of Interhalogen compounds :

(1) They are used as non-aqueous solvents.

(2) They act as fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U + 3ClF_3 \longrightarrow UF_6 + 3ClF$$

9.9 PSEUDOHALIDE IONS AND PSEUDOHALOGENS :

The ions consisting of two or more electronegative atoms of which atleast one is nitrogen and have properties similar to those of halide ions are called **pseudohalide ions**.

These pseudohalide ions also form dimeric molecules, like the halide ions. These dimers are called **pseudohalogens** as they show properties similar to those of halogens. A few examples of pseudohalide ions and pseudohalogens are given below :

Pseudohalides	Pseudohalogens
Cyanide, CN^-	Cyanogen $(CN)_2$
Thiocyanate, SCN^-	Thiocyanogen $(SCN)_2$
Cyanate, OCN–	Oxycyanogen $(OCN)_2$

Cyanamide ion (NCN^{2-}), fulminate ion (ONC^-) and azide ion (N_3^-) are examples of a few other pseudohalide ions.

CHAPTER (9) AT A GLANCE

1. **Elements of Halogen family :** Fluorine, chlorine, bromine, iodine and astatine (radioactive).
2. **Electronic configuration :** The general electronic configuration in the outermost orbit is ns^2np^5.
3. **Oxidation states :** Fluorine exhibits only –1 oxidation states. In addition to these status higher positive oxidation states of +3, +4, +5, +6 and +7 are also exhibited.
4. O_2F_2 is a strong fluorinating agent. It is employed for removing plutonium from spent nuclear fuel, as it oxidise plutonium to PuF_6.
5. ClO_2 is as a bleaching agent for paper pulp and textiles.
6. Br_2O, BrO_2 and BrO_3 are the oxides of bromine unstable at higher temperature and are powerful oxidising agents.
7. I_2O_5 is a good oxidising agent and is used for estimation of CO.
8. Fluorine shows anomality in its behaviour due to (a) its small size, (b) high electronegativity, (c) low F-F bond dissociation enthalpy and (d) non-availability of d-orbital in valence shell.

9. HF is a liquid and also a weak acid because of intermolecular hydrogen bonding.

10. Fluorine is usually called as super halogen.

11. **Chlorine** is a greenish yellow, pungent, suffocating poisonous gas fairly soluble in water. It combines with several metals and nonmetals except nitrogen, oxygen, carbon and inert gases. It is prepared by the oxidation of hydrochloric acid, heating an electrovalent chloride with conc H_2SO_4 in presence of MnO_2 or by electrolysis of concentrated sodium chloride solution.

$$4\,HCl + MnO_2 \longrightarrow MnCl_2 + 2H_2O + Cl_2.$$

$$2\,KMnO_4 + 16\,HCl \longrightarrow 2\,MnCl_2 + 2KCl + 8H_2O + 5Cl_2.$$

$$2\,NaCl + 3H_2SO_4 + MnO_2 \longrightarrow 2\,NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Moist chlorine acts as an oxidising and bleaching agent. Bleaching action of chlorine is due to oxidation and it is permanent.

12. **Hydrochloric acid** is a colourless gas with pungent odour, highly soluble in water, heavier than air. It acts as a reducing agent in presence of strong oxiding agent.

13. **Aquaregia** is a mixture of concentrated HCl and concentrated HNO_3 in the ratio 3 : 1. It dissolves noble metals like gold and platinum.

$$3\,HCl + HNO_3 \longrightarrow NOCl + 2H_2O + 2Cl.$$

14. **Hydrogen chloride** gas is prepared in the laboratory by heating NaCl with conc H_2SO_4.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl \text{ (on heating)}$$

15. HCl gas is collected by upward displacement of air, and dried by bubbling it through Conc. H_2SO_4.

16. Interhalogen compounds or Interhalogens are compounds of one halogen with every other halogen. These are generally covalent compounds and are more reactive than halogens.

17. The interhalogen compounds of XY_3 type have sp3d hybridisation and possess bent T-shaped structure, of XY_5 type have sp^3d^2 hybridisation and square pyramidal structure and of XY_7 type sp^3d^3 hybridisation showing pentagonal bipyramidal structure.

18. Halogens form oxo-acids commonly known as

(a) Hypohalous acid (b) Halous acid (c) Halic acid and (d) Perhalic acid.

19. The nuclear fuels like Uranium-235, are enriched by fluorinating agents.

QUESTIONS

A. Very short answer type questions (1 mark each)

1. Give any two uses of fluorine
2. HF is less volatile than HCl. Why is it so ?
3. What happens when HCl gas is passed through concentrated solution of sodium chloride ?
4. Arrange the halogen hydrides in the increasing order of bond lengths.
5. Among the hydracids of halogens which is the weakest ?
6. Which of the halogens forms hydrogen bond ?
7. Name an element which can belong both to Group I and Group 7 of the periodic table.
8. Which is the most electronegative element in the periodic table ?
9. Which halogen shows only one oxidation number in its compounds ?
10. Give the electronic configuration of chlorine atom.
11. Which halogen does not exhibit the oxidation state of +1
12. Arrange the following in order of increasing electronegativity.
    Cl, I, F, Br
13. Arrange the following in order of increasing size. Cl, Cl^+, Cl^-
14. Which hydracid of halogen has the highest bond energy ?
15. What is the oxidation number of oxygen in OF_2 ?
16. What is the role of MnO_2 in the preparation of Cl_2 from HCl.
17. Which is the strongest of the halogen acids ?
18. Write two uses of ClO_2.
19. What is the shape of IF_7 molecule ?
20. BrF_3 or ClF_5, which has bent T-shaped structure ?
21. Name two poisonous gases which can be prepared from chlorine gas.

B. Short answer type questions (2 marks each)

1. Electron affinity of fluorine is less than that of chlorine, why ?
2. What happens when NaCl is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 ?
3. Glass apparatus are not used for isolation and storing of fluorine. Why ?
4. Why is the boiling point of hydrofluoric acid abnormally high ?
5. Why is HF a liquid where as other hydrides of halogens are gases ?
6. Between the acids HBr and HI which is more easily oxidised ? Give reasons.
7. Explain on the basis of electronic configuration why fluorine and chlorine are put in 17 group of periodic table.

8 What happens when chlorine water is added to potassium iodide solution in small quantity ? Give equation.

9 What happens when H_2S is passed into chlorine water ?

10. Why Hydrogen fluoride is a liquid where as other Hydrogen halides are gases ?

11. Explain what happens when HCl gas is passed through concentrated NaCl solution.

12. Arrange F_2, Cl_2, Br_2, I_2 in the increasing bond dissociation enthalpy. Justify your answer.

13. Why are halogens coloured ?

14. HCl reacts with finely divided Iron forming ferrous chloride and not ferric chloride. Why?

15. Arrange HF HCl, HI, HBr in the increasing order of their acidity. Justify your answer.

C. Long questions (3 Marks each)

1. What happens when Cl_2 reacts with hot concentrated NaOH. Show with equation that, this is a disproportionation reaction.
2. Why are halogens strong oxidising agents ? Name the strongest oxidising halogen.
3. Explain why fluorine forms only one oxoacid HOF.
4. Give the reasons for anomalous behaviour of fluorine.
5. How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.
6. What happens when :
   (a) NaCl is heated with conc. H_2SO_4 in presence of MnO_2
   (b) Cl_2 gas is passed into the aqueous solution of NaI.
7. Write the reactions of F_2 and Cl_2 with water.
8. Predict the products obtained due to hydrolysis of ICl, ClF_3 and IF_7.
9. Fluorine never acts as the central atom in polyatomic interhalogen compounds.

D. Long questions (7 Marks each)

1. Give a comparative account of Group 17 elements of periodic table.
2. Write notes on the general characteristics of halogens.
3. Write two methods of preparation of Chlorine ? Discuss its reaction with metals & non-metals. Write two of its uses.
4. What happens when ? Write equations.
   (a) Dry slaked lime reacts with Cl_2.
   (b) NH_3 reacts with excess Cl_2
5. Write notes on hydrides of halogens.

MULTIPLE CHOICE TYPE QUESTIONS

1. The electronic configuration of halogen is

(a) ns^2 (b) ns^2np^3

(c) ns^2np^5 (c) ns^2np^4

2. Which of the following shows only one oxidation state ?

(a) F (b) Cl

(c) Br (d) I

3. Most electropositive halogen is

(a) F (b) Cl

(c) Br (d) I

4. The smallest atom is

(a) F (b) Cl

(c) Br (d) I

5. Fluorine doesn't show positive oxidation state due to absence of

(a) p - orbitals (b) d - orbitals

(c) s - orbitals (d) None

6. Bromine gas turns starch iodine paper

(a) Blue (b) Red

(c) Yellow (d) Colourless

7. Halogen having highest bond energy

(a) F_2 (b) Cl_2

(c) I_2 (d) Br_2

8. Bleaching powder is

(a) $CaClO_3$ (b) $CaClO$

(c) $CaOCl_2$ (d) $Ca(OCl)_2$

9. Which of the following statement is correct

(a) Br_2 is more reactive than Cl_2 (b) I_2 is more reactive than Br_2

(c) Cl_2 is insoluble in water (d) Iodine is solid

10. Sea weeds are important source of

(a) Fe (b) I_2

(c) Cl_2 (d) Br_2

11. Among the C-X bond (where X = Cl, Br, I) the correct bond energy is

(a) $C - Cl > C - Br > C - I$ (b) $C - I > C - Cl > C - Br$

(c) $C - Br > C - Cl > C - I$ (d) $C - I > C - Br > C - Cl$

12. The strongest oxidising element is

(a) F (b) Cl

(c) Br (d) I

13. Which of the following has the highest molar heat of vaporisation

(a) HF (b) HCl

(c) HBr (d) HI

14. Which of the following radicals can bring about the highest oxidation state of a transition metal

(a) F^- (b) Cl^-

(c) Br^- (d) I^-

15. The halogen that is most readily reduced is

(a) Chlorine (b) Bromine

(c) Iodine (d) Fluorine

16. Which of the following has greatest reducing power

(a) HCl (b) HI

(c) HF (d) HBr

17. The halogen that is most easily reduced is

(a) F_2 (b) Cl_2

(c) Br_2 (d) I_2

18. Oxidising action increases from left to right in the following order

(a) $Cl < Br < I < F$ (b) $Cl < I < Br < F$

(c) $I < F < Cl < Br$ (d) $I < Br < Cl < F$

19. The no. of electrons in a halogen in its outermost orbit in comparision with corresponding noble gas is

(a) One electron less (b) One electron more

(c) Two electrons less (d) Two electrons more

20. Tear gas is

(a) $COCl_2$ (b) $CaOCl_2$

(c) NH_3 (d) CCl_3NO_2

21. The element present in combined state in laminaria stenophylla is

(a) Bromine (b) Iodine

(c) Fluorine (d) Chlorine

22. The compounds used as refrigerants are

(a) NH_3 (b) CCl_4

(c) CF_4 (d) CF_2Cl_2 (e) CH_2F_2

23. Which of the following displaces Br_2 from an aqueous solution containing bromide ion.

(a) Cl_2 (b) Cl^-

(c) I_2 (d) I_3^-

24. Which of the following compounds exists?

(a) $KHCl_2$ (b) KHF_2

(c) $KHBr_2$ (d) KHI_2

25. Which of the followin has the highest reducing power?

(a) HCl (b) HI

(c) HBr (d) HF

26. Structure of IF_5 is

(a) Linear (b) Pentagonal bipyramidal

(c) Bent T-shaped (d) Square pyramidal

ANSWERS TO MULTIPLE TYPE QUESTIONS

1. c
2. a
3. d
4. a
5. b
6. c
7. b
8. c
9. d
10. b
11. a
12. a
13. a
14. a
15. d
16. b
17. a
18. d
19. a
20. d
21. b
22. a, d
23. a
24. b
25. b
26. d

* * *

CHAPTER - 10

GROUP 18 ELEMENTS : NOBLE GASES

(ZERO GROUP ELEMENTS)

10.1 INTRODUCTION :

The elements helium, neon, argon, krypton, xenon and radon are included in the zero group of the periodic table. All these elements are monoatomic gases. Except helium, which has $1s^2$ electronic configuration, all other elements have eight electrons (ns^2np^6) in their outermost shell. All these gases except radon are found in atmosphere in traces and hence they are called **rare gases**. Radon is radioactive and is obtained from radioactive disintegration of radium. These gases are called **inert gases** or **noble gases**, because they are relatively unreactive. However, recently some of the inert gases are found to form compounds under suitable conditions. The electronic configurations of these elements account for their high degree of chemical inertness in ordinary chemical reactions.

10..2 OCCURRENCE :

(i) **Atmosphere :** All the noble gases except radon are present in the atmospheric air. The relative abundance of these gases in atmosphere is given in Table - 10.1

TABLE - 10.1

Relative abundance of Noble gases in Atmosphere

Element (Symbol)		**Percentage by Volume**
Helium (He)	–	5.2×10^{-4}
Neon (Ne)	–	1.8×10^{-3}
Argon (Ar)	–	9.3×10^{-1}
Krypton (Kr)	–	1.4×10^{-4}
Xenon (Xe)	–	8.7×10^{-6}

It may be noted that **Argon** is the most abundant **noble gas**.

(ii) **Natural gas :** Natural gas contains about 2–7% helium.

(iii) **Minerals :** Minerals like monazite sand, pitch blende, thorianite and clevite contain helium. Small amounts of helium and argon are also found in some mineral springs.

(iv) **Sun :** Helium is also found is sun's atmosphere where it is formed from hydrogen by nuclear fusion.

(v) **Radioactive element :** Radon is produced in the radioactive decay of radium.

10.3 POSITION OF INERT GASES IN THE PERIODIC TABLE :

The inert gases were not known during Mendeleef's time when the original classification of element was proposed. Moreover, the existence and discovery of such elements, devoid of chemical activity could not be visualised at that time and no space was provided for these elements in the periodic table though several vacant places were left for elements to be discovered. Basing on the critical analysis of the periodic table, Juliot Thomson suggested that there must be a chemically inert group of elements between highly electronegative halogens (Group 17) and highly electropositive alkali metals (Group 1). After the discovery of the inert gas elements, the new group was introduced into the periodic table as zero group.

The electronic configurations of these elements are considered to be most stable which account for their inertness.

The electronic configurations are –

He (2) → $1s^2$

Ne (8) → $1s^2, 2s^2, 2p^6$

Ar (18) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

Kr (36) → $1s^2, 2s^6, 2p^2, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6$

Xe (54) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6$

Rn (86) → $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6$

which suggest that these elements have saturated shells. Therefore, they have no tendency either to lose or gain or share electrons with atoms of other elements. In other words, their valency or combining capacity is zero. Hence, they are placed in **zero group.**

TABLE - 10.2

Some Physical Properties of Noble Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic Numer	2	10	18	36	54	86
Atomic mass/g-mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic Configuration	$1s^2$	[He] $2s^2 2p^6$	[Ne] $3s^2 3p^6$	[Ar]$3d^{10} 4s^2 4p^6$	[Kr]$4d^{10} 5s^2 5p^6$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^6$
Ionisation Enthalpy/kJ.mol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy/kJ.mol^{-1}	48	116	96	96	77	68
Atomic radios ($\overset{0}{A}$)	1.20	1.60	1.90	2.00	2.20	-
M.P/K	0.9	24	84	116	161	202
B.P/K	4.2	27.1	87.4	120.3	165.2	211

Though these elements are chemically inactive, their reactivity increases with the increase in the atomic number. This is because of the fact that the ionisation potential decreases as we go down the group (Table - 10.2) The decrease in the ionisation potential makes the electron available for chemical reaction.

10.4 PROPERTIES OF ZERO GROUP ELEMENTS :

The general trend in the physical properties of inert gas elements are given in Table-10.2. All these elements are colourless and odourless gases.

10.4.1 Monoatomic nature :

These gases exist as monoatomic gases. This has been established from the specific heat ratio (Cp/Cv) for all inert gases which has been found to be 1.66 (theoretical value of all monoatomic gases). Other physical constansts such as refractive index, dielectric constant etc. also confirm their monoatomic character. This is because the atoms of inert gas elements have saturated shells and they have no tendency to combine amongst themselves.

10.4.2 Solubility in water :

Noble gases are slightly soluble in water. Neon and Argon gases are more soluble in water than nitrogen. The solubility in water increases from He to Rn. Noble gases are soluble in water because polar water molecule induces dipole in those molecules. As water molecule is polar in nature when it comes near a noble gas atom, it induces a dipole in the noble gas atom by polarizing its symmetrical electron cloud. This induced dipole interacts with the dipole of water molecule and hence the noble gas dissolves (Fig. 10.1). On moving from He to Rn the size of the noble gas increases and also the extent of polarization of it, resulting in the increase of the dipole-induced dipole interaction or extent of solubility in water. They are slightly soluble in water. Neon and argon are more soluble in water than nitrogen.

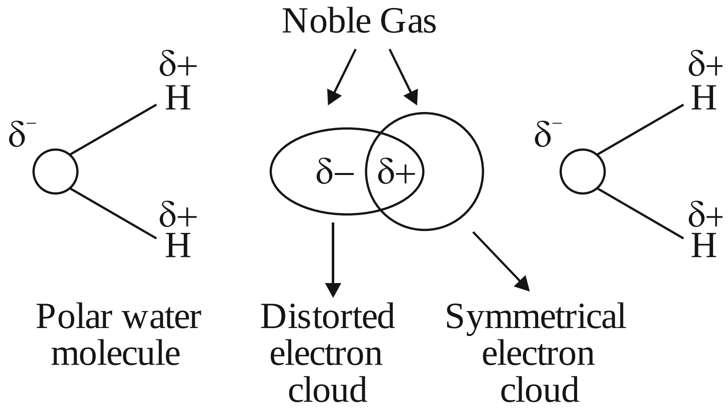


Fig 10.1 : Polarization of noble gas by polar water molecules

10.4.3 Liquefaction of the Noble Gases :

On account of **weak van der Waals force of attraction** existing in these gases, these are relatively difficult to be liquified. However, they can be liquified and solidified at very low temperature. Liquefaction of these gases increases from helium to xenon, since the vander Waals forces increase in the same order. For the same reason, the boiling points and melting points of these gases are very low and increase with the increase in the atomic number. The m.p (0.9K) and b.p. (4.2K) of helium are the lowest of any known element.

10.4.4. Ionisation Enthalpy :

As already discussed, the outermost shells have stable electronic configuration and therefore the ionisation energies are very high. They decrease with increase in atomic number. Thus, the reactivities increase due to availability of electrons for chemical reaction. The outermost electrons in Kr and Xe are away from the nucleus and therefore less firmly held. Thus, Krypton and Xenon can combine with highly electronegative elements like oxygen or fluorine which has strong tendency to attract electrons towards itself and leaves Krypton and Xenon with a net positive charge.

10.4.5 Electron Affinity :

The stable electronic configurations of these elements do not allow them to accept electrons. Hence, they have **zero electron affinity.**

10.4.6 Atomic radii :

Noble gases are monotomic. They have only van der Waals radii (not the covalent radii). So in a period the atomic radius of the noble gas present in it is largest. The **atomic radii** increase with the increase in atomic numbers from Helium to Radon, because new shells are added.

10.4.7 Adsorption by activated charcoal :

All noble gases are **adsorbed** by **activated charcoal** at low temperature. The capacity of adsorption increases with increase in atomic mass. Helium has the minimum adsorption capacity.

Each of these noble gases has a **characteristic spectrum** by which it can be easily identified.

These elements are fairly good conductors of heat and electricity. The thermal conductivity of helium is very high at room temperature (even much higher than copper).

Unusual Properties of liquid Helium

It is observed that if the temperature is lowered below 2.1K, a new form of helium, called He (II) is formed. He (I) boils vigorously, but if the temperature is lowered to 2.1K, the boiling stops and the liquid continues to vanish. He (II) is superconductive and therefore does not boil vigorously and only evaporates. When He (II) is poured in a beaker to a level much below the top, it rises up the wall against gravity and passes over the top and flows down outside. It solidifies at 0.9K and 25 atmospheric pressure.

10.5 CHEMICAL PROPERTIES :

The inert gas elements have stable electronic configuration. However, under suitable conditions elements like xenon and krypton have been found to react chemically and the reactivity increases with increase in atomic number. That is why, the inert gases are now called **noble gases.** Highly electronegative elements such as oxygen and fluorine are capable of forming compounds, because chemical reactivity of noble gases involves loss of electrons. Xenon, having the least ionisation energy forms a large number of compounds. Krypton forms only a few number of compounds, but with difficulty. Helium, neon and argon do not form compounds.

Platinum hexafluoride, PtF_6 is a powerful oxidising agent which is capable of oxidising molecular oxygen forming an ionic compound $O_2^+ PtF_6^-$. This observation led to suggest that xenon which has almost same ionisation potential can form similar compounds. In 1962, Bartlett could isolate similar type of compound, $Xe^+(PtCl_6)^-$ by the reaction of xenon with platinum hexachloride at room temperature.

A few compounds of xenon, especially the fluorides are discussed below.

FLUORIDES OF XENON

A number of fluorides of xenon have been prepared and studied. They are XeF_2, XeF_4 and XeF_6.

1. Xenon difluoride, XeF_2 :

Preparation : It is prepared

(i) by heating a mixture of xenon and fluorine in the ratio 1:3 in a nickel tube at 673K. On cooling the vapour, xenon difluoride is obtained as a colourless solid.

$$Xe + F_2 \xrightarrow[673K]{Ni-tube} XeF_2$$

(ii) **by photochemical combination** of xenon and fluorine under the influence of mercury vapour.

$$Xe + F_2 \xrightarrow{\text{Mercury vapour}} XeF_2$$

(iii) by reaction of xenon with excess amount of O_2F_2 at 155K.

$$Xe + O_2F_2 \xrightarrow{155K} XeF_2 + O_2$$

PROPERTIES

Physical : Xenon difluoride is a colourless, crystalline solid and melts at 300K. It is the least volatile of all the fluorides of xenon.

Chemical :

(i) **With hydrogen :** It reacts with hydrogen forming xenon and hydrogen fluoride.

$$XeF_2 + H_2 \rightarrow Xe + 2HF$$

(ii) **With water :** It oxidises water to oxygen and hydrogen chloride to chlorine.

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

$$XeF_2 + 2HCl \rightarrow Xe + 2HF + Cl_2$$

(iii) **With PF_5 :** XeF_2 reacts with fluorine ion acceptors like PF_5,

SbF_5 to form cationic species.

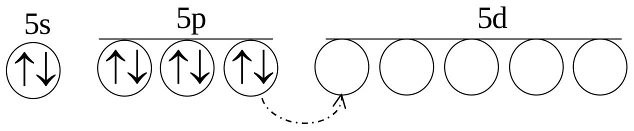
$$XeF_2 + PF_5 \rightarrow [XeF]^+[PF_5]^-$$

Uses : (i) It is an effective fluorinating agent.

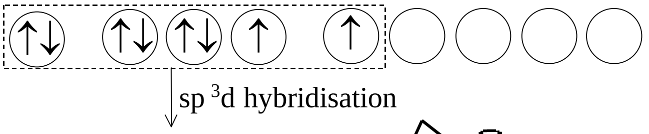
(ii) Xenon can be prepared from it (by reactions with H_2 and H_2O)

Structure : XeF_2 molecule has a **linear** structure (F–Xe–F) which can be explained in the light ofhybridisation.

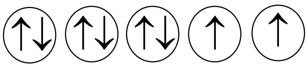
The electronic configuration of Xe atom in the ground state :



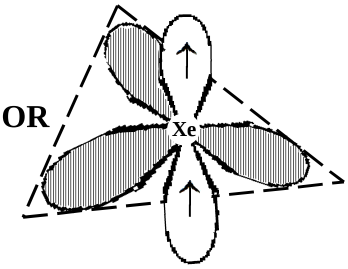
and in the excited state :



Xe atom in the hybridised state :



OR



Five sp^{3}d hybrid orbitals

After hybridisation, they form five sp^{3}d hybrid orbitals with three orbitals having lone pairs and two, having one electron each, which overlap with 2p orbitals of fluorine and form two Xe–F sigma bonds.

Thus, the molecule assumes a **linear** shape as shown in **Fig. 10.2**

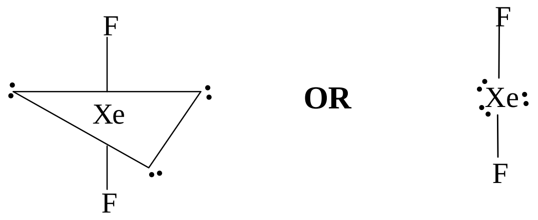


Fig. 10.2 : Linear structure of XeF$_2$

2. Xenon tetrafluoride, XeF$_4$

Preparation – It is prepared

(i) by passing electric discharge through a mixture of xenon and fluorine at 193K and 2-15mm pressure.

$$Xe + 2F_2 \xrightarrow[\substack{193K \\ \text{2-15 mm press.}}]{\text{Electronic discharge}} XeF_4$$

(ii) by heating a mixture of xenon and fluorine in molecular ratio 1:10 to 673K under 6 atmospheric pressure in a nickel vessel for a few hours and cooling the vapour immediately.

$$Xe(g) + 2F_2(g) \xrightarrow[400^0C,\ 6\ atm.\ Press.]{\text{Nickel vessel}} XeF_4(s)$$

PROPERTIES

Physical – It is a colourless crystalline solid which melts at 100^{0}C and sublimes on heating. It is quite stable in pure and dry state and can be stored in a nickel vessel. It dissolves in liquid HF without any chemical reaction.

Chemical :

(i) **With hydrogen :** XeF_4 reacts with hydrogen liberating xenon.

$$XeF_4 + 2H_2 \rightarrow Xe + 4HF$$

(ii) **With water :** It reacts with water forming a highly explosive compound XeO_3

$$2XeF_4 + 3H_2O \rightarrow Xe + XeO_3 + 6HF + F_2$$

(iii) **With potassium iodide :** It oxidises KI to I_2

$$4KI + XeF_4 \rightarrow Xe + 4HF + 2I_2$$

(iv) **With sulphur tetrafluoride :** Xenon tetrafluoride fluorinates sulphur tetrafluoride to sulphur hexafluoride.

$$2SF_4 + XeF_4 \rightarrow Xe + \underset{\text{(Sulphur hexafluoride)}}{2SF_6}$$

(v) **With SbF_5 :** It reacts with fluoride ion acceptors like antimony pentafluoride to form cationic species.

$$XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$$

Uses

(i) For the preparation of xenon.

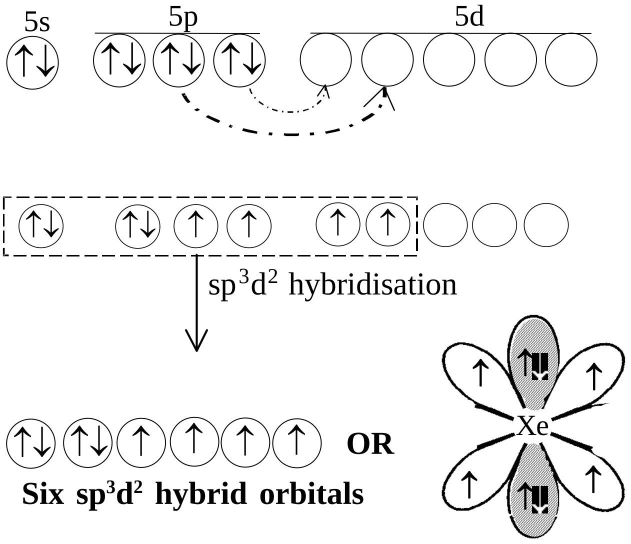
(ii) As a fluorinating agent.

Structure : Xenon tetrafluoride molecule has a **square planar** structure which can be explained in terms of sp^3d^2 hybridisation.

Xenon atom in its ground state :

In the excited state :

Xe atom in sp^3d^2 hybridised state :



Six sp^3d^2 hybrid orbitals

After hybridisation, they form six sp^3d^2 hybrid orbitals with two hybrid orbitals containing lone pairs in axial positions and four hybrid orbitals centaining one electron each in equitorial position which overlap with 2p orbitals of 4F atoms forming sigma bonds. The molecule assumes **square planar** structure. (Fig. 10.3)

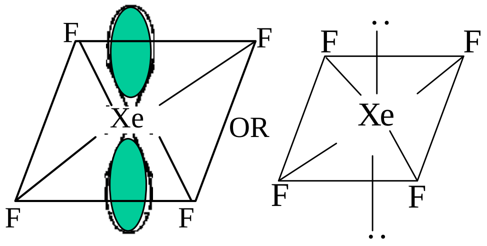


Fig. 10.3 : Square planar structure of XeF_4 molecule.

3. Xenon hexafluoride, XeF_6

Preparation : It is prepared

(i) by heating a mixture of xenon and fluorine in molecular ratio 1:20 to 523K – 573K under 50 atmospheric pressure in a nickel vessel. The yield is about 95%.

$$Xe + 3F_2 \xrightarrow[\text{50 atm. press}]{\substack{\text{Ni-vessel} \\ \text{523K – 573K}}} XeF_6$$

(ii) by the direct interaction of XeF_4 with O_2F_2 at 143K

$$XeF_4 + O_2F_2 \xrightarrow{143K} XeF_6 + O_2$$

PROPERTIES :

Physical : Xenon hexafluoride is a colourless crystalline solid which melts at 322.5K giving a yellow liquid. It is volatile.

Chemical :

(i) **With hydrogen :** XeF_6 reacts with H_2 liberating xenon.

$$XeF_6 + 3H_2 \rightarrow Xe + 6HF$$

(ii) **With moisture :** Slow hydrolysis of xenon hexafluoride by atmospheric moisture gives solid XeO_3.

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Small quantity of water brings about partial hydrolysis of XeF_6 producing a colourless liquid containing xenon oxyfluoride, $XeOF_4$.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

Complete hydrolysis forms XeO_3 as the final product.

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

(iii) **With HF :** XeF_6 veacts with HF and forms $[XeF_5]^+[HF_2]^-$ which is appereciably ionised.

$$XeF_6 + HF \rightarrow [XeF_5]^+[HF_2]^- \rightarrow [XeF_5]^+ + [HF_2]^-$$

(iv) **With silica :** It reacts with silica readily and hence can not be stored in glass vessels.

$$2\,XeF_6 + \underset{\text{(silica)}}{SiO_2} \rightarrow 2XeOF_4 + SiF_4$$

(v) **With Alkali metal fluorides :** It reacts with fluoride ion donors like alkali metal fluorides to form fluoroanions.

$$XeF_6 + MF \rightarrow M^+ [XeF_7]^- \text{ (M = Na, K, Rb or Cs}$$

Uses : (i) As an oxidising agent, it oxidises hydrogen to HF, HCl to Cl_2 and NH_3 to N_2.

(ii) As an effective fluorinating agent.

Structure :

The structure of XeF_6 is a controversial issue. The molecule is believed to have **distorted octahedral** structure in gaseous state. (Fig 10.4) This can be explained by sp^3d^3 hybridisation in Xe atom in the molecule.

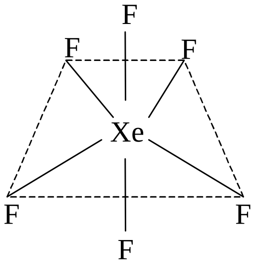


Fig. 10.4 : Distorted octahedral shape of XeF_6 molecule.

4. Xenon trioxide (XeO_3)

Preparation : It is prepared by hydrolysis of XeF_4 and XeF_6 with water

$$6\ XeF_4 + 12\ H_2O \rightarrow 4\ Xe + 2XeO_3 + 24\ HF + 3O_2$$

$$XeF_6 + 3\ H_2O \rightarrow XeO_3 + 6\ HF$$

Properties :

(1) It is a colourless explosive solid. The xenon atom is sp^3 hybridised and the molecule has a pyramidal structure (Fig. 10.5)

(2) It acts as a powerful oxidising agent. It oxidises Pu^{2+} to Pu^{4+} in the presence of H+ ions.

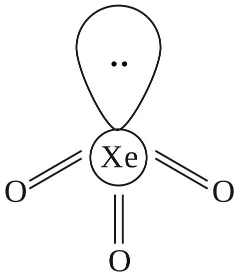


Fig. 10.5 Structure of XeO3

$$3\ Pu^{2+} + XeO_3 + 6H^+ \rightarrow 3Pu^{4+} + Xe + 3\ H_2O$$

(3) Xenon trioxide reacts with aqueous alkali to form the hydrogen xenate ion, $HXeO_4^-$. $HXeO_4^-$ slowly undergoes disproportionation to give xenon and perxenate ion, XeO_6^{4-}, which is a powerful oxidising agent.

$$XeO_3 + OH^- \rightarrow HXeO_4^-$$

Hydrogen xenate ion

$$2\ HXeO_4^- + 2OH^- \rightarrow XeO_6^{4-} + Xe + O_2 + 2\ H_2O$$

Perxenate ion

5. Xenon oxyfluorides :

Preparation : Partial hydrolysis of XeF_6 give oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$$

Properties :

(1) $XeOF_4$ is a colourless volatile liquid. Here the central 'Xe' atom is sp^3d^2 hybridised and it has a square pyramidal structure.

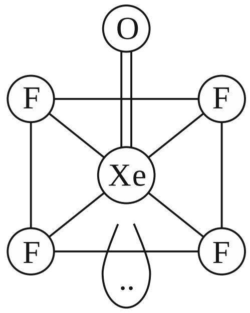


Fig. 10.6 : Structure of $XeOF_4$

(2) XeO_2F_2 (Xenon dioxydifluoride) has trigonal bipyramidal structure. Here the 'Xe' atom is sp^3d hybridised.

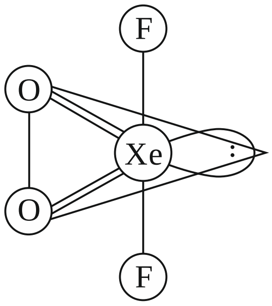


Fig.: 10.7 Structure of XeO_2F_2

10.6 USES OF NOBLE GASES :

Of all the noble gases only helium and argon are plentily and easily available. The uses are due to their chemical inertness and low boiling points. Some important uses of the noble gases are given below.

Uses of Helium :

1. **Filling airships and balloons :** In lightness, helium is next to hydrogen. Being non-inflammable and light, it is used for filling weather balloons and airships. For this purpose 85% helium and 15% hydrogen is usually used. Helium is also used for inflating the tyres of big aeroplanes.

2. **Relief in respiratory diseases :** A mixture of helium and oxygen is used in the artificial breathing of asthma patients. This keeps the breathing steady. Helium is also used for the treatment of some respiratory diseases.

3. **Respiration of sea divers :** The mixture of helium and oxygen (20:80) is used for respiration by sea divers. The air proves harmful, because nitrogen of the air dissolves in the blood at high water pressure when the diver is in the deep sea. When he comes out to the surface, the pressure suddenly decreases and the dissolved nitrogen from the blood escapes in form of bubbles and gives a painful sensation, called **bends.**

4. **Gas thermometer :** Helium is used for filling gas thermometers, used for low temperature measurement.
5. **Welding of metals :** It is used for providing inert atmosphere is the welding of metals and alloys.
6. **Production of low temperature :** Liquid helium (b.p. 4.2K) is used as a cryogenic fluid for producing low temperature required for research work.
7. **Space programme :** It is used as a pressuring agent in rockets to expel liquid oxygen and liquid hydrogen.
8. **Clinical diagnosis :** It is used to produce and sustain powerful super condcuting magents which form essential part of NMR spectrometers and MRI (Magnetic Resoanance Imaging) systems used for clinical diagnosis.

Uses of Neon :

1. **Production of coloured glow :** Neon is used in discharge lamps and tubes to produce brilliant coloured glow, often used for advertising purposes since neon lights are visible from long distances. Mixed with mercury vapour, neon produces blue or green colour.
2. **Beacon light :** Neon light can penetrate through fog and mist. Therefore neon signs are used in beacon lights for ships and aeroplanes.
3. **Electrical devices :** Neon is used in certain protective electric devices like voltage stabilisers, current rectifiers etc.

Uses of Argon :

1. **Electric bulbs and radio valves :** A mixture of argon with 15% nitrogen is filled in electric bulbs to increase the life of filaments. It is also used for filling radio valves.
2. **Production of inert atmosphere :** Argon is also used for producing inert atmosphere in welding and in metallurgy of certain metals which are easily oxidised.
3. **Coloured glow :** A mixture of argon and mercury vapour produces blue or green colour in the discharge tubes.

Uses of Krypton and Xenon :

These gases are used for filling electric bulbs and tubes. They are better than argon for this purpose.

Uses of Radon :

1. **Treatment of cancer :** Radon, being radioactive is used in the treatment of cancer and radiotherapy for treatment of malignant growths and non-healing wounds.
2. **Industry :** It is used for locating the defects in steel castings.

CHAPTER (10) AT A GLANCE

1. Zero group of the periodic table comprises of elements like helium, neon, argon, krypton, xenon and radon.
2. These elements are called rare gases, inert gases or noble gases.
3. The outermost shell of all these elements are fully saturated. Except helium, others have the general outermost electronic configuration ns^2np^6.
4. Although present in a very small quantity, atmospheric air is the main source of these elements except radon, which is obtained by the radioactive disintegration of radium. Argon is the most abundant noble gas.
5. The mixture of rare gases is obtained from dry air or liquid air and separated by physical and chemical methods.
6. The inert gas elements are monoatomic. ($C_P/C_V = 1.66$)
7. The atomic radii, boiling points, melting points, and the capacity of being adsorbed increase with increase in atomic number.
8. The electron affinity of these elements is zero. The ionisation potential is very high and decreases with increase in atomic number.
9. Noble gases are soluble in water because of polarization of their molecules by the dipole interaction of polar water molecules.
10. Inert gases find a large number of applications because of their unique properties.
11. The ionisation potential of xenon being less compared to other inert gases, it can form compounds with highly electronegative elements like oxygen and fluorine. Krypton forms relatively less number of compounds than xenon.
12. The most important fluorides of xenon are XeF_2, XeF_4 and XeF_6. They are stable XeF_2 has a linear structure. XeF_4 has a square planar structure and XeF_6 has a distorted octahedral structure in the gaseous state.
13. XeO_3 is payramidal in shape where the Xe atom is sp3 hybridised. Xenon oxyfuorides i.e. $XeOF_4$ and XeO_2F_2 have square pyramidal and trigonal bipyramidal structures respectively.

QUESTIONS

(A) Very short answer type questions (1 mark) :

1. Why sea divers use a mixture of helium and oxygen instead of air for respiration ?
2. What lamp is used as beacon lights for ships and aeroplanes ?
3. Two of the following are inert gases. Identify them.
   Oxygen, Neon, Nitrogen and Helium
4. Why the noble gases, in general, are chemically inert ?
5. Which are of the following inert gases is the most abundant in air ?
   Ne, Ar, Kr, He
6. Why argon is monoatomic ?
7. Which gas is used in beacon lights ?
8. The most abundant noble gas present in the atmosphere is ————
9. Give one use of xenon tetrafluoride.
10. Why zero group elements do not form diatomic molecules ?
11. Give the electronic configuration of argon atom.
12. Write any one use of xenon difluoride.
13. Which of the noble gases is radioactive ?
14. Which noble gas is used for treatement of cancer.
15. Show the product that is formed by the interaction of xenon with excess of O_2F_2 at 155K.
16. Give any two uses of xenon tetrafluoride.
17. Write two uses of Helium.
18. Write the electronic configuration of krypton.
19. Write the structure of XeO_2F_2 molecule.
20. Write the shape of xenon difluoride.
21. Which of the following noble gases is used in weather balloons
    i) He, ii) Xe, iii) Ne, iv) Kr
22. Why has it been difficult to study the chemistry of radon ?

(B) Short answer type questions (2 marks each) :

1. Explain why neon is monoatomic.
2. Mention one use of each of four noble gases.
3. Chemical activity of noble gases vary in the group, how ?
4. Give a brief account of the preparation, properties and structure of XeF_6

5. Which inert gas contains less than eight electrons in its outer shell ? What is its atomic number ? Write down its electronic configuration.
6. The inert gas molecules are monoatomic. Why it is so ?
7. Write the electronic configuration of krypton, Why is it inert ?
8. Name the zero group elements and give their atomic numbers.
9. Give a method of preparation of xenon tetrafluoride.
10. Give the shapes of Xenon di and tetrafluorides.
11. Why do Noble gases have low boiling points ?
12. Noble gas atoms have highest atomic radius than other elements present in that period. Why ?
13. Amongst all noble gases only xenon is known to form compounds with oxygen and fluorine. Given reasons.
14. Which compound led to the discovery of noble gases ? How?

(C) Short Questions (3 marks each) :

1. Xenon forms fluorides easily. Explain in two or three sentences.
2. Give the hybridisation of Xe in XeF_2, XeF_4 and $XeOF_4$.
3. Write down the structure of XeO_4 and XeF_4
4. Complete the following chemical equations :
   (a) $XeF_2 + PF_5 \rightarrow$
   (b) $XeF_4 + H_2O \rightarrow$
   (c) $XeF_4 + O_2F_2 \rightarrow$
5. Write the hybridization and also draw the melecular structure of
   (a) XeO_3
   (b) $XeOF_4$
   (c) XeO_2F_2

(D) Long Questions (7 Marks each) :

1. Write a short account of the fluorides of xenon stating their preparation and properties.
2. Why the zero group elements are also known as inert gases ? Which inert gas contains less than eight electrons in its outer shell ? Give the preparation of Xenon tetrafluoride.
3. Name the zero group elements and give their atomic numbers. How xenon difluoride is prepared and what is its use ?
4. On the basis of electronic configuration discuss the position of inert gases in the periodic table.
5. How will you account for the formation of Xenon fluorides ? Give the preparation and structures of xenon difluoride and xenon tetrafluoride.

MULTIPLE CHOICE QUESTIONS

1. Noble gas used in radiotherapy is

   (a) Kr (b) Ar

   (c) Rn (d) Xe

2. Deep sea divers respirate in a mixture of

   (a) oxygen and argon (b) oxygen and helium

   (c) oxygen and nitrogen (d) oxygen and hydrogen.

3. Shape of XeF_4 is

   (a) Linear (b) trigonal pyramidal

   (c) pyramidal (d) square planar

4. Which of the following is not correct about the rare gases ?

   (a) They are used to provide inert atmosphere in many chemical reactions.

   (b) They are sparingly soluble in water.

   (c) They form diatomic molecules

   (d) Some of them are used for advertising signboards.

5. The first noble gas compound obtained was

   (a) XeF_2 (b) $XePtF_6$

   (c) XeF_4 (d) XeO_2F_2

6. The valency of noble gas is

   (a) zero (b) one

   (c) two (d) three

7. Which of the following noble gases is the least polarisable ?

   (a) He (b) Ne

   (c) Kr (d) Xe

8. Which of the following fluorides of xenon is impossible ?

   (a) XeF_2 (b) XeF_3

   (c) XeF_4 (d) XeF_6

9. The outermost shell of the elements of inert gases in characterised by

   (a) ns^2np^6 (b) ns^2np^5

   (c) ns^2np^4 (d) ns^2np^3

10. The coloured discharge tubes for advertisement contain

    (a) Xenon (b) Helium

    (c) Argon (d) Neon

11. Monazite on heating gives.
    (a) Ra (b) Ar
    (c) He (d) Ne
12. The maximum number of compounds are formed by
    (a) He (b) Xe
    (c) Kr (d) Ne
13. The inert gas abundantly found in atmosphere is
    (a) Xe (b) Kr
    (c) Ar (d) He
14. Which of following is called stranger gas ?
    (a) Kr (b) Xe
    (c) He (d) Ne
15. Which of the following rare gases shows least ionisation potential ?
    (a) Ar (b) Kr
    (c) He (d) Xe
16. The noble gas which behaves abnormally in liquid state is.
    (a) Xe (b) Ne
    (c) He (d) Ar
17. Which of the following liquids can climb up the wall of the glass vessel in which it is placed ?
    (a) Alcohol (b) Liquid He
    (c) Liquid N_2 (d) Water
18. The compound that attacks pyrex glass is
    (a) XeF_2 (b) XeF_4
    (c) XeF_6 (d) None
19. How many lone pairs are associated with xenon difluoride ?
    (a) 1 (b) 2
    (c) 3 (d) 4
20. In XeO_3 molecule Xe atom shows which hybridisation.
    (a) sp^3 (b) sp^3d
    (c) d^3sp^2 (d) sp^3d^2

ANSWERS TO MULTIPLE CHOICE QUESTIONS

E 1. (c), 2. (b), 3. (d), 4. (c), 5. (b), 6. (a), 7. (a) 8. (b),
9. (a), 10. (d), 11. (c), 12 (b), 13. (c), 14. (b) 15. (d). 16. (c).
17. (b), 18. (c). 19. (c). 20. (a).

* * *

UNIT - VIII

d and f - BLOCK ELEMENTS

CHAPTER - 11

d- BLOCK ELEMENTS : TRANSITION ELEMENTS

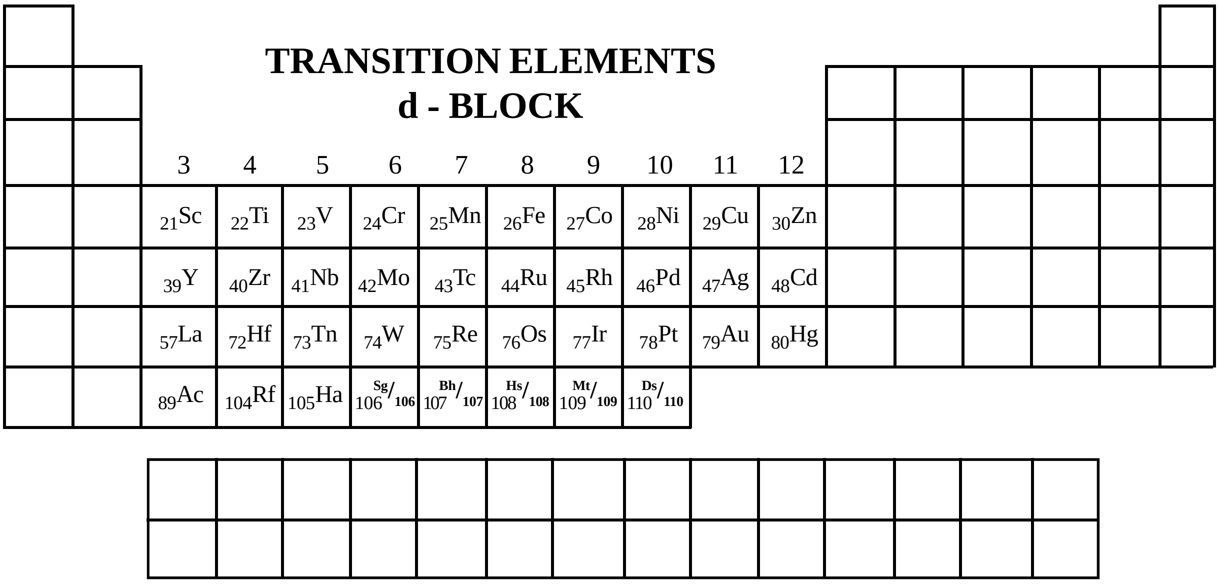
11.1 TRANSITION METALS :

A transition metal may be defined as one that has an incomplete inner d-orbital. A transition metal is also called a transition element or a d-block element.

The general electronic configuration of transition elements is (n-1)d^{1-10} ns^{1-2}, whereas the general electronic configuration of representative elements is ns^{1-2} or ns^{1-2} ns^{2} np^{1-6}.

In the case of d-block (transition) elements, electrons are added successively to the inner d-orbitals.

The elements are called transition elements (Table 11.1) as they are placed between the s- and p-block elements and their properties represent a transition between the highly reactive electropositive elements of the s-block and the electronegative elements of the p-block.



TRANSITION ELEMENTS
d - BLOCK

3	4	5	6	7	8	9	10	11	12
$_{21}$Sc	$_{22}$Ti	$_{23}$V	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{28}$Ni	$_{29}$Cu	$_{30}$Zn
$_{39}$Y	$_{40}$Zr	$_{41}$Nb	$_{42}$Mo	$_{43}$Tc	$_{44}$Ru	$_{45}$Rh	$_{46}$Pd	$_{47}$Ag	$_{48}$Cd
$_{57}$La	$_{72}$Hf	$_{73}$Tn	$_{74}$W	$_{75}$Re	$_{76}$Os	$_{77}$Ir	$_{78}$Pt	$_{79}$Au	$_{80}$Hg
$_{89}$Ac	$_{104}$Rf	$_{105}$Ha	$106^{Sg}/_{106}$	$107^{Bh}/_{107}$	$108^{Hs}/_{108}$	$109^{Mt}/_{109}$	$110^{Ds}/_{110}$		

Table : 11.1 Position of transition elements in the periodic table

As shown above (Table 11.1) the d-block elements belong to groups 3 to 7, 8 and 11 to 12 of the periodic table.

These transition elements are present in the periodic table in four series.

Table : 11.2 Series of transition elements

Series	**Number of elements**	**Element present**	**Electronic configuration**
1st Series (3d Series)	10	Sc_{21}(Scandium) to Zn_{30} (Zinc)	$[Ar]3d^{1-10}4s^{1-2}$
2nd Series (4d Series)	10	Y_{39}(Yttrium) to Cd_{40} (cadmium)	$[Kr]4d^{1-10}5s^{1-2}$
3rd Series (5d Series)	10	La_{57}(Lanthanum), Hf_{72}(Hafnium) to Hg_{80} (Mercury)	$[Xe]4f^{14}5d^{1-10}\ 6s^{1-2}$
4th Series (6d incomplete series)		Ac_{89} (Actinium),Rf_{104} and newly discovered elements, At.No. 105-110	$[Rn]5f^{14}\ 6d^{1-10}\ 7s^{1-2}$

Just after the transition element Lanthanum La_{57} ($[Xe]4f^{0}5d^{1}6s^{2}$) (Table.11.2), the next transition element is Hafnium Hf_{72} $[Xe]4f^{14}5d^{2}6s^{2}$. The elements occurring just after Lanthanum is Cerium, Ce_{58}($[Xe]4f^{2}5d^{0}6s^{2}$). A series of 14 elements from Ce_{58} to Lu_{71}, Lutetium ($[Xe]4f^{14}5d^{1}6s^{2}$) ae called as 1st series of inner transition elements or f-block elements. These are known as **Lanthanides** or **4f-block elements**. The 2nd series of inner transition elements are elements occurring just after the transition element Actinium, Ac_{89}.These are the **actinides** or **5f-block elements** beginning with Thorium, Th_{90} ($[Rn]5f^{0}6d^{2}7s^{2}$) and ending till now in Lawrencium, Lw_{103}($[Rn]5f^{14}6d^{1}7s^{2}$). **Inner transition elements** contain incomplete 4f and 5f orbitals respectively in addition to their incomplete (n-1)d orbitals. Inner transition elements are special type of transition elements.

There are three transition series of elements (Table 11.2). The 1st series or **3d series** begins with the element Scandium, Sc_{21} ($[Ar]3d^{1}4s^{2}$) and ends with the element Zinc, Zn_{30}-($[Ar]3d^{10}4s^{2}$). The 2nd series or **4d series** begins with the element Yttrium, Y_{39} ($[Kr]4d^{1}5s^{2}$) and ends with the element Cadmium, Cd_{48} ($[Kr]4d^{10}5s^{2}$). The 3d series begins only with Lanthanum, La_{57}, ($[Xe]4f^{0}5d^{1}6s^{2}$),and then begins with Hafnium, Hf_{72} ($[Xe]4f^{14}5d^{2}6s^{2}$)

and ends with the element Mercury, Hg_{80} (Xe]$4f^{14}5d^{10}6s^{2}$). The elements Zn, Cd and Hg remain at the end of 3d,4d and 5d series respectively whose atoms have completely filled d-orbitals for which they are non-transitional.

The first transition series :

The first transition series or **3d-series** is present in the 4th period of the periodic table (Sc_{21} to Cu_{29}). Zn_{30} ([Ar]$3d^{10}4s^{2}$) remains at the end of the series whose atom has completely filled 3*d*-orbital for which it is non-transitional.

Table : 11.3 The outer electronic configurations of the atoms and ions of the first transition series

Elements	Atomic number	Outer E. C	Ions and their outer E.C			
			Ions	E.C	Ions	E.C
Scandium (Sc)	21	$3p^63d^14s^2$			Sc^{3+}	$3p^6$(non-transitional)
Titanium (Ti)	22	$3p^63d^24s^2$	Ti^{2+}	$3p^63d^2$	Ti^{3+}	$3p^63d^1$
Vanadium(V)	23	$3p^63d^34s^2$	V^{2+}	$3p^63d^3$	V^{3+}	$3p^63d^2$
Chromium (Cr)	24	$3p^63d^54s^1$	Cr^{2+}	$3p^63d^4$	Cr^{3+}	$3p^63d^3$
Manganese (Mn)	25	$3p^63d^54s^2$	Mn^{2+}	$3p^63d^5$	Mn^{3+}	$3p^63d^4$
Iron (Fe)	26	$3p^63d^64s^2$	Fe^{2+}	$3p^63d^6$	Fe^{3+}	$3p^63d^5$
Cobalt (Co)	27	$3p^63d^74s^2$	Co^{2+}	$3p^63d^7$	Co^{3+}	$3p^63d^6$
Nickel (Ni)	28	$3p^63d^84s^2$	Ni^{2+}	$3p^63d^8$		
Copper (Cu)	29	$3p^63d^{10}4s^1$	Cu^{2+}	$3p^63d^9$	Cu^{+}	$3p^63d^{10}$ (non-transitional)
Zinc (Zn)	30	$3p^63d^{10}4s^2$	Zn^{2+}	$3p^63d^{10}$	(non-transitional)	

Based on experimental evidence the outer electronic configurations of chromium and copper are $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively. It may be noted that the electronic configuration of chromium and copper unlike the others, show a single electron in the $4s$ orbital. This is due to the additional stability gained by the atom when the d-orbital is exactly half-filled (in the case of chromium) or completely filled (in the case of copper).Accordingly one of the $4s$ electrons shifts to the $3d$ orbital in the atoms of chromium and copper.

11.2 GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS :

Transition elements are solid metals hard,malleable and ductile. They have relatively high densities, high melting points and high boiling points. These properties indicate that the atoms in these elements are held together by strong metallic bonds. Such metallic bonds are even present in their molten states. The properties of transition (d-block) elements are intermediate between the properties of s and p block elements.

Table : 11.4 Properties of elements of the first transition metal series

	Element								
Property	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
Atomic mass	45.00	47.88	50.95	52.00	54.94	55.85	58.93	58.69	63.54
Atomic radius, A^0	1.64	1.47	1.35	1.29	1.26	1.26	1.25	1.24	1.28
Ionic radius,A^{0}M^{2+}	—	0.80	0.73	—	0. 90	0.85	0.80	0.76	0.69
M^{3+}	0.69	0.63	0.62	0.62	0.63	0.63	0.56	—	—
1st.Ionisationenergy kJmol^{-1}	635	659	650	654	713	762	759	736	745
Density g.cc^{-1}	3	4.5	6.0	6.9	7.4	7.9	8.7	8.9	8.9
Melting point, K	1200	1660	1710	1600	1260	1535	1490	1450	1083
Boiling point,K	2730	3260	3450	2660	2150	3000	2900	2730	2600

1. Atomic radii :

The atomic radii of the transition elements of a particular series decrease slightly with increase in atomic number. In the case of these elements, the electrons are added successively to the inner (n-1)d orbitals and these electrons screen the outer ns electrons from the nucleus. The effective nuclear charge thus increases slightly. Therefore, there is a slight decrease in atomic radii.

In the first transition series the atomic radius value increases from Ni (1.24) to Cu (1.28). This is due to increased force of repulsion between added electrons which overcome effective nuclear charge (nuclear attraction force).

2. Ionisation enthalpy :

Ionisation enthalpies of transition elements increase across a transition series with increase in atomic number. This trend is, however, not regular. This is because though the nuclear charge increases, the screening effect of added electrons also increases. These two effects almost cancel each other. Ionisation enthalpies are in between s- and p- block elements and these elements are less electropositive than s-block elements.

Zinc, cadmium and mercury have comparativly higher ionisation enthalpy values, because they have stable outer electronic configuration, $(n-1)d^{10}ns^2$.

There is a general increase in the second ionisation enthalpy as the atomic number increases. The exception is manganese.

The second ionisation enthalpy of Cr and Cu involves the removal of one electron from the 4s orbital and another electron from the half-filled and completely filled $3d$-orbital respectively. The half-filled and filled orbitals have extra stability associated with them. Therefore, the second ionisation enthalpy of these elements are relatively larger. Eventhough transition elements form ionic compounds, the tendency is less than the s-block elements. In higher valency state, there is also a tendency for covalent bond formation.

3. Metallic properties :

Transition elements are all hard metals except mercury which is a liquid.These elements are harder and more brittle than s-block elements.

The atoms in these elements are held together by strong metallic bonds. The strength of such metallic bonding depends upon the interaction between the electrons in the outermost shell. In general, the greater the number of valence electrons available, the stronger is the bond. Further electrons in the *d*-orbitals form stronger metallic bonds. In transition elements, a minimum of three electrons, $(n-1)d^x\ ns^2$ are available for interaction with other atoms for the metallic bond formation.Again greater the number of unpaired electrons greater is the strength of the bond. In the first transition series Cr is very hard having five unpaired d-electrons. In the case of Zn_{30} $(3d^{10}4s^2)$, the metal is not hard because there is complete pairing of 3d electrons. In the third transition series $Hg_{80}(5d^{10}6s^2)$having complete pairing of 5d electrons exists as a liquid. These metals are, as expected, good conductors of heat and electricity.

4. Denisities, melting and boiling points :

The high densities of transition elements are due to their relatively small atomic radii. The densities of the first transition series elements increase across the period with the increase in atomic number.

Transition elements have high melting and boiling points. The high melting and boiling points are due to strong inter-atomic bonding which invloves the participation of both 4s and 3d electrons.

5. Variable oxidation states :

Transition elements show more than one oxidation states in their compounds. The oxidation states shown by the first transition series are given in (Table9.5)The most usual oxidation states are indicated as bold.

Tabe : 11.5 Different oxidation states of elements of first transition series

Elements ⟶	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
Oxidation states		+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**
	+3	+3	+3	**+3**	+3	**+3**	+3		
		+4	+4		+4		+4	+4	
			+5		+5				
				+6	+6	+6			
					+7				

Transition metals have their valence electrons in two different sets of orbitals ns and (n-1)d which have nearly the same energies. All these elements use their two ns electrons and thus show +2 oxidation states. When oxidation states are greater than +2, the unpaired **(n-1)**d electrons are involved in bonding in addition to the **ns** electrons. The elements thus show +3 and higher oxidation states besides +2 oxidation state. Scandium has exclusively an oxidation state of +3. In the case of tansition elements the oxidation states vary by one unit whereas in some of the p-block elements variable oxidation states marked by a difference of two units. This is due to the *inert pair effect*. Thallium shows oxidation states +1 and +3 and lead has two oxidation states +2 and +4.

The element manganese exhibits six number of oxidation states from +2 to +7 in its oxides MnO, Mn_2O_3, and MnO_2 and Mn_2O_5. In manganate, $MnO_4^{2-}$and permanganate, MnO_4^- its oxidation states are +6 and +7 respectively.

6. Formation of coloured compounds :

Majority of transition metal compounds are coloured. In contrast the compounds of s-and p-block elements are often colourless or are generally not strongly coloured.

When a compound absorbs light of a particular wavelength,it is able to promote and electron from one energy level to another higher energy level.

If E_1 is the energy associated with the electron in one energy level and E_2, the energy associated with the elctron in the higher energy level, then $E_2 - E_1 = \Delta E$ i.e. energy of absorbed light or radiation. Since $\Delta E = h\nu = h\frac{c}{\lambda}$, the energy of absorbed radiation is inversely proportional to the wavelength λ .

Coloured substances such as compounds of transition elements absorb in the visible region 4000–7500A^0or longer wavlength. Colourless substancees such as compounds of s– and p– block elements absorb in the u.v(ultraviolet) region below 4000A^0 or shorter wavelength.

The compounds of transition metals are coloured due to the presence of unpaired d-electrons in the partly filled d- orbitals of the metal. Here the light radiation is absorbed in the visible region (λ =4000 –7500 A^0) with a fairly small energy to promote d– electron to a higher energy level within the d- orbital, resulting d– d transitions of electrons. The colour of the compound is complementary to the observed colour. $CuSO_4.5H_2O$ is blue in colour since it absorbs orange colour from visible light (λ =6000 – 6500A^0) and emits the complementary colour blue (blue is complementary to orange).

Relation between absorbed and observed colours

Wave length (A^0)	Absorbed colour	Observed complementary colour
4000- 4500	violet	yellow
4500-5000	blue	orange
5000- 5500	green	red
5500- 6000	yellow	violet
6000- 6500	orange	blue
6500- 7000	red	green

The compounds of Sc^{3+} ($3d^0\ 4s^0$) and Zn^{2+}($3d^{10}\ 4s^0$) are colourless because they do not contain any unpaired *d*-electron .

In case of s– and p– block elements, there may not be a d– orbital, if any one is completely full. For such elements there cannot be any d–d transition of electrons. However, *s* or *p* electron can be promoted to a higher energy level provided the element receives much greater energy corresponding to wavelengths of ultraviolet region. Here there is no absorption of radiation from the visible region. Therefore compounds of s– and p–block elements do not appear coloured in the visible region.

Table : 11.6 Colour shown by some hydrated transition metal ions.

Ion	Outer electronic Configuration	No. of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{+}	$3d^4$	4	Violet
Mn^{2+}	$3d^5$	5	Pink
Fe^{3+}	$3d^5$	5	Yellow
Fe^{2+}	$3d^6$	4	Green
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^{+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

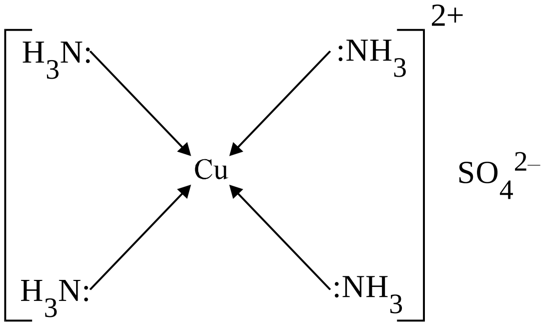
7. Formation of Complex compounds :

Transition metal ions have greater tendency to form complexes in contrast to s– and p–block elements.This is because the transition metals have (i) **small size of highly charged cations** and (ii) **vacant inner d–orbitals of approximately the same energy to accept lone pairs of electrons donated by the groups called ligands** and (iii) **high effective nuclear charge in the cation.**

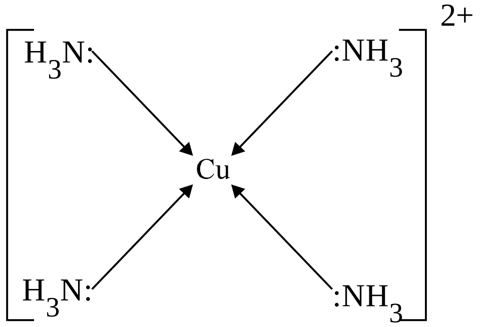
In a complex, a central atom or ion is surrounded by a number of other atoms, ions or molecules called **ligands.** The bonding between ligand and the transition metal ion can be either predominantly electrostatic or predominantly covalant.In many cases the attachment of ligands to the central metal atom or ion is by coordinate covalent bonds. The number of attached ligands is called **coordination number (C.N)** of the central metal atom or ion. The complex is said to be unstable if the ligands are easily removed. If it is difficult to remove the ligands from the complex, then the complex is stable one.

Complex ions such as cuprammine ion, $[Cu(NH_3)_4]^{2+}$ (tetramminecopper (II) ion), ferrocyanide ion, $[Fe(CN)_6]^{4-}$ (hexacyanoferrate(II) ion) and ferricyanide ion,$[Fe(CN)_6]^{3-}$ (hexacyanoferrate (III)) are well known.

In the complex tetrammine copper (II) sulphate,$[Cu(NH_3)_4]SO_4$ the complex ion is tetrammine copper (II) cation, $[Cu(NH_3)_4]^{2+}$. Here four ammonia molecules are bonded to the central Cu^{2+} by coordinate covalent bonds.Each ammonia molecule donates a lone pair of electrons located on its nitrogen atom to the Cu^{2+} ion.Ammonia molecules are called as ligands and are neutral in nature.



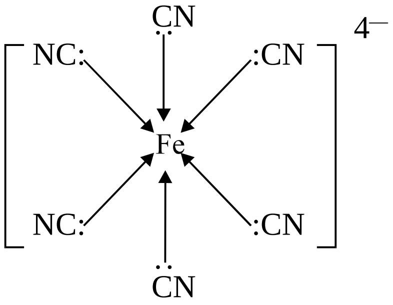
Tetrammine copper (II) sulphate



Tetrammine copper (II) cation

Since ammonia is a neutral ligand, the charge 2+ on Cu is transferred on to the total complex ion indicated by square bracket. In this complex, the complex ion is a cation and thus the complex is called a **cationic** complex. In this complex, the coordination number of Cu^{2+} is 4.

In the complex potassium ferrocyanide, $K_4[Fe(CN)_6]$ (IUPAC name: Potassium hexacyanoferrate (II)), the complex ion is hexacyanoferrate(II) ion, $[Fe(CN)_6]^{4-}$.



Hexacyanoferrate (II) anion

Since the complex ion is an anion the complex is called an **anionic complex**. In the complex the coordination number of Fe^{2+} is 6.

In the complex diammine silver chloride $[Ag(NH_3)_2]Cl$, the complex ion is

$$[H_3N: \rightarrow Ag \leftarrow :NH_3]^+$$

Diamminesilver (I) cation.

diammine silver(I) cation. two ammonia molecules are coordinated to the Ag^+ and hence the coordination number of Ag^+ is 2.

9. Paramagnetism :

Transition metals and their compounds are paramagnetic in nature i.e. they are attracted by magnetic field. Paramagnetism arises due to the presence of unpaired d- electrons. These electrons can be regarded as spinning around their axes, just as an electric current through a wire generates a magnetic moment. Magnetic moment due to electron spin is given by $\mu_{eff} = \sqrt{n(n+2)}$ where n = number of unpaired electrons.A substance become strongly paramagnetic if it contains more number of unpaired electrons.Mn^{2+} ($3d^5\,4s^0$) and Fe^{3+} ($3d^5\,4s^0$)are most paramagnetic, whereas Sc^{3+} ($3d^{10}\,4s^0$)and Zn^{2+} ($3d^{10}\,4s^0$) are diamagnetic in nature. A diamagnetic (non-magnetic) substance is repelled by a magnetic field. In such cases, the paired electrons possess opposite spins and cancel the magnetic moments.

In the case of Fe, Co and Ni the spins of the unpaired electrons are much pronounced.As a result, these elements are much more paramagnetic than the rest of the elements. These element are called **ferromagnetic** which means that they can be magnetised.

10. Catalytic activity :

Many transition metals and their compounds show catalytic activity due to their variable oxidation states. In the variable oxidation states these are capable of forming unstable intermediate compounds with catalysts. The metal ions while functioning as catalysts change their oxidation states. They can also provide greater surface area for the reactants to the absorbed and thus come closer to one another for the reaction to occur readily on their (catalyst)surfaces.

The catalytic activity of nickel in the hydrogenation of oils, the use of platinum and vanadium pentoxide, V_2O_5 in the contact process for manufacturing sulphuric acid and the use of iron in Haber's process for manufacturing ammonia are well known.

11. Alloys and interstitial compounds :

Transition metals form intermetallic alloys because they have atoms of nearly the same size. Their atoms can mutually substitute each other in the metal lattice. They also form interstitial alloys like stainless steel, chrome steel etc.

Transition metals form interstitial compounds. In interstitial hydrides, the hydrogen is accommodated in the lattice of the transition element. Interstitial nitrides and carbides of transition metals are known, which are similar to interstitial hydrides in structure.

11.3 POTASSIUM DICHROMATE $K_2Cr_2O_7$:

It is an important oxidant used for preparation of many azo compounds. Besides it finds its use in leather industry.

Preparation :

Steps involved

(i) Chromite ore ($FeCr_2O_4$) is fused with sodium or potasium carbonate in free access of air producing sodium chromate.

$$4FeCr_2O_4 + Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

(ii) The yellow solutions of Sodium dichromate is filtered and acidified with Sulphuric acid to give a solution from which orange sodium dichromate $Na_2Cr_2O_7.2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$

(iii) The hot saturated solution of $Na_2Cr_2O_7$ is treated with KCl to produce potasium dichromate. Sodium dichromate is more soluble than potasium dichromate.

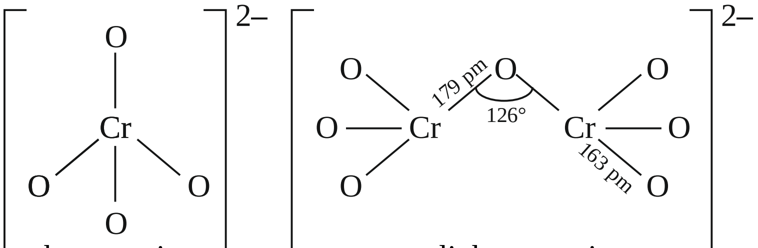
$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium chloride precipitates out from the hot solution and is removed by filtration. On cooling the mother liquor orange crystals of $K_2Cr_2O_7$ crystllise out. The oxidation state of chromium in CrO_4^{2-} and $Cr_2O_7^{2-}$ is the same. These ions are interconvertible in aqueous solution depending upon pH of the solution.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

Structure of CrO_4^{2-} & $Cr_2O_7$2–



chromate ion dichromate ion

Physical properties :

Potasium dichromate form orange red crystals melting at 671K. It is moderately soluble in cold water but highly soluble in hot water.

Chemical properties :

1. On strong heating it decomposes to chromic oxide and oxygen

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

2. It reacts with hydrochloric acid evolving chlorine

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

3. When heated with Conc. H_2SO_4 and a soluble chloride such as NaCl, gives red vapours of chromyl chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 2H_2O$$

4. In volumetric analysis it is used as a primary standard. It is a powerful **oxidising agent**. In acidic solution ie the presence of dilute H_2SO_4 its oxidising action is represented as

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

Some oxidation reactions are given below.

(i) It liberates I_2 from KI solution

$$\begin{array}{l} 6I^- \rightarrow 3I_2 + 6e \\ Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3I_2 \end{array}$$

(ii) It oxidises Fe^{2+} to Fe^{3+}

$$\begin{array}{l} 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e \\ Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

(iii) It oxidises H_2S to S & SO_2 to sulphuric acid.

$$\begin{array}{l} 3H_2S \rightarrow 6H^+ + 3S + 6e \\ Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O \end{array}$$

$$\begin{array}{l} 3SO_2 + 6H_2O \rightarrow 3SO_4^{2-} + 12H^+ + 6e \\ Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 2Cr^{3+} + H_2O + 3SO_4^{2-} \end{array}$$

(iv) It oxidises sulphite ion to SO_4^{2-} ion.

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

5. In dichromate solution $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

Orange red Yellow

(a) On addition of alkali the orange colour changes to yellow

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

Orange red Yellow

(b) On addition of acid to the above solution the yellow colour again changes to orange red.

$$2K_2CrO_4 + 2H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Yellow Orange red.

Uses :

(i) In volumetric analysis for estimation of Fe^{2+}, I^- ions.

(ii) In the preparation of several chromium compounds like $ZnCrO_4$, $PbCrO_4$ etc.

(iii) In photography.

(iv) As a cleansing agent ($K_2Cr_2O_7$ + Conc H_2SO_4) for glassware.

(v) In dyeing, chrome tanning etc.

11.4 POTASSIUM PERMANGANATE ($KMnO_4$) :

Method of preparation :

(i) It is prepared from K_2MnO_4 by the action of dil H_2SO_4

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2\downarrow + 2H_2O$$

MnO_2 is removed by filtration. Potassium permanganate being less soluble than K_2SO_4, crystallises out first.

(ii) Solid manganese (IV) oxide is fused with KOH and the melt is stirred in contact with air

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Chlorine gas is then passed through green solution of potassium manganate to produce potassium permanganate.

$$2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$$

Since KCl is more soluble than $KMnO_4$, on concentrating the solution $KMnO_4$ separates out first leaving behind KCl in solution.

(iii) **By electrolysis :** The manganate solution is taken in the anodic compartment and the cathodic compartment is filled with dilute alkali solution. Oxidation is carried out electrolytically using Ni anode and iron cathode.

Reaction at anode :

The manganate ion is oxidised to permanganate ion in the anodic compartment.

$$MnO_4^{2-} \xrightarrow[\text{oxidation in}]{\text{Electrolytic}} MnO_4^-$$

manganate ion alkaline solution permanganate ion

Reaction at cathode :

$$2H^+ + 2e \rightarrow 2H \rightarrow H_2$$

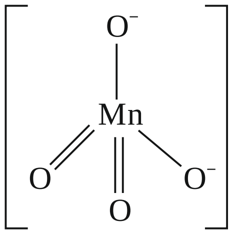
From ionisation
of water

Physical properties :

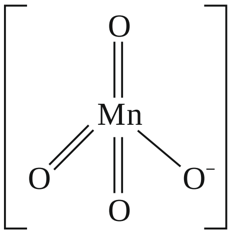
Potasium permanganate forms dark purple (almost black) crystal isostructural with those of $KClO_4$.

It is not very much soluble in water, about 6.4 gms dissolving in 100 gms of water at 293K.

Both manganate and permanganate ions are tetrahedral. The green manganate is paramagnetic with one unpaired electron whereas the purple permanganate is diamagnetic. The π bonding is due to overlap of p-orbital of oxygen with d-orbital of manganese.



Tetrahedral manganate ion (green)



Tetrahedral permanganate ion (purple)

Chemical properties :

1. It decomposes evolving oxygen when heated alone or with alkali.

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$$

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2$$

2. When treated with Conc H_2SO_4 it produces Mn(VII) oxide which decomposes explosively when heated.

$$2KMnO_4 + H_2SO_4 \rightarrow Mn_2O_7 + K_2SO_4 + H_2O$$

3. It is a powerful oxidising agent. A powdered mixture of sulphur, charcoal and potassium permanganate is like gunpowder. It burns when heated and explodes when rubbed. Similarly a powdered mixture of $KMnO_4$ and oxalic acid catches fire spontaneously.

4. $KMnO_4$ is a strong **oxidising agent** in solution. The course of reaction depends upon the nature of the solution in which the reaction is carried out i.e. whether it is acidic, neutral or alkaline.

(a) **In alkaline solution :** MnO_4^- ion is first reduced to MnO_4^{2-} ion and then to manganese (IV) oxide. The colour of the solution changes from purple to green and finally becomes colourless.

$$2MnO_4^- + 2OH^- \rightarrow 2MnO_4^{2-} + H_2O + [O]$$

$$2MnO^{2}{}_{4}^{-} + 2H_2O \rightarrow 2MnO_2 + 4OH^- + 2[O]$$

$$2MnO_4^- + H_2O \xrightarrow{\text{alkali}} 2MnO_2 + 2OH^- + 3[O]$$

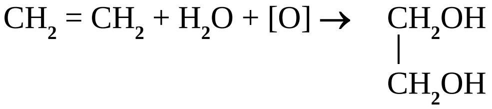
In alkaline solution as is evident from the above overall reaction, 2 molecules of $KMnO_4$ give 3 atoms (or 6 equivalents) of available oxygen. Hence the equivalent mass of $KMnO_4$ is alkaline solution as an oxidising agent is one third its molar mass.

Example :

(1) Iodides are oxidised to Iodates.

$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(2) Ethylene is oxidised to glycol.



$$CH_2 = CH_2 + H_2O + [O] \rightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

(3) Toluene is oxidised to benzoic acid.

$$C_6H_5 - CH_3 + 3\,[O] \rightarrow C_6H_5 - COOH + H_2O$$

(b) **In neutral solution :** The reaction is almost same as in case with faintly alkaline solution.

$$2MnO_4^- + H_2O \rightarrow 2OH^- + 2MnO_2 + 3[O]$$

Examples :

(1) H_2S is oxidised to sulphur.

$$2MnO_4^- + 3H_2S \rightarrow 2MnO_2 + 3S + 2H_2O + 2OH^-$$

(2) Thiosulphate is oxidised to sulphate and sulphur.

$$2MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 3S + 2OH^-$$

(c) **In acidic solution :** In acidic solution MnO_4^- ion is reduced to Mn(II) ion.

$$2MnO_4^- + 6H^+ \rightarrow Mn^{2+} + 3H_2O + 5[O]$$

The best acid to be used is dilute sulphuric acid, Permanganate titrations with HCl are not satisfactory since HCl is oxidised to Cl_2 during the titration.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

Most of the volumetric analysis in carried out in acid medium. The end point is marked by change of colour from purple (MnO_4^-) to almost colourless [Mn (II) ion]

Examples :

(1) Fe^{2+} ion is converted to Fe^{3+} ion.

$$\underset{\text{green}}{5Fe^{2+}} + MnO_4^- + 8H^+ \rightarrow 2Mn^{2+} + 4H_2O + \underset{\text{yellow}}{5Fe^{3+}}$$

(2) I_2 is liberated from KI.

$$10I^- + 2\,MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(3) Oxalic acid is oxidised to CO_2.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 10\,CO_2$$

(4) Sulphites are oxidised to sulphates

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3\,H_2O$$

(5) H_2S is oxidised to sulphur

$$H_2S \rightarrow 2H^+ + S^{2-}$$

$$5S^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$$

(6) SO_2 is oxidised to H_2SO_4

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

(7) Nitrites are oxidised to Nitrates.

$$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

Uses :

(1) In qualitative analysis for detection of halides, sulphites, oxalates etc.

(2) In volumetric estimations.

(3) In the manufacture of saccharine, benzoic acid, acetaldehyde etc.

(4) As a disinfectant.

(5) Alkaline $KMnO_4$ soln. is Bayer's reagent which finds its use in organic reactions.

CHAPTER (11) AT A GLANCE

1. A d-block element or transition element may be defined as one that has a partially filled inner d-orbital. The general configuration for transition element is $(n-1)\ d^{1-10}\ ns^{1-2}$.
2. Transition elements are solid metals hard, malleable and ductile. They have high densities, high melting points and boiling point. They show variable valencies and variable oxidation states.
3. Transition elements form coloured as well as complex compounds.
4. Transition elements and their compounds are paramagnetic in nature and show catalytic activity.
5. Transition metals form intermetallic alloys and form interstitial compounds.
6. Potassium dichromate is a very important oxidising agent. It finds application in volumetric analysis as a primary standard and a powerful oxidising agent in acidic solution. It is used in photography, dyeing and chrome tanning.
7. Potassium permanganate is another useful compound in qualitative and quantitatve analysis. It is a strong oxidising agent in solution. The oxidation reactions are carried out in acidic, alkaline and neutral medium. Potassium permanganate is used as a disinfectant. It finds its application in the manufacture of saccharine, benzoic acid, acetaldehyde etc. Alkaline potassium permangnate is known as Bayer's reagent.

QUESTIONS

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

1. Define a transition element.
2. Mention two characteristic feature of transition elements.
3. What is the oxidation number of Mn in MnO_4^-?
4. What is the oxidation number of Cr in $Cr_2O_7^{2-}$?
5. What is the reason of paramagnetism in transition metals ?
6. What is the magnetic property of dipositive Zinc ?
7. What is the general electronic configuration of d-block elements ?
8. What is the maximum oxidation state of manganese ?
9. Name a transition element which is not a solid.
10. What happens when acid is added to the yellow coloured potassium chromate solution?

B. Short anwer type. (2 marks each)

1. Transition elements form alloys easily. Give reasons.
2. Why most of the compounds of transitional elements are paramagnetic ?

3. Why Zinc salts are colourless ?
4. Why Cu^{1+} salts are colourless ?
5. Write the structure of chromate and dichromate ions ?
6. What happens when potassium dichromate is heated ?
7. Mention two uses of potassium dichromate.
8. Write the structure of manganate and permanganate ions.
9. Explain why conversion of chromate ion to dichromate ion is not a redox reaction.
10. Mention two important uses of potassium permanganate.

C. Short answer type. (3 marks each)

1. Explain why $CuSO_4$ is paramagnetic while $ZnSO_4$ is diamagnetic.
2. Why do transition metal ions form complexes ?
3. Transition metals and their compounds act as catalysts- Explain.
4. What happens when $KMnO_4$ is heated alone and with alkali.
5. Why are transition metal compounds coloured ?
6. What happens when H_2S gas is passed through acidified $K_2Cr_2O_7$ solution?
7. What is the equivalent mass of $KMnO_4$ in alkaline solution ? Explain.
8. What are the uses of potassium permanganate ?

D. Long answer type. (7 marks each)

1. What are transition elements ? Describe any four characteristic properties of transition elements.
2. Describe the preparation of potassium permanganate. How does acidified potassium permagnate solution react with

   (a) KI (b) SO_2 (c) iron (II) (d) H_2S
3. Discuss the oxidising action of KMnO4 in acidic, alkaline and neutral solutions with suitable examples.
4. Describe the preparation of potassium dichromate from iron chromite ore. Discuss the effect of pH on a solution of potassium dichromate.
5. Discuss the oxidising action of $K_2Cr_2O_7$ and write the ionic equations for its reaction with (a) KI (b) Fe^{2+} (c) H_2S.

E. Multiple choice type. (Choose correct answers)

1. Which of the following is a transition element ?

   (a) Ca (b) Al

   (c) Co (d) Na
2. The d-block elements form alloys among themselves, because.

   (a) their atomic sizes are nearly same (b) they have unpaired electrons

   (c) their ionisation enthalpies are similar (d) they are all metals.

3. Which of the following statements(s) is (are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?
   (a) A deep red vapour is evolved.
   (b) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4.
   (c) Chlorine gas is use evolved.
   (d) Chromyl chloride is formed.

4. Out of the following indentify the d-block element.
   (a) Ca (b) U
   (c) Mn (d) Al

5. Which of the following statements about transition metals in wrong ?
   (a) They form coloured compounds
   (b) All their compounds are diamagnetic
   (c) They exhibit variable valency.
   (d) They contain partially filled d-orbitals.

6. Acidified potassium permanganate solution is decolourised by
   (a) Bleaching powder (b) White vitriol
   (c) Mohr's salt (d) Microcosmic salt.

7. Which one of the metals does not form amalgam ?
   (a) Zn (b) Ag
   (c) Cu (d) Fe

8. Which ion is not coloured ?
   (a) Cu^+ (b) Cr^{2+}
   (c) Co^{2+} (d) Cr^{3+}

9. Paramagnetic behaviour in transition metal is due to the presence of
   (a) lone pair of electron (b) even number of electrons
   (c) unpaired electron (d) odd number of electrons.

10. The general electronic configuration of transition elements is
   (a) $(n-1)d^{1-5}$ (b) $(n-1)d^{1-10}ns^1$
   (c) $(n-1)d^{1-10}ns^{1 \text{ or } 2}$ (d) none

ANSWER TO MULTIPLE CHOICE QUESTIONS

1. (c) 2. (a) 3. (a) (b) (d) 4. (c) 5. (b) 6. (c) 7. (d) 8. (a)
9. (c) 10. (c) 11. (c)

❑❑❑

CHAPTER - 12

THE f-BLOCK ELEMENTS

THE LANTHANOIDS AND THE ACTINOIDS

12.1 INTRODUCTION :

The elements in which the last electron enters the ante-penultimate energy level, i.e. (n–2) f-orbitals are called **f-block elements**. They are also regarded as inner transition metals / rare earth metals (due to their occurence in traces in nature).

The f-block elements consists of two series :

Lanthanoids : The group of 14 elements following Lanthanum (Z = 58 to 71) are known as Lanthanoids.. Lanthanum though a d-block element, is included in any discussion of lanthanoids because it closely resembles them in its properties. The study of lanthanoids is comparatively easier because they show only one stable oxidation state.

Actinoids : The group of 14 elements following Actinium (Z = 90 to 103) in which the last electron enters into the ‘5f’ orbital are known as “Actinoids”. Actinium also resembles them in its properties. The elements of this series are radioactive and exhibit complicated gradation in properties. They show wide range of oxidation states.

12.2 THE LANTHANOIDS :

12.2.1 Electronic Configuration :

Lanthanoids possess common electronic configuration $6s^2\ 5d^{0-1}\ 4f^{1-14}$ (Table 12.1) The exceptional electronic configuration of few elements can be explained on the basis of stability.

(i) The electronic configuration of Cerium (Z = 58) is $4f^2\ 5d^0\ 6s^2$.

(ii) Europium (Z = 63) has electronic configuration $4f^7\ 6s^2$ and that of Gadolinium is $4f^7\ 5d^1\ 6s^2$, because of the extrastability due to half-filled orbitals.

(iii) Ytterbium (Z = 70) has electronic configuration $4f^{14}\ 6s^2$ and Lutetium (Z = 71) is $4f^{14}5d^16s^2$, which is explained on the basis of extra stability of the completely filled 4f orbitals.

Table 12.1 : Electronic Configuration and Radii of Lanthanum and Lanthanoids

Atomic Number	Name	Symbol	Electronic Configuraton				Raddi / pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^{\circ}$		187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^{\circ}$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$		-	-

12.2.2 Atomic and Ionic sizes :

In the lanthanoid series there is a regular decrease in atomic and ionic radii from Lanthanum to Lutetium. (Table 12.1, Fig. 12.1). The cumulative effect of this regular decrease (contraction) in the atomic and ionic radii of lanthanoids with increasing atomic number is known as **'Lanthanoid contraction'**. Lanthanoid contraction is a unique feature in the chemistry of Lanthanoids.

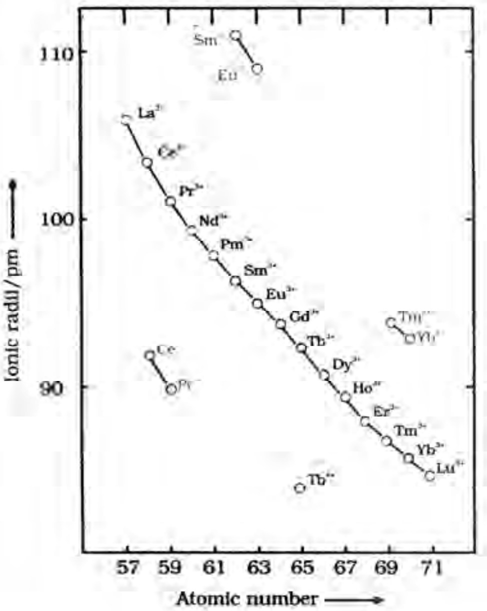


Fig. 12.1 : Trends in ionic radii of lanthanoids

Cause of Lanthanoid contraction :

Lanthanoid contraction is attributed to the imperfect shielding of one electron by another in the same sub-shell (i.e. 4f), as the '4f' orbital is more diffused in space. This imperfect shielding is unable to counter balance the effect of the increased nuclear charge. So the net result is a contraction in size.

Consequences of Lanthanoid contraction :

(1) Similarity in size of elements of same group of second and third transition series :

The size of an atom of third transition series is nearly same as that of the atom of the element lying in the same group of the second transition series, due to lanthanoid contraction.

Ex : $_{40}$Zr – 160 pm $_{41}$Nb – 146 pm

and $_{72}$Hf – 159 pm and $_{73}$Ta – 146 pm

(2) Difficulty in separation Lanthanoids :

The change in sizes of the lanthanoid ions along the series are very small. So their chemical properties are similar with each other and it is difficult to separate the lanthanoids in the pure state. However, the slight difference in sizes results in differences in properties like solubility, hydration, complex ion formation which enable the separation of lanthanoid elements individually by ion exchange methods.

12.2.3 Oxidation States :

Lanthanoids possess common oxidation state +3.

The Lanthanoids which acquire a stable configuration of f^0, f^7 or f^{14} by losing 2 or 4 electrons, they show +2 or +4 oxidation state.

Ex. Eu^{2+} [Xe] $4f^7$; Yb^{2+} [Xe] $4f^{14}$

Ce^{4+} [Xe] $4f^0$; Tb^{4+} [Xe] $4f^7$

Exceptions :

Pr^{4+} [Xe] $4f^1$; Nd^{2+} [Xe] $4f^4$; Sm^{2+} [Xe] $4f^6$;

Dy^{4+} [Xe] $4f^8$; Nd^{4+} [Xe] $4f^2$

The lanthanoids in +2 or +4 oxidation state tend to show +3 oxidation state by loss or gain of electron.

Sm^{2+}, Eu^{4+} and Yb^{2+} ions loose electrons in solutions to show +3 oxidation state and are good reducing agents.

Ce^{4+}, Tb^{4+} in their aqueous solution are good oxidising agents as they gain electron and change to +3 oxidation state.

Though the formation of Ce^{4+} is favoured by its noble gas configuration, it has a tendency to show +3 oxidation state and enables it to behave as a strong oxidant.

The E^0 value for Ce^{4+} / Ce^{3+} is + 1.74 V. So it can oxidise water at a very slow rate and Ce (IV) is a good analytical reagent. Praseodymium, Neodymium, Terbium and Dysprosium exhibit +4 oxidation state only in oxides. Their oxides have general formula MO_2. (M = Pr, Nd, Tb or Dy)

12.2.4 General characteristics of Lanthanoids :

1. **Softness :** All the lanthanoids are silvery white soft metals. They tarnish rapidly in air. Their hardness increases with increasing atomic number. Samarium is exceptionally hard like steel.

2. **Melting points :** The melting points of lanthanoids range between 1000K to 1200K. Samarium has melting point 1623K.

3. **Thermal and Electrical conductivity :** The lanthanoids have metallic structure. They are good conductors of heat and electricity.

4. **Density :** They have high densities in the range of 6.77 to 9.77 $g.cm^{-3}$. Their density and other properties vary smoothly with increasing atomic number. Europium and Ytterbium show exceptions.

5. **Colour :** Lanthanoids are silvery white metals. Most of the trivalent metal ions are coloured both in the solid state and in aqueous solution. This is due to f-f transitions of the electrons present in partly filled f–orbitals. The lanthanoid ions with ‘n’ electrons or (14–n) electrons in f-subshells have similar colour.

   Ex: (a) La^{3+} and Lu^{3+} are colourless, n = 0

   (b) Sm^{3+} and Dy^{3+} are yellow, n = 5

   (c) Eu^{3+} and Tb^{3+} are pink, n = 6

6. **Magnetic behaviour :** The lanthanoid ions are paramagnetic due to presence of unpaired electrons in the 4f subshell, except La^{3+}, Ce^{4+} (f^0 configuration) and Lu (f^{14} configuration). The paramagnetism is maxium in Neodymium.

(7) **Ionisation Enthalpy :** The first IE of lanthanoids are 600 kJ mol^{-1} and second IE are 1200 kJ mol^{-1}. The second Ionisation Enthalpy of Lanthnoids are comparable with that of Ca^{2+}. That is why the first few members of the series have reactivity similar to Calcium.

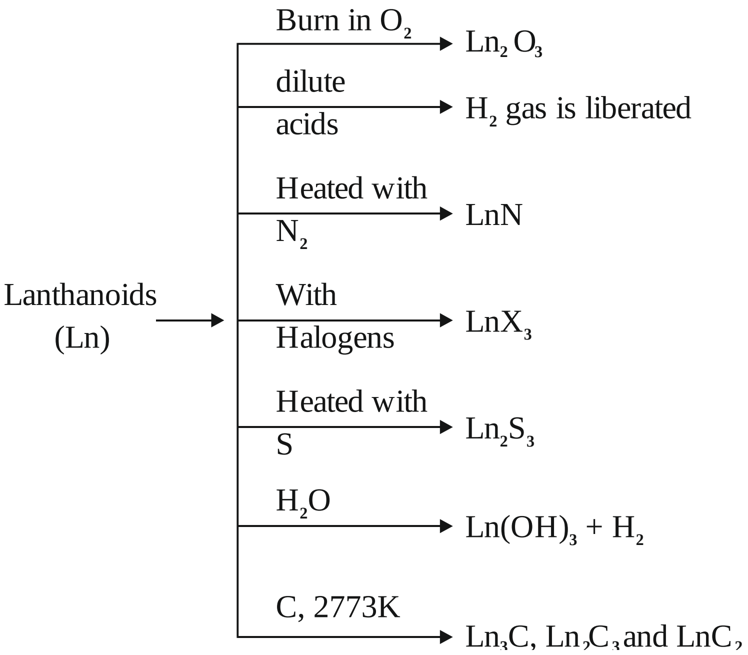
Lanthanum, Gadolinium and Lutetium possess abnormally low values of 3rd Ionisation Enthalpy because removal of third electron leads to empty, half-filled and completely filled f-orbitals respectively.

(8) Chemical behaviour : As discussed previously, the earlier members of lanthanoid series have reactivity similar to Calcium with increasing atomic number they resemble Aluminium in their chemical behaviour.

(a) With non-metals : They combine with hydrogen on gentle heating and form carbides on heating with carbon. With halogens respective halides are formed. Oxides and hydroxides of the type M_2O_3 and $M(OH)_3$ are formed due to reaction with oxygen and water respectively, which are basic in nature.

(b) With dilute acids : They react with dilute acids to liberate hydrogen gas.

SUMMARY



12.2.5 Uses :

(1) **Mischemetal :**

Composition : 50% Cerium, 40% Lanthanum and other Lanthanoids, 5% iron, traces of S, C, Ca and Al.

It is used in making magnesium-based alloy. Because of its pyrophoric nature (tendency to emit spark when struck), it is employed in production of bullets, shells and flints.

(2) Their oxides are used for making UV protective lenses.

(3) Ceric sulphate is a well-known oxidising agent.

12.3 THE ACTINOIDS :

As mentioned earlier, Actinoids are radioactive. The earlier members of the series have relatively long half-lives and the later ones have half-lives ranging from a day to 3 minutes for Lawrencium.

12.2.1 Electronic Configuration :

The general electronic configuration of Actinoids is $7s^2\ 6d^{0-1}\ 5f^{1-14}$ (Table 12.2). The actinoids have their stable configuration for f^0, f^7 and f^{14} occupancy. So there is certain irregularity in their electronic configuration.

Ex : Am – [Rn] $7s^2 5f^7$

Cm – [Rn] $7s^2 6d^1 5f^7$

The 5f orbitals are not as buried as 4f orbitals. So they can participate in bonding to a greater extent.

Table 12.2 : Some properties of Acitinium and Actinoids

Aotmic Number	Name	Symbol	Electronic congiguration			Raddi/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	-	-
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$		
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	-	-
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	-	-
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	-	-

12.3.2 Oxidation states :

The 5f, 6d and 7s subshells are of comparable energies. So the actinoids show a greater range of oxidation states (Table 12.3).

Table 12.3 : Oxidation states of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

However, like lanthanoids the +3 oxidation state is common to all of them. As evident from the table the oxidation state of actinoids increases upto the middle of the series and then decreases for the succeeding elements. This is because the 5f, 6d and 7s subshells are of comparable energies and all their electrons can take part in bond formation.

12.3.3 Ionic sizes :

The actinoids also show **"actinoid contraction"** (like lanthanoids) due to the poor shielding effect of '5f' subshells. As a result, the radii of these atoms or ions decrease across the series. (Table 12.2)

12.2.4 General characteristics of Actinoids :

1. The actinoid metals are all silvery in appearance.
2. **Structure :** The actinoids display a variety of structures due to irregularities in metallic radii.
3. **Colour :** The actinoid cations are coloured due to f–f transition. Those ions having no 5f-electron or seven 5f-elecrons (i.e. exactly half-filled f-subshell) are colourless.

Ex :

Ac^{3+}	$5f^0$ colourless	Am^{3+}	$5f^6$ pink
U^{3+}	$5f^3$ red	Cm^{3+}	$5f^7$ colourless
Np^{3+}	$5f^4$ blue	Th^{3+}	$5f^0$ colourless
Pu^{3+}	$5f^5$ violet	etc.	

4. **Melting and Boiling points :** Actinoids have high melting and boiling points. But they do not show any regular trend.
5. **Density :** They have high densities.
6. **Ionization enthalpies :** The actinoids have lower ionization enthalpies than lanthanoids because '5f' is less penetrating than '4f' and hence is more effectively shielded from nuclear charge.
7. **Electropositive character :** Actinoids are highly electropositive like the Lanthanoids.

8. **Magnetic behaviour :** The actinoids are strongly paramagnetic. The magnetic susceptibility of actinoids are higher than the lanthanoids.

9. **Chemical behaviour :**

   (a) Actinoids react with boiling water to give oxides and hydroxides.

   (b) They react with most of the non-metals at moderate temperature.

   (c) They are rendered passive by action of nitric acid.

12.3.5 Uses of Actinoids :

(1) Thorium : It is used as a nuclear fuel, anti-carcinogen and for manufacture of mantles of incandescent lamps.

(2) Uranium : It is used as nuclear fuel, textiles, ceramics, medicines and to impart colour (green) to bulbs.

(3) Plutonium : It is used in nuclear reactors and manufacture of atomic bombs.

12.4 COMPARISON BETWEEN LANTHANOIDS AND ACTINOIDS :

Though Lanthanoids and Actinoids resemble each other in certain properties there are also some dissimilarities between them.

Similarities :

(1) +3 oxidation state is common for both the series of elements.

(2) Both are electropositive and have low value of Ionisation Enthalpy.

(3) Both exhibit magnetic and spectral properties.

(4) Lanthanoids show ‘Lanthanoid contraction’ and Actinoids show ‘Actinoid contraction’.

Differences :

(1)	They are non-radioactive. Exception-Promethium.	(1)	They are radioactive.
(2)	Besides +3 oxidation state they show +2 and +4 oxidation states only in a few cases.	(2)	They show higher oxidation states +4, +5, +6, +7 besides +3 oxidation state
(3)	Do not form oxocation.	(3)	UO_2^{+}, UO_2^{2+}, PuO_2^{2+} etc. oxocation are formed by them.

CHAPTER (12) AT A GLANCE

1. The elements in which last electron enters the ante-penultimate energy level, i.e. (n–2) f-orbitals are called f-block elements.
2. The group of 14 elements following Lanthanum (Z = 58 to 71) are known as Lanthanoids.
3. The group of 14 elements following Actinium (Z = 90 to 103) in which the last electron enters into the '5f' orbital are known as Actinoids.
4. The general electronic configuration of Lanthanoids is $6s^2 5d^{0-1} 4f^{1-14}$ and of Actinoids is $7s^2 6d^{0-1} 5f^{1-14}$.
5. Due to imperfect shielding of one '4f' electron by another of same sub-shell there is regular decrease in the atomic and ionic radii of lanthanoids with increasing atomic number. This phenomenon is known as 'Lanthanoid contraction'.
6. Both Lanthanoids and Actinoids show common oxidation state +3. The Lanthanoids also show +2 and +4 oxidation state whereas the higher oxidation states +4, +5, +6 and +7 are shown by actinoids.
7. Ce (IV) is used as good analytical reagent because Ce^{4+}/Ce^{3+} has E^0 value + 1.74 V.
8. The trivalent Lanthanoids and Actinoid ions are coloured due to f-f transitions of the electrons present in partly filled f-orbitals. But those with f^0, f^7 and f^{14} configuration are colourless.
9. Mischmetal is an alloy of cerium. Lanthanides are used in making magnesium-based alloy with a wide range of applications.

QUESTIONS

A. Short answer type (1 mark each) :

1. What is the general electronic configuration of lanthanoids?
2. Write down the electronic configuration of

   (a) Lu^{2+} (b) Pm^{3+}
3. Indentify the atomic number of the inner transition elements.

   24, 35, 59, 65, 73, 87, 91, 102, 105
4. What are the different oxidation states exhibited by lanthanoids?
5. Name an important alloy containing some of the lanthanoid metals.
6. Write the electronic configuration of (a) Yb^{2+} (b) Sm^{2+}
7. Which lanthanoid shows maximum paramagnetism.

8. Name the common mineral containing lanthanoids.
9. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

B. Short answer type (2 marks each) :

1. Define Lanthanoid contraction. Write two consequences of it.
2. 'Eu' and 'Yb' show +2 oxidation state, whereas +4 oxidation state is shown by Ce and Tb. Why?
3. Explain with correct reason whether Sm^{2+} and Eu^{2+} act as good oxidising or reducing agent.
4. La^{3+} and Lu^{3+} are colourless, whereas Sm^{3+} and Eu^{3+} are coloured. Why?
5. Mention important uses of uranium and plutonium.
6. Chemistry of all lanthanoids is quite similar. Why?
7. Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

   (Hint : The 5f electrons are more effectively shielded from nuclear charge)
8. Give reason why : Chemistry of all the lanthanoids is quite similar.

C. Short answer type (3 marks each) :

1. Compare the chemistry of actinoids with that of lanthanoids with special reference to :

   (a) electronic configuration (b) atomic and ionic radii (c) oxidation states.
2. Name an important alloy containing some of the lanthanoid metals. Mention its uses.
3. Which is the last element in the series of Actinoids? Write its electronic configuration. Comment on its oxidation states.
4. La $(OH)_3$ is more basic than Lu $(OH)_3$, why ?

   (Hint : As the size of Lanthanide ions decrease from La^{+3} to Lu^{3+}, the covalent character of the hydroxide increases).
5. Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents, but an aqueous solution of Ce^{4+} is a good oxidising agent.

D. Long answer type (7 marks each) :

1. (a) Write the general electronic configuration of lanthanoids.

   (b) Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents ?

   (c) Why is the separation of lanthanoid elements difficult ?
2. Compare the chemistry of actinoids with that of lanthanoids with special reference to

   (a) electronic configuration (b) oxidation state

   (c) atomic and ionic sizes (d) chemical reactivity

E. Multiple choice questions (Choose the correct answer) :

1. Which of the following pairs have same size.

(a) Zn^{2+}, Hf^{4+} (b) Fe^{2+}, Ni^{2+}

(c) Zr^{4+}, Ti^{4+} (d) Zr^{4+}, Hf^{4+}

2. The main cause of Lanthanide contraction is

(a) Poor shielding of one of the 4f-electrons by another in the subshell.

(b) Greater shielding of 5d electrons by 4f electrons.

(c) Poorer shielding of 5d electrons by 4f electrons.

(d) Effective shielding of one of the 4f electrons by another in the subshell.

3. The maximum oxidation state exhibited by actinide ions is

(a) +4 (b) +5

(c) +7 (d) +8

4. The most common mineral containing lanthanoids is :

(a) pyrites (b) monazite sand

(c) rock salt (d) none

5. Which is the strongest base among the following:

(a) La $(OH)_3$ (b) Lu $(OH)_3$

(c) Yb $(OH)_3$ (d) Ce $(OH)_3$

6. The general electronic configuration of inner transition elements is :

(a) $ns^2 (n–1) d^{0–1} (n–2)f^{1-14}$ (b) $ns^2 (n–1) d^{1–2} (n–2)f^{0-14}$

(c) $ns^2 (n–1) d^{0–1} (n–2)f^{0-14}$ (b) $ns^2 (n–1) d^1 (n–2)f^{1-14}$

7. Which of the following oxidation states is the most common among the lanthanoids?

(a) + 4 (b) +2

(c) +5 (d) +3

8. The lanthanoid ions are coloured due to

(a) p–p transition (b) d–d transition

(c) d–f transition (d) f-f transition

ANSWER

1. (d), 2. (a), 3 (c), 4. (b), 5. (a), 6. (a), 7. (d), 8. (d)

❑❑❑

UNIT - IX

CHAPTER - 13

CO-ORDINATION COMPOUNDS

13.1 NORMAL SALT :

A **normal salt** is *formed by the replacement of all replaceable hydrogen atoms in an acid by the metal atoms.* Thus a **normal salt** is formed by the complete neutralisation of a strong acid by a strong base. A normal salt gives almost a neutral solution in water.

Some examples are : NaCl, K_2SO_4, $NaNO_3$ etc.

All types of salts are fully ionised when dissolved in water. When NaCl dissolves in water, it ionises fully while water ionises slightly.

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

$$H_2O \rightleftharpoons H^+ + OH^-$$

H^+ ion has no tendency to combine with Cl^- ions as HCl is fully ionised. Similarly, OH^- ions have no tendency to combine with Na^+ ions as NaOH is fully ionised.

There are certain exceptions. For example, though Na_2CO_3 and $CuSO_4$ are normal salts their aqueous solutions are basic and acidic respectively. Due to hydrolysis,

$$Na_2CO_3 + 2H_2O \longrightarrow 2(Na^+ + OH^-) + H_2CO_3.$$

Due to free OH^- the solution is alkaline. Similarly, solutions of copper (II) salts are acidic due to hydrolysis.

On evaporation of solutions containing two or more salts in simple molar proportions, it is found that crystals of new compounds separate out. These new compounds are of two types namely (a) Double salts (b) Co-ordination compounds.

13.2 DOUBLE SALTS :

The compounds which when dissolved in water or any other solvent decompose into their constituent compounds and which exist only in crystal lattices are known as **double salts**. The physical and chemical properties of these compounds are almost the same as those of individual compounds.

Examples include

(i) $Al_2(SO_4)_3.K_2SO_4.24H_2O$ (Potash Alum)

(ii) $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)

(iii) $KCl.MgCl_2.6H_2O$ (Carnallite)

So a solution of potash alum shows the same physical and chemical properties as a mixture of solutions of Aluminium sulphate and Potassium sulphate.

13.3 CO-ORDINATION COMPOUNDS :

The compounds which when dissolved in water or any other solvent retain their identity are known as **co-ordination compounds**. The physical and chemical properties of these compounds are completely different from those of the constituents. Some common examples are

(i) $[Co(NH_3)_6]Cl_3$ - Hexaamminecobalt (III) chloride

(ii) $K_4[Fe(CN)_6]$ - Potassium hexacyanoferrate (II)

(iii) $[Ni(NH_3)_6]Cl_2$ - Hexaamminenickel (II) chloride

Hexaamminenickel (II) chloride ionises in solution as

$$[Ni(NH_3)_6]Cl_2 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 2Cl^-$$

On evaporating the solution, the compound can be recovered. The compound in solution does not show the properties of Ni^{2+} ions or ammonia molecules.

13.4 DEFINITIONS OF SOME IMPORTANT TERMS :

(i) Coordination Complex and Complex ions

Two or more stable chemical species combine to form a compound known as **Co-ordination complex**. The compound retains its identity both in the solid as well as in dissolved state.

e.g. $CuSO_4$ and NH_3 are two stable chemical species and they combine to form a coordination complex $[Cu(NH_3)_4]SO_4$.

A water-soluble co-ordination compound invariably contains a complex ion. For example, $[Cu(NH_3)_4]SO_4$ contains $[Cu(NH_3)_4]^{2+}$ complex ion and $K[Ag(CN)_2]$ contains the complex ion $[Ag(CN)_2]^-$. A complex ion is thus electrically charged ion which contains a central metal atom or ion surrounded by a group of ions or neutral molecules. So $[Cu(NH_3)_4]^{2+}$ contains a central ion Cu^{2+} surrounded by four ammonia molecules.

(ii) Central ion

The ion to which a fixed number of ions or neutral molecules are bound in a definite geometrical arrangement around it is known as the **central ion**. For example, in complex ion $[Ni(NH_3)_6]^{2+}$, Ni^{2+} is the central ion and in $[Fe(CN_6]^{3-}$, Fe^{3+} is the central ion. The central ion is a Lewis acid.

(iii) Ligands

The ions or molecules bound to the central ion in the coordination compounds are called **ligands**. For example, in complex ions $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$ the ligands are molecules of ammonia and cyanide ions respectively. The ligands may be simple ions like Cl^-, small molecules like H_2O and NH_3, larger molecules like $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules like proteins.

(iv) Coordination Number

The ligands are attached to the central ion through coordinate bonds. The number of ligands attached to the central ion is known as the **coordination number** of that ion. For example, co-ordination number of Ag^+ in $[Ag(CN)_2]^-$ is 2. Co-ordination number of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4. The most common coordination numbers are 2, 4, and 6.

(v) Coordination sphere

The central ion bonded to the ligands constitute the **co-ordination sphere**. The co-ordination sphere is written within the square bracket.

e.g. $[Ag\,(CN)_2]^-$

Types of Ligands

A ligand necessarily contains one or more donor atoms for co-ordination with the central ion. On the basis of number of donor atoms the ligands may be classified as follows :

(1) Unidentate or monodentate ligands

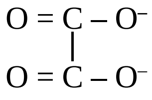
The ligands which can coordinate to the central ion through only one donor atom are known as **unidentate** or **monodentate** ligands. The common examples are-

H_2O, Cl^-, NH_3, OH^-, NO_2^- etc.

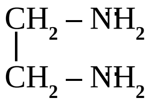
(2) Bidentate or didentate ligands

The ligands which can coordinate to the central ion through two donor atoms are called **bidentate** or **didentate** ligands.

The examples are



$$\begin{array}{l} O = C - O^- \\ \quad\;\, | \\ O = C - O^- \end{array}$$

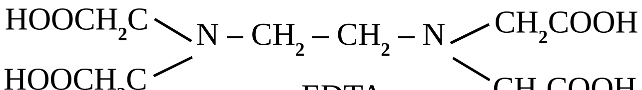


$$\begin{array}{l} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array}$$

(3) Polydentate ligands

The ligands which can co-ordinate to the central ion through more than two donor atoms are called **polydentate** ligands. They may be **tridentate, tetrandentate, pentadentate** and **hexadentate** depending upon the number of donor atoms as 3, 4, 5, and 6 respectively.

e.g. Ethylene diamine tetracetic acid (EDTA) is an important hexadentate ligand. It binds through two nitrogen and four oxygen atoms of four –COOH groups to the central metal ion.

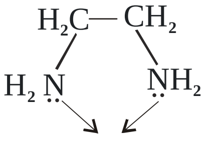


EDTA

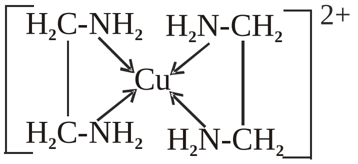
(4) Chelating ligands and Chelates

A bidentate or polydentate ligand may link to central metal ion through two or more donor atoms forming a ring structure. The ligand is called a **chelating ligand** and the complex is called a **chelate**.

For example, ethylene diamine (a bidentate ligand) coordinates through both the Nitrogen atoms to central Cu^{2+} ion forming a ring structure.



Ethylene diamine
Bidentate ligand
acting as chelating ligand



Chelate cation

13.5 WERNER'S CO-ORDINATION THEORY :

To explain the formation and structure of complex compounds **Werner** in 1823 put forward the theory of coordination for which he was awarded Nobel prize in chemistry. He is known as the the father of coordination chemistry.

Postulates

(1) Metal atoms in coordination compounds exhibit two types of valencies (a) **Primary valency** (b) **Secondary valency.** The primary valency is non-directional and ionisable. It corresponds to oxidation state. The secondary valency is directional and non-ionisable. It corresponds to coordination number.

(2) Each metal atom exhibits a fixed number of secondary valencies i.e. it has a fixed coordination number.

(3) The primary valencies are satisfied by negative ions whereas the secondary valencies are satisfied either by negative ions or by neutral molecules.

(4) The secondary valencies are responsible for imparting a particular geometry to the coordination compound. For example, if the central metal ion has four secondary valencies, then they form either a tetrahedral or square planar arrangement around the central metal ion. If the central metal ion has six secondary valencies, then these are arranged octahedrally around the metal ion. In otherwords the **stereochemistry** of the complex is determined by the **secondary** valencies.

Explanation of Structure of complexes on the basis of Werner's theory

The structures of various cobalt ammines may be explained by Werner's theory. In all such compounds cobalt exhibits a primary valency of three and secondary valency of six. The primary valencies are represented by dotted lines whereas the secondary valencies by thick lines in the following figures.

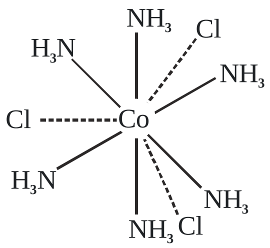


Fig.13.1 Structure of $CoCl_3.6NH_3$ complex

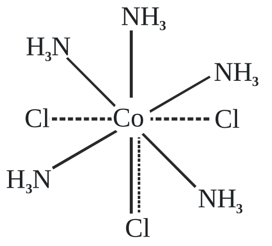


Fig.13.2 Structure of $CoCl_3.5NH_3$ complex

(a) Total no. of ions = 4
(3 numbers of Cl^- ion,
1 complex ion $[Co(NH_3)_6]^{3+}$)

(b) The complex = $[Co(NH_3)_6]Cl_3$

(c) The number of Cl^- ions getting precipitated on addition of $AgNO_3$ = 3

(a) Total number of ions = 3
(2 numbers of Cl^- ion,
1 complex ion)

(b) The complex = $[CoCl\ (NH_3)_5]Cl_2$

(c) The number of Cl^- ions getting precipitated on addition of $AgNO_3$=2

(d) One Cl^- ion exhibits a dual character. It is held by a secondary as well as a primary valency.

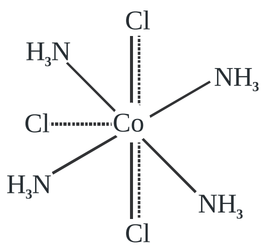


Fig.13.3 : Structure of $CoCl_3$.$4NH_3$ complex

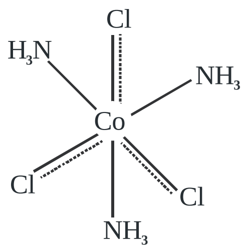


Fig.13.4 : Structure of $CoCl_3$. $3NH_3$ complex

(a) Total no. of ions = 2 (one Cl^- ion), one complex ion

(b) The Compex = $[CoCl_2(NH_3)_4]Cl$

(c) The number of Cl^- ion getting precipitated on addition of $AgNO_3$ = 1

(d) Two number of Cl^- ions are held by primary as well as secondary valencies.

(a) Total number of ions = zero.It is a neutral molecule.

(b) The complex $[CoCl_3(NH_3)_3]$

(c) The number of Cl^- ions getting precipitated on addition of $AgNO_3$ = nil.

(d) Three numbers of Cl^- ions are held by primary as well as secondary valencies

13.6 NOMENCLATURE OF COORDINATION COMPOUNDS: IUPAC SYSTEM :

The International Union of Pure and Applied Chemistry (IUPAC) publication, Nomenclature of Inorganic Chemistry (1989), Blackwell Scientific Publishers, has given the rules for systematic naming of coordination compounds. The basic rules are as follows:

I. Order of naming ions: In ionic complexes, the cation is named first and then the anion. For example:

$[Ni(NH_3)_6]Cl_2$ is named as Hexaamminenickel (II) chloride.

$[Cr(NH_3)_6](NO_3)_3$ is named as Hexaamminechromium (III) nitrate.

and $K_2[PtCl_6]$, as Potassium hexachloroplatinate (IV).

II. Non-ionic complexes: They are given one-word name.

For example: $[Pt(NH_3)_2Cl_4]$ is named as Diamminetetrachloroplatinum (IV)

$[Co(NH_3)_3(NO_2)_3]$ is named as Triamminetrinitrocobalt(III).

III. Naming the complex:

i) When the name of the complex is written, the ligands are written in **alphabetical order** regardless of their charge, followed by the metal.

For example: $[Pt.Cl.NO_2(NH_3)_4]SO_4$ is named as Tetraammine–chloronitroplatinum(IV) sulphate.

ii) When the formula of the complex is written, the complex ion should be enclosed in square brackets. The metal is written first, then the coordinated groups are listed in the order– negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).

a) The name of the negative ligands end in ‘o’.

Thus,

F^-	fluoro	H^-	hydrido	HS^-	mercapto	NO_2^-	nitro
Cl^-	chloro	OH^-	hydroxo	S^{2-}	thio	CH_3COO^-	acetato
Br^-	bromo	O^{2-}	oxo	SO_4^{2-}	sulphato	$S_2O_3^{2-}$	thiosulphato
I^-	iodo	O_2^{2-}	peroxo	CN^-	cyano	NO_3^-	nitrato

b) Neutral ligands are named as the molecule. Thus, water (H_2O) is named as *aqua*, ammonia (NH_3) as *ammine*, CO as *carbonyl* and NO as *nitrosyl*. The ligands N_2 is called *dinitrogen* and O_2 is called *dioxygen*. Organic ligands are given their common names as *phenyl*, *methyl*, *ethylenediamine* (shortly as ‘*en*’), *pyridine* (shortly as ‘*py*’) glycine (Gly), dimethyl glyoxime (DMG) etc.

(c) Positive ligands end in ‘*ium*’ For example, $NH_2 - NH_3$ is named as *hydrazinium*. (But when NO^+ ligand is used, it is called *nitroso*).

IV) **Prefixes to indicate number of ligands:** When there are several simple ligands of the same kind, their number is indicated by di, tri, tetra, penta and hexa. If the ligands have complex names, to avoid confusion bis, tris, tetrakis are used instead of di, tri and tetra and the name of the ligand is kept within brackets. For example- $K_3[Al(C_2O_4)_3]$ is named as Potassium trioxalatoaluminate (III) and $[CoCl_2(NH_2CH_2CH_2NH_2)_2]_2SO_4$ or $[CoCl_2(en)_2]_2SO_4$ is named as Dichlorobis (ethylene diammine) cobalt(III) sulphate.

V) **Oxidation state of central metal** is shown by Roman numerals (I, II, III etc) in brackets immediately following its name. For zero oxidation state, (0) is written.

VI) **Ending of names :** The complex negative ions end in ‘*ate*’ but complex positive ions and neutral molecules have no special ending.

For example: $K_4[Fe(CN)_6]$ is named as Potassium hexacyanoferrate(II)

and $K_3[Fe(CN)_6]$ is Potassium hexacyanoferrate (III).

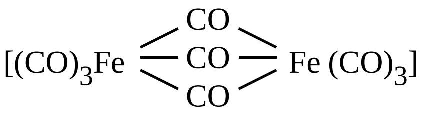
$K[PtCl_5(NH_3)]$ is named as Potassium amminepentachloroplatinate(IV)

and $[Co(NO_2)_3(NH_3)_3]$ as Triamminetrinitrocobalt(III).

VII) **Bridging groups:** Ligands which link two centres of coordination are usually separated from the rest of the complex by a '*hyphen*'(_) and are denoted by the prefix $\mu -$. If there are two or more bridging groups of the same kind, this is indicated by di $-\mu-$, tri $-\mu-$ etc. Bridging groups are listed alphabetically with other groups unless the symmetry of the molecule allows a simpler name.

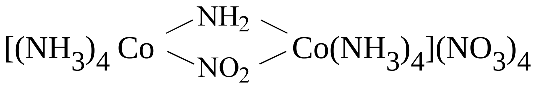
For Example: $[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)_5$ is named as

$\mu-$ Amidobis [pentaamminecobalt(III)] nitrate,



$[(CO)_3Fe(CO)_3Fe(CO)_3]$ as Tri $-\mu-$ carbonyl-bis (tricarbonyliron(0))

and

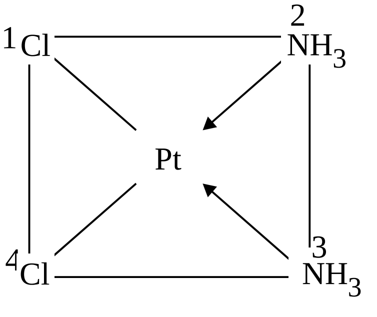


$[(NH_3)_4Co(NH_2)(NO_2)Co(NH_3)_4](NO_3)_4$ as

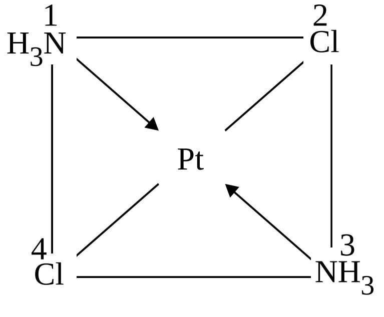
$\mu-$ Amido $-\mu-$ nitrobis [tetraamminecobalt(III)] nitrate.

VIII) Sometimes a ligand may be attached through different atoms. Thus, M-NO_2 is called *nitro* whereas M-ONO is called *nitrito*. Similarly, M-SCN in called *thiocyanato* and M-NCS is called *isothiocyanato*. Systematically they are named as thiocyanato-S or thiocyanato-N to indicate which atom is bonded to the metal. This convention is extended to other cases where the mode of linkage is ambiguous. For example, $NH_4[Cr(NCS)_4(NH_3)_2]$ is named as Ammonium diamminethiocyanato-N-chromate(III) and $[Cd(SCN)_4]SO_4$ as Tetrathiocyanato-S-cadmium(II) sulphate. Such ligands are called **ambidentate** ligands.

IX) **Naming Geometrical isomers:-** Geometrical isomers are named by the use of *cis* to indicate the adjacent positions of two similar ligands and *trans* to indicate the opposite. For a square planar complex such as $[Pt(NH_3)_2Cl_2]$ which is isolated in two forms *cis* and *trans* can be shown as



cis (1,4 or 2,3 positions are *cis*)



trans (1,3 or 2,4 positions are *trans*)

X) Naming optical isomers:- *Dextro* and *laevo* rotatory optically active complex compounds are designated as(+) and (–) or as *d-* and *l-* respectively.

A few IUPAC names are given below with their formulae.

$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt (III) chloride
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechlorocobalt (III) ion.
$[Co.Cl.CN.NO_2(NH_3)_3]$	Triamminechlorocyanonitrocobalt(III).
$[Co.SO_4(NH_3)_4]NO_3$	Tetraamminesulphatocobalt(III) nitrate.
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III). (Pot.ferricyanide).
$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate(III) (Here, NO is neutral)
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	Potassium amminedicyanodioxoperoxochromate(VI).
$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato)argentate(I).
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosoferrate(II) (Here, NO is NO^+) (Sodium nitroprusside)
$[Fe(H_2O)_5NO]SO_4$	Pentaaquanitrosoiron(I) sulphate (Here, NO is NO^+) (This complex is formed during *brown-ring* test for nitrate)
K_2HgI_4	Potassium tetraiodomercurate (II)
$LiAIH_4$	Lithium tetrahydridoaluminate(III)
$[CuCl_2(CH_3NH_2)_2]$	Dichlorobis(methylamine) copper (II)
$[Pt(py)_4]\ [PtCl_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II).
$[Cr\ (NH_3)_6][Co(C_2O_4)_3]$	Hexaamminechromium (III) trioxalatocobaltate (III)
$[Pt(NO_2)(NH_3)(C_5H_5N)(H_2O)]Cl$	Ammineaquanitropyridine platinum(II) chloride.
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (A hydrated complex)	Tetraaquadichlorochromium(III) chloride 2-water.
$Ni\ (DMG)_2$	Bis(dimethylglyoxamato) nickel (II)
$Fe\ (CO)_5$	Pentacarbonyliron (O)

13.7 ISOMERISM IN COORDINATION COMPOUNDS :

Compounds which have the same chemical composition but different arrangements of their atoms are called **isomers** and this phenomenon is known as *isomerism*. The isomers differ in one or more physical or chemical properties.

Metal complexes exhibit different kinds of isomerism. The main types are

(a) Stereoisomerism and (b) Structural asomerism Steroisomerism is further subdivided into

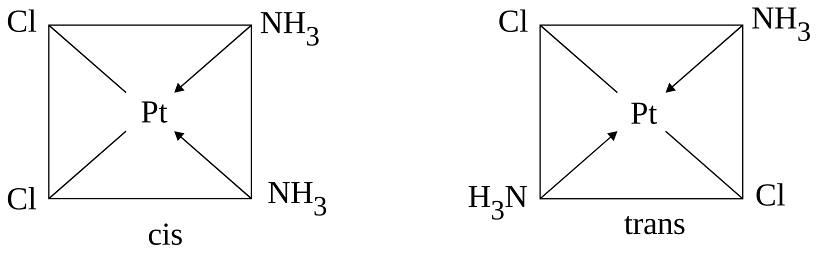
(I) *Geometrical isomerism* (II) *Optical isomerism.*

Stereoisomers have the same chemical formula and chemical bonds, but they have different spatial arrangements. Structural isomers have different bonds.

(I) **Geometrical isomerism —** Geometrical isomerism is due to *ligands occupying different positions around central ion.* Ligands occupy postions either *adjacent to one another or opposite to one another* and are termed as *cis-form and trans-form* respectively. Geometrical isomerism of compounds with coordination numbers 4 and 6 is most important.

Coordination Number 4 — In these complexes two principal geometries are found i.e. **tetrahedral** and **square planar.** Cis-trans isomerism is not possible in tetrahedral complexes. However, *cis-trans isomerism* is very common amongst square planar complexes.

In complexes of type Ma_2b_2 such as $[Pt(NH_3)_2Cl_2]$ or $[Pd(NH_3)_2(NO_2)_2]$ cis-trans isomers are found. Similar complexes of Ni(II), Cu (II) and Co(II) are also known

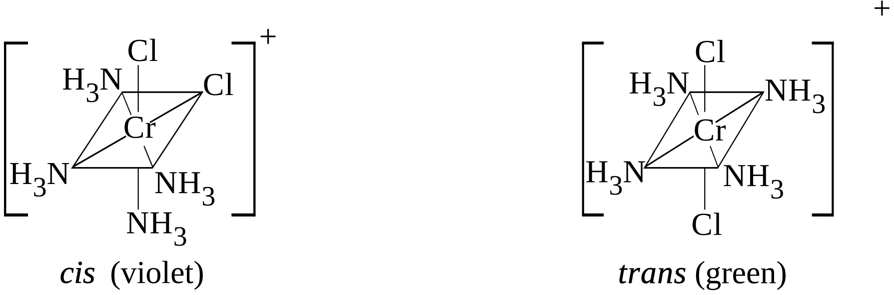


cis trans

Fig. 13.1 Cis-trans forms of $[Pt(NH_3)_2Cl_2]$

In complexes of type Ma_2bc where M = Pt, a = NH_3 and b, c = Cl^-, Br^-, NO_2^-, SCN^- etc. cis-trans isomers exist.

Coordination Number 6 — The regular geometric arrangement is *octahedral.* Tetraammine dichlorochromium(III) ion exists as *cis* (violet) and *trans* (green) forms.



cis (violet) *trans* (green)

Fig.13.2 Cis-trans forms of $[Cr(NH_3)_4Cl_2]^+$

Large number of octahedral complexes of the type Ma_4b_2 or Ma_2b_4 or Ma_4xy where M=Co(III), Cr (III), Rh (III) and Pt (IV) exist as isomers.

Complexes of the type Ma_3b_3 exist in two isomeric forms.

For example: $[Rh(py)_3Cl_3]$, where py = pyridine.

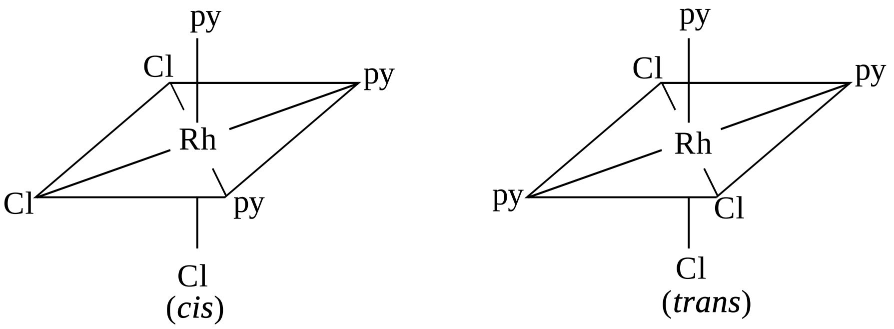


Fig. 13.3 Cis-trans forms of $[Rh(py)_3Cl_3]$

(II) **Optical isomerism** — Optical activity is due to lack of symmetry of the molecule. It is known that *d*– and *1*– isomers are just mirror images of one another just as the left hand is the mirror image of the right hand. *Optical isomers have identical chemical and physical properties and differ only in the direction in which they rotate the plane of polarised light.* The *dextro* form rotates the plane towards the right and *laevo* form, towards the left.

Only *tetrahedral* complexes (coordination number-4), containing two unsymmertrical bidentate ligands of Be (II), B (III) and Zn (II) can be resolved into optically active forms. *Square planar* complexes are seldom optically active.

Coordination Number 6 — Common examples are compounds or ions of the type $[M(aa)_2]$ whose aa = bidentate ligand (occupies two coordination positions). For example, trioxalatochromate (III) ion exists in two optically active forms.

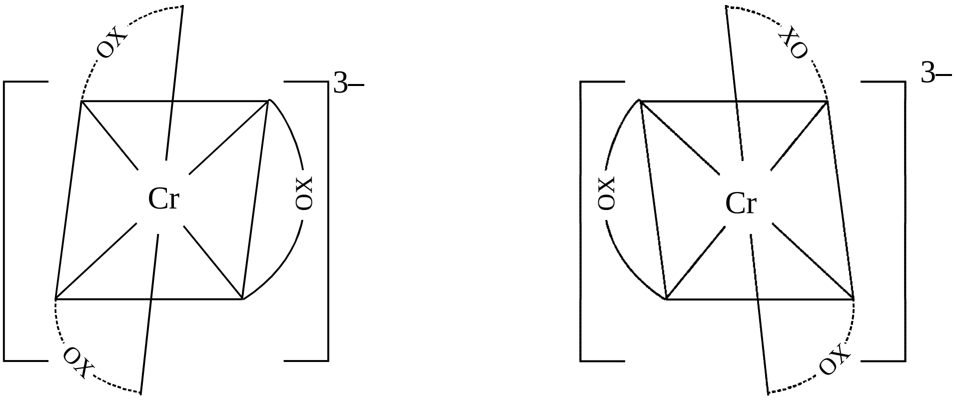


Fig. 13.4 Optical isomers of trioxalatochromate (III) ion

Some other common complexes with coordination number 6, belong to the type $[M(aa)_2b_2]$ where 'aa' = bidentate ligand. The *cis*-form of these complexes have been resolved into ***d***- and *l*-isomers but the ***trans***-form does not show optical isomerism.

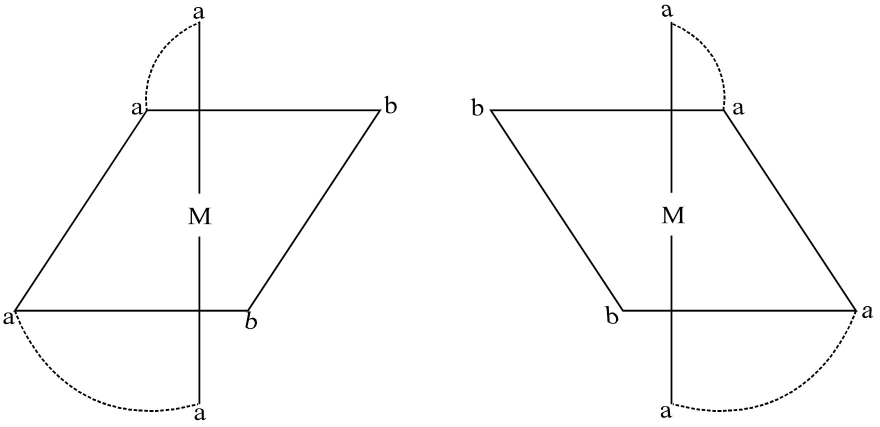


Fig. 13.5. *d*- and *1*-isomers of *cis*-form of the complex $[M(aa)_2b_2]$

An example of this type is the *cis*-form of dichloro bis (ethylenediamine) rhodium (III). Also complexes of the type $[M(aa)_3]$ where 'aa' = bidentate ligand, for example, tris(ethylenediamine)cobalt(III) cation gives the *d*-and *1*-isomers.

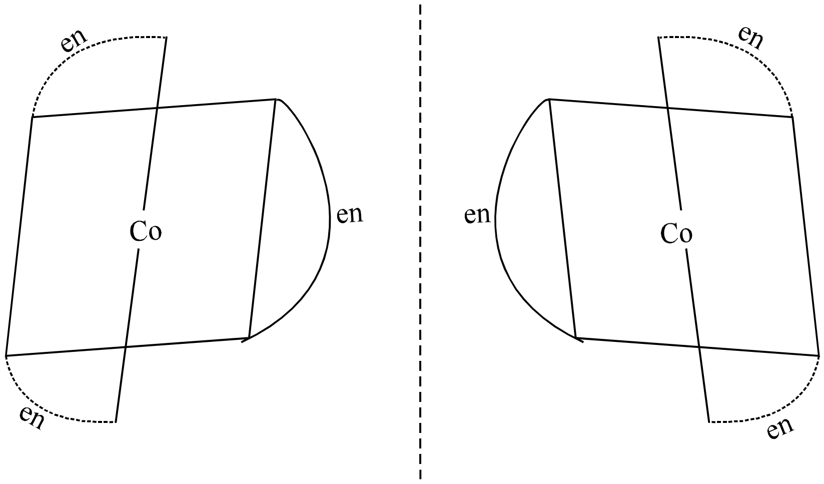


Fig. 13.6 *d*– and *1*– isomers of tris (ethylenediamine) cobalt(III).

Structural isomerism : This is shown by compounds having different ligands within their coordination sphere. Various types of such isomerism are discussed below.

1) **Ionisation isomerism —** This type of isomerism is shown by such compounds which have same composition but liberate different ions in solution. In such isomers, the position of groups whithin or outside the coordination sphere differs.

Examples : $[Co(NH_3)_5SO_4]Br$ (Red) – liberates Br^- ions in solution.

and

$[Co(NH_3)_5Br]SO_4$ (Purple) – liberates SO_4^{2-} ions in solution.

2) **Hydrate isomerism —** This type of isomerism results from the replacement of a coordinated group by water of hydration. These isomers differ widely in their physical and chemical properties.

Examples : $[Cr(H_2O)_6]Cl_3$ (Violet) – Does not lose water molecules but three Cl^- ions are precipitated by $AgNO_3$ solution.

$[Cr(H_2O)_5Cl]Cl_2(H_2O)$(Light green)– Loses one molecule of water but two Cl^- ions are precipitated by $AgNO_3$ solution.

$[Cr(H_2O)_4Cl_2]Cl(2H_2O)$(Dark green)– Loses two molecules of water on dehydration, but one Cl^- ion is precipitated by $AgNO_3$ solution.

3) **Linkage isomerism —** This type of isomerism is shown by such complexes which contain a monodentate ligand having more than one donor atom. Thus, cyanide ion $:C \equiv N^-:$ can attach itself to metal M either through the carbon $M - C \equiv N^-:$ or the nitrogen $M - N \equiv C{:}^{-}$: Similarly, $:N \equiv C-S{:}^{-}$ (through N or S), $:C \equiv O:$ (through C or O).

4) **Coordination isomerism—** This type of isomerism is shown by such compounds which contain both cationic and anionic species and it results from random distribution of ligands.

Example : $[Co(NH_3)_6]\,[Cr(CN)_6]$ and $[Cr(NH_3)_6]\,[Co(CN)_6]$.

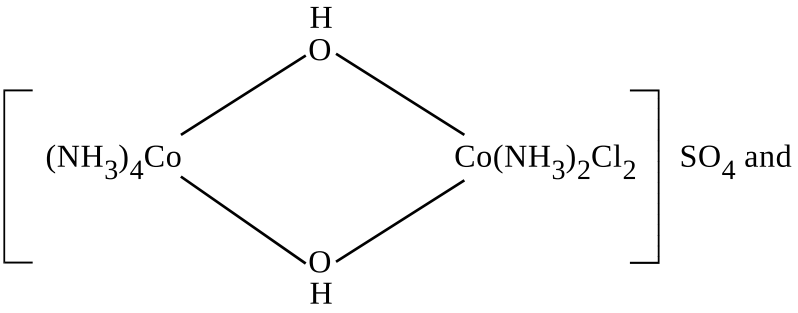
5) **Ligand isomerism —** When isomeric ligands are associated into complexes, the complexes are isomers of each other.

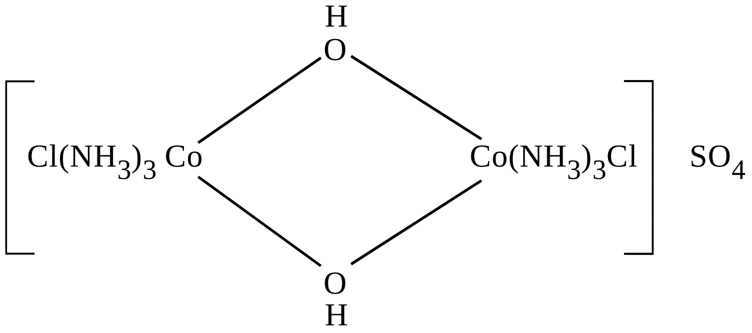
Example: $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$

pn=1, 2 – diaminopropane, tn = 1, 3 – diaminopropane

6) **Coordination position isomerism—** This type of isomerism is shown by bridged complexes and involve different placement (attachment) of ligands. It is a special type of coordination isomerism.

Examples :





13.8 BONDING IN COORDINATION COMPOUNDS :

Though the bonding features in coordination compounds were described by Werner, his theory could not explain the following basic questions.

(a) Why the coordination compounds are formed by only certain elements ?

(b) Why the bonds present in coordination compounds have directional properties ?

(c) Why certain coordination compounds appear coloured and they possess characteristic magnetic and optical properties ?

Three modern theories have been developed with a view to explaining the nature of bonding and properties of coordination complexes. These are

(a) The Valence Bond Theory

(b) The Crystal Field Theory

(c) The Molecular Orbital Theory

13.8.1 THE VALENCE BOND THEORY

This theory was develoved by **Pauling.**

Postulates

1. During the formation of coordination compounds the ligands coordinate with the central metal ion. For the formation of coordinate bond the central metal ion provides an adequate number of empty orbitals to accomodate the electron pairs from the ligand. The number of empty orbitals is equal to the coordination number of the central ion.

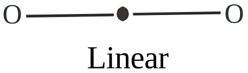
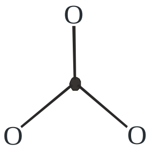
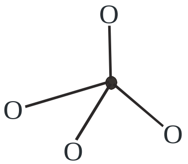
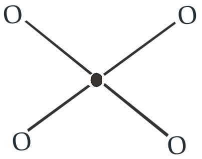
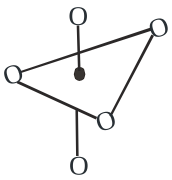
2. The atomic orbitals (*s*, *p* and *d*) of the metal hybridise giving hybrid orbitals of equivalent energies. The number of hybridising orbitals is equal to the number of hybrid orbitals. The hybrid orbitals are directed to the positions of the ligand depending upon the geometry of the complex. (see Table -1)

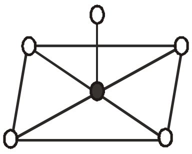
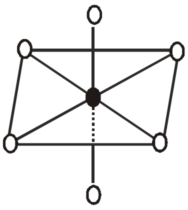
3. Each ligand must have atleast one orbital containing a lone pair of electrons.

4. The inner *d*-orbitals i.e. (n–1)*d* or the outer *d*-orbitals i.e. n *d-* orbitals participate in hybridisation. For example, in case of octahedral structure the hybridisation is of (n–1) d^2sp^3 type or n sp^3d^2 type. The complexes thus formed are known as *low spin* and *high spin* complexes respectively.

5. The ligand -metal coordinate bond is formed by the overlapping of vacant hybrid orbitals of metal ion with completely filled orbitals of the ligand. The number of such bonds varies with the number of vacant orbitals made available by the central metal ion.

Table - 1

Coordination number	**Hybrid orbitals**	**Molecular geometry**	**Examples**
2	*sp*	 Linear	$Ag(NH_3)_2^+$, $Ag(CN)_2^-$
3	sp^2	 Trigonal planar	$[HgI_3]^-$
4	sp^3	 Tetrahedral	$[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2 The *d*-orbital involved in $d_{x^2-y^2}$ of the inner i.e (n–1)th shell.	 Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 The *d*-orbital involved i.e. d_{z^2} of the inner i.e. (n–1)th shell.	 Trigonal bipyramidal	$[Fe(CO)_5]$

5	sp^3d The d-orbitals involved i.e. $d_{x^2-y^2}$ of the outer i.e. nth shell	 Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3 or sp^3d^2 The d orbitals involved are $d_{x^2-y^2}$ and d_{z^2} of the inner in (n–1)th shell in the 1st case and of the outer i.e. nth shell in the second case	 Octahedral	$[Co(NH_3)_6]^{2+}$ (n-1)d orbitals are involved. $[CoF_6]^{3-}$ nd orbitals are involved.

The stereochemical and magnetic properties of co-ordination compounds can be predicted by Valence bond theory. We know that the substance which contains no unpaired electron is known as **diamagnetic** substance and it is repelled by the magnetic field. On the other hand, the substance which contains unpaired electron is known as **paramagnetic** substance and it is attracted by the magnetic field. It is possible to predict the geometry of the complex, the number of unpaired electrons and the type of hybridisation involved on the basis of Valence bond theory.

Examples of Octahedral complexes

Consider the formation of complexes of Co (III) on the basis of Valence bond theory.

1. Hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$

The outer electronic configuration of Co (III) is $3d^6$. The six electrons are to be distributed among the five numbers of 3d orbitals. The hybridisation scheme is as shown below in the diagram (Fig.13.5)

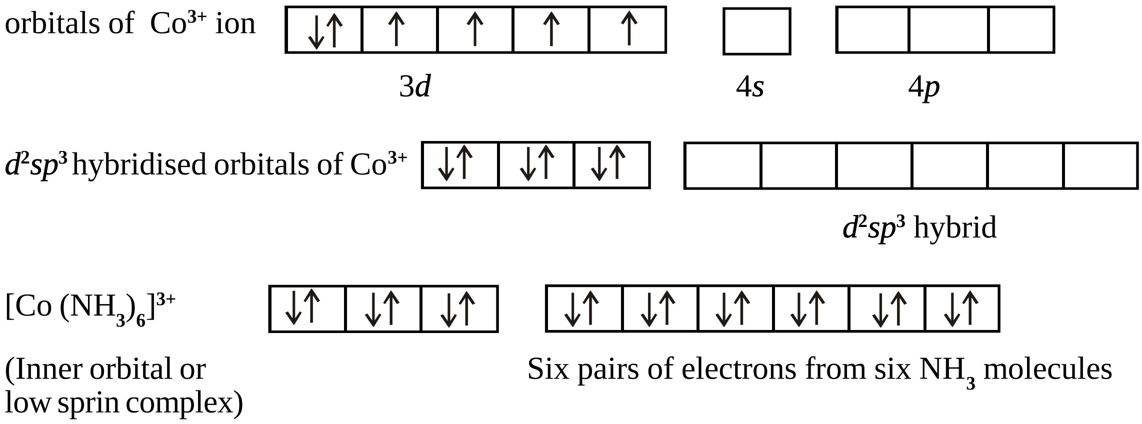


Fig.13.5 Formation of octahedral complex $[Co(NH_3)_6]^{3+}$ involving d^2sp^3 hybridisation of Co^{3+} ion orbitals

The six number of hybrid orbitals are occupied by six pairs of electrons one from each NH_3 molecule. The complex has octahedral geometry and because of absence of unpaired electrons it is diamagnetic in nature . In the formation of this complex the inner orbital 3*d* is used in hybridisation. Hence the complex is known as **inner orbital** or **low spin** or **spin paired** complex.

2. Hexafluorocabalt (III) ion, $[CoF_6]^{3-}$

Hexafluorocobalt (III) ion is paramagnetic. In this case the 3*d* orbitals do not take part in hybridisation, rather the 4*d* orbitals are involved. The hybridisation scheme is as shown below in diagram (Fig.13.6).

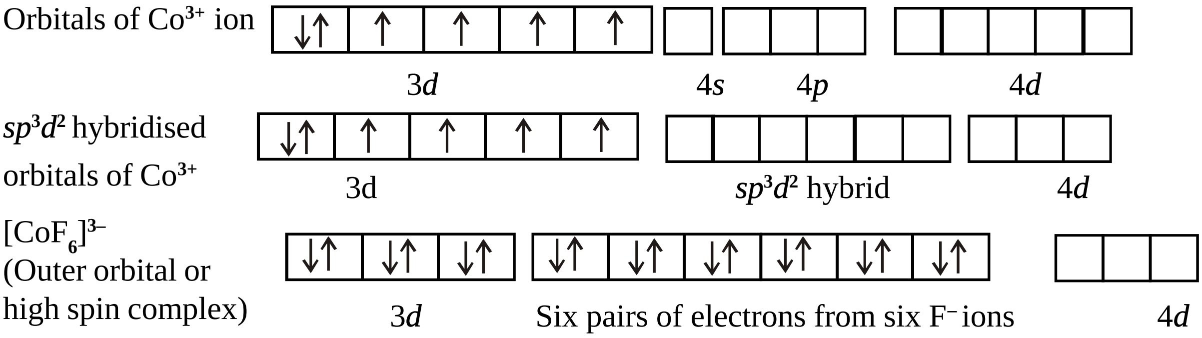


Fig. 13.6 Formation of octahedral $[CoF_6]^{3-}$ complex involving sp^3d^2 hybridisation of Co^{3+} ion orbitals

The six number of hybrid orbitals are occupied by six pairs of electrons one from each F^- ion.

The complex has octahedral geometry and because of the presence of unpaired electrons it is paramagnetic in nature. In the formation of the complex the outer 4*d* orbitals are used in hybridisation. Hence the complex is known as **outer orbital** or **high spin** or **spin free complex**.

Examples of Square planar and Tetrahedral complexes

Consider the complexes of Ni in which the coordination number of the metal ion is 4.

(i) Tetracyanonickelate (II) ion, $[Ni(CN)_4]^{2-}$

The Ni (II) ion has $3d^8$ outer electronic configuration. The 8 electrons are to be distributed in five *d* orbitals. According to Hund's rule, there are two unpaired electrons. The hybridisation scheme is as show below in diagram (Fig. 13.7).

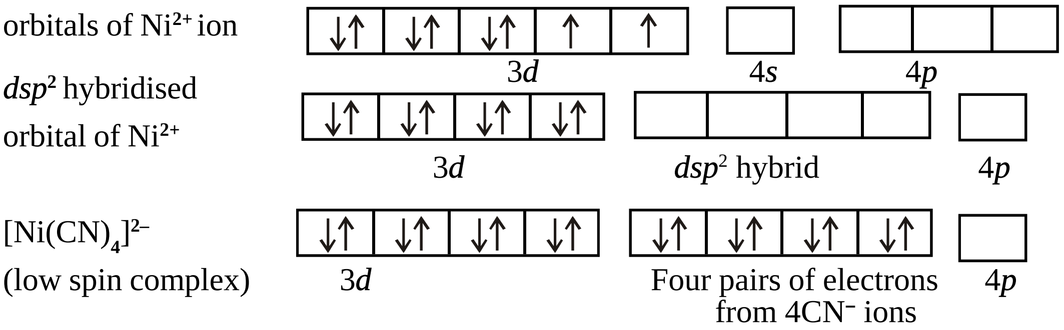


Fig 13.7 Formation of square planar $[Ni(CN)_4]^{2-}$ complex involving dsp^2 hybidisation of Ni^{2+} ion orbitals

The hybridisation involved here in *dsp*^{2} and the structure is square planar. In this case one of the 3*d* orbitals is made empty and available for hybridisation. This is possible only by the fact that the two unpaired electrons are paired by the energy available due to the approach of the ligands. The four hybrid orbitals are occupied by four pairs of electrons, one from each CN^- ion. Since there are no unpaired electrons the complex is considered to be diamagnetic in nature. The empty hybrid orbitals of the metal overlap with the completely filled orbitals of CN^- ions to form metal- ligand co-ordinate bonds.

(2) Tetrachloronickelate (II) ion, $[Ni(Cl)_4]^{2-}$

The nickel (II) ion has two unpaired electrons as shown below in Fig(10.8). Since the complex is paramagnetic it would involve unpaired electrons and *sp*^{3} hybridisation. The structure is tetrahedral.

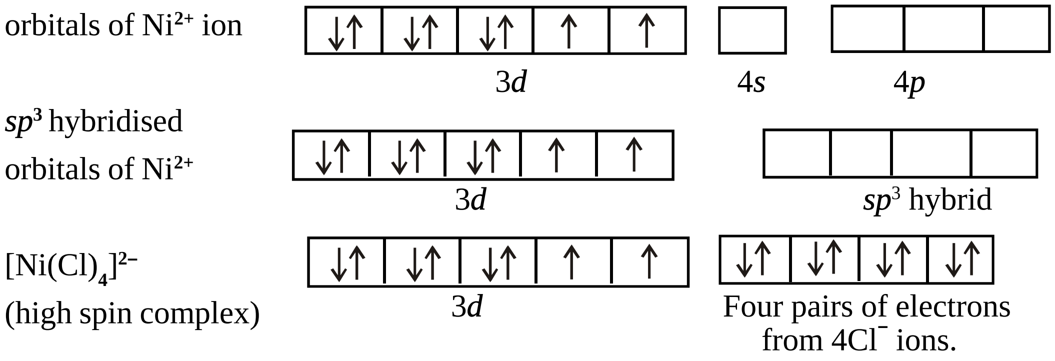


Fig. 13.8 Formation of tetrahedral $[NiCl_4]^{2-}$ complex involving *sp*^{3} hybridisation of Ni^{2+} oritals.

The four hybrid orbitals are occupied by four pairs of electrons, one from each Cl^- ion. Since there are unpaired electrons the complex is considered to be paramagnetic.

Magnetic Properties of Co-ordination Compounds

Magnetic susceptibility experiment measures the magnetic moment of coordination compounds. The results obtained reveal the structures adopted by the metal complexes.

Let us take the cases of 1st row transition metal series. The magnetic data of co-ordination compounds of these metals reveal some complications. In case of metal ions Ti^{3+} (d^1), V^{3+}(d^2), Cr^{3+} (d^3), two vacant *d*-orbitals are available for d^2sp^3 hybridisation with 4*s* and 4*p* orbitals having octahedral geometry. The magnetic behaviour of coordination compounds of these ions are similar.

But when there are more than three 3*d* electrons, the vacant pair of *d*-orbitals is available only by pairing. So for d^4 (Cr^{2+}, Mn^{3+}), d^5(Mn^{2+}, Fe^{3+}) and d^6(Fe^{2+}, Co^{3+}), as a result of pairing of *d*-orbitals two, one and zero unpaired electrons are left respectively. Maximum complications arise with species having d^4 and d^5 ions, e.g. $[Mn(CN)_6]^{3-}$ has a magnetic moment of two unpaired electrons whereas $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons whereas $[Co\ (C_2O_4)_3]^{3-}$ is diamagnetic. $[Fe(CN)_6]^{3-}$ has a magnetic moment of a single unpaired electron whereas $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.

This anomaly is, however, explained by Valence Bond Theory on the basis of inner orbital and outer orbital complex formation. The co-ordination complex ion like $[Mn(CN)_6]^{3-}$, $[Fe\,(CN)_6]^{3-}$ and $[Co\,(C_2O_4)_3]^{3-}$ are inner orbital complexes involving ***d²sp³*** hybridisation. But the former two are paramagnetic whereas the latter one is diamagnetic. Similarly, the complexes like $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic having 4,5 and 4 unpaired electrons respectively.

Limitations of Valence Bond Theory

(1) The colour exhibited by co-ordination compounds can not be explained by the theory.

(2) The quantitative interpretation of magnetic data can not be made by this theory.

(3) The thermodynamic and kinetic stability of co-ordination compounds can not be explained by the theory.

(4) The theory can not distinguish between weak and strong ligands.

(5) The theory fails to predict the number, position and intensities of the bonds observed in electronic spectra of coordination compounds.

(6) The theory does not explain satisfactorily why some complexes of a metal ion in a particular oxidation state are low spin (inner orbital) whereas some other complexes of the same metal ion in the same oxidation state are high spin (outer orbital) e.g. $[Co\,(NH_3)_6]^{3+}$ is diamagnetic and $[CoF_6]^{3-}$ is paramagnetic.

(7) Exact predictions regarding the structure of 4-coordinate complexes whether tetrahedral or square planar can not be made by this theory.

13.8.2 CRYSTAL FIELD THEORY

The theory was developed by **H. Bethe** and **V. Bleck.** According to this theory the bonding between a central metal ion and its ligand arises from purely electrostatic interactions. The ligand may be an anion or a neutral molecule having unshared or lone pair of electron. In case of anion the ligands are treated as point charges whereas in case of neutral molecules these are treated as dipoles. If the ligand is an anion the attraction between the central ion and the ligand is same as that between two oppositely charged particles. If the ligand is a dipole the negative end of the dipole is attracted towards the central positive ion.

The five *d*-orbitals is an isolated gaseous atom or ion are degenate i.e. they have the same energy. The degeneracy is maintained if the metal ion is surrounded by spherically symmetrical field of negative charges. But when the metal ion is surrounded by the ligands in a complex, the negative field becomes asymmetrical and the degeneracy of the *d*-orbital is destroyed or lifted. It results in splitting of *d*-orbitals. The nature of crystal field affects the pattern of splitting.

Orientation of *d*-orbitals and Crystal field splitting of Energy levels.

Depending upon the nature of orientation in space the *d*-orbitals are divided into two groups (Fig.10.9). Three orbitals belonging to one group are oriented in the regions in between the coordinate axes and are designated as d_{XY}, d_{YZ}, d_{XZ} while the other two orbitals belonging to another group or oriented along the axes and are designated as $d_{X^2-y^2}$ and d_{Z^2}. In case of a free metal ion, all the five *d*-orbitals are degenerate i.e. they are of equal energies.

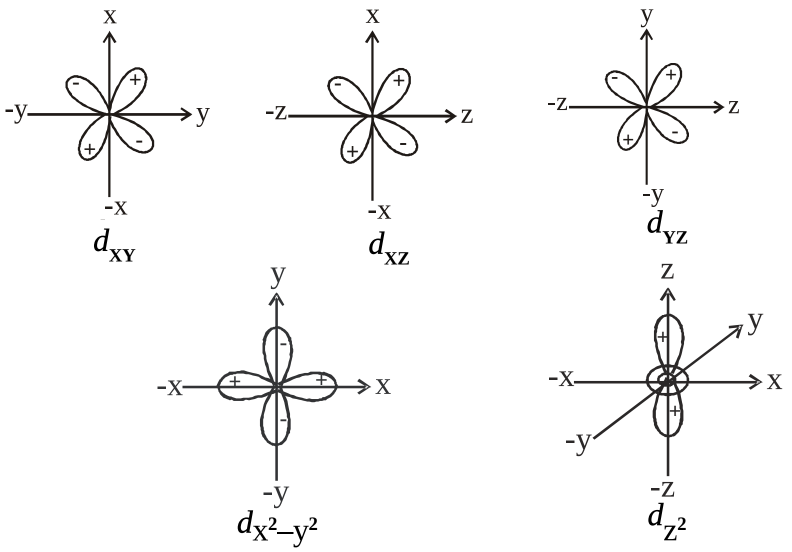


Fig. 13.9 Shape of d-orbitals

Now consider the case when the five *d*-orbitals of the metal ion are surrounded by the negative charge of the ligands (anion or dipole). The energy of the orbitals lying along the axes i.e in the direction of point charges would be raised to a larger extent than that of the orbitals lying in between the axes. The splitting of five degenerate *d*-orbitals of the metal ion into set of orbitals having different energies is called **crystal field splitting.**

Crystal field splitting in Octahedral complexes

In an octahedral complex there are six ligands surrounding the metal atom or ion. Repulsion takes place between the electrons in metal *d*-orbitals and electrons of the ligands. The repulsion is more pronounced when the metal *d*-orbital is directed towards the ligand than when directed away from the ligand. As a result $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion than d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes. The energy of $d_{x^2-y^2}$ and d_{z^2} will be raised while that of d_{xy}, d_{yz} and d_{xz} will be lowered compared to the average energy in spherical Crystal field. Thus due to metal electron - ligand electron repulsion the degeneracy of the *d*-orbitals has been lost in octahedral complex. Two sets of *d*-orbitals are formed.

(i) t_{2g} set comprising of three orbitals of lower energy

(ii) e_g set having two orbitals of higher energy.

The energy separation between the two sets is represented by Δ_0 (The subscript 'o' is for octahedral) (Fig.10.10). The energy of two e_g orbitals increases by (3/5) Δ_0 or $0.6\Delta_0$ or 6Dq and that of three t_{2g} decreases by (2/5) Δ_0 or 0.4 Δ_0 or 4Dq

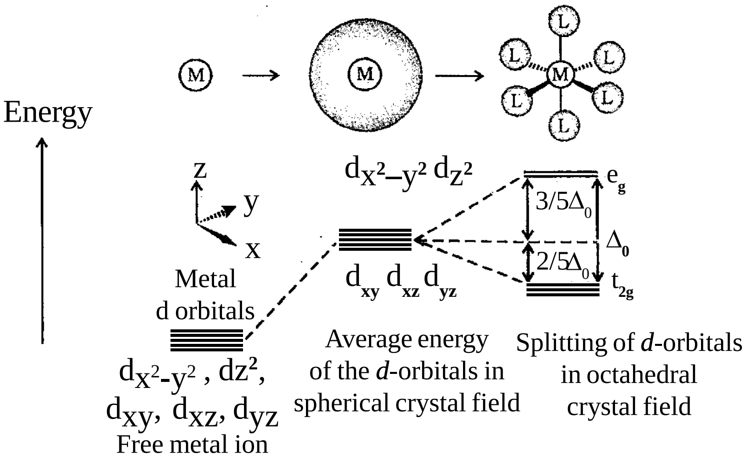


Fig. 13.10 *d*-orbital splitting in an octahedral crystal field

The factors that affect the crystal field splitting are (i) charge on the meal ion (ii) field produced by the ligand. The splitting will be large if the ligands produce strong field whereas the splitting will be small if the ligands produce weak field. The ligands may be arranged in the increasing order of the field strength produced by them in a series known as **spectrochemical series** as shown below.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

The series is based on absorption of light by complexes with different ligands.

Crystal Field Stabilisation Energy (CFSE)

The electron always prefers to occupy orbital of lower energy. In an octahedral complex containing one *d*-electron, it is evident that the electron would occupy one of the t_{2g} orbitals. This orbital has energy $-0.4\ \Delta_0$ compared to energy zero for hypothetical degenerate *d*–orbitals. Thus the complex will be 0.4 Δ_0 more stable than predicted by electrostatic theory. The decrease in energy $0 - (-0.4\ \Delta_0) = 0.4\ \Delta_0$ is known as the **crystal field stabilisation energy** of the complex under consideration.

For a d^2 system, the two *d*-electrons will prefer to occupy t_{2g} orbitals. The CFSE is $2\times0.4\ \Delta_0 = 0.8\ \Delta_0$. For a d^3 system the CFSE similarly is $3 \times 0.4 = 1.2\ \Delta_0$

But for a d^4 system these are two possibilities.

(i) All the four may occupy the three 2g orbitals. So one electron must be paired.

(ii) Three electrons occupy t_{2g} orbitals and one electron e_g orbital

(See Table.2 for CFSE energies for metal ions having different number of *d*-electrons in octahedral complexes).

Table - 2
Crystal Field Stabilisation Energies for Metal Ions having Different Number of *d*-Electrons in Octachedral Complexes.

No. of *d* electrons in metal ions	Distribution of Electrons (High Spin)		CFSE*	Distribution of Electrons (Low Spin)		CFSE
	t_{2g}	e_g		t_{2g}	e_g	
1	(↑) ○ ○	○ ○	4Dq			
2	(↑) (↑) ○	○ ○	6Dq**			
3	(↑) (↑) (↑)	○ ○	12 Dq			
4	(↑) (↑) (↑)	(↑) ○	6Dq	(↑↓) (↑) (↑)	○ ○	16 Dq
5	(↑) (↑) (↑)	(↑) (↑)	0	(↑↓) (↑↓) (↑)	○ ○	20 Dq
6	(↑↓) (↑) (↑)	(↑) (↑)	4Dq	(↑↓) (↑↓) (↑↓)	○ ○	24 Dq
7	(↑↓) (↑↓) (↑)	(↑) (↑)	6Dq**	(↑↓) (↑↓) (↑↓)	(↑) ○	18 Dq
8	(↑↓) (↑↓) (↑↓)	(↑) (↑)	12 Dq			
9	(↑↓) (↑↓) (↑↓)	(↑↓) (↑)	6 Dq			
10	(↑↓) (↑↓) (↑↓)	(↑↓) (↑↓)	0			

* Calculated by including the effects of interelectronic repulsions amonst the *d* electrons and the effects of *d* orbital splitting.

** CFSEs of these configurations are 8 Dq if we consider the effects of *d* orbital splitting alone and neglect the effects of interelectronic repulsions amongst the *d* electrons.

Table - 3
Crystal Field Stabilisation Energies for Tetrahedral Complexes with Metal Ions having different Electronic Configurations

Electronic configuration	Distribution of Electrons		CFSE
	e	t_2	
d^1	(↑) ○	○ ○ ○	6 Dq
d^2	(↑) (↑)	○ ○ ○	12 Dq
d^3	(↑) (↑)	(↑) ○ ○	6 Dq*
d^4	(↑) (↑)	(↑) (↑) ○	4 Dq
d^5	(↑) (↑)	(↑) (↑) (↑)	0
d^6	(↑↓) (↑)	(↑) (↑) (↑)	6 Dq
d^7	(↑↓) (↑↓)	(↑) (↑) (↑)	12 Dq
d^8	(↑↓) (↑↓)	(↑↓) (↑) (↑)	6 Dq*
d^9	(↑↓) (↑↓)	(↑↓) (↑↓) (↑)	4 Dq
d^{10}	(↑↓) (↑↓)	(↑↓) (↑↓) (↑↓)	0

* CFSEs of these configurations are 8 Dq if we consider the effect of *d* orbital splitting alone and neglect the effects of interelectronic repulsions amongst the *d* electrons

The actual configuration is decided by taking into account Δ_0 and P (Pairing energy i.e the energy required for pairing the electrons)

(a) If $\Delta_0 > P$, configuration (1) is possible. The complex has less number of unpaired electrons and it is known as low spin or **strong field complex.**

(b) If $\Delta_0 < P$, configuration (2) is possible. The complex has maximum number of unpaired electrons and it is known as high spin or **weak field complex.**

From detailed calculation it is found that d^4 to d^7 coordination complexes are more stable for strong field as compared to weak field cases.

Crystal Field splitting in Tetrahedral complexes

In a tetrahedral complex there are four ligands surrounding the metal atom or ion. The *d*-orbital splitting in this case is inverted and is smaller as compared to the octahedral splitting. For the same metal ion and same ligand and metal-ligand distance it is observed that $\Delta_t = 4/9\ \Delta_0$ (see Fig. 13.11)

Pairing of electrons in the orbital does not take place easily since orbital splitting energies are not sufficiently large for forcing pairing. So low spin configurations are almost not observed.

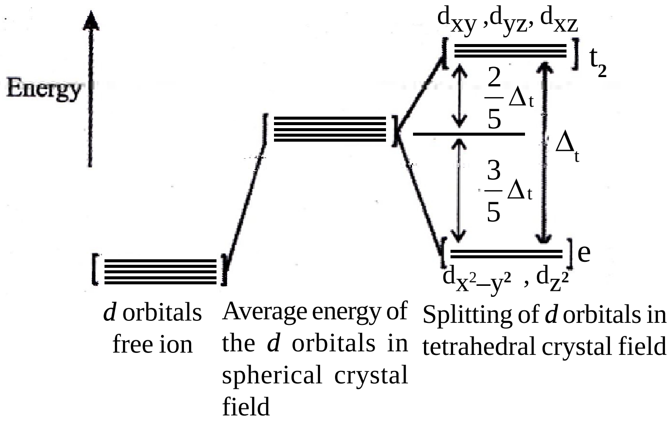


Fig. 13.11 *d* orbital splitting in an tetrahedral crystal field.

Colours in Coordination compounds.

A substance which possesses the property of absorbing certain radiations from the visible region ($3800A^0 - 7600A^0$) of the spectrum exhibits colour. So when white light in passed through the sample of co-ordination compound some of the visible spectrum is removed from the white light. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour produced from the wave length of visible light left over. For example if red light is absorbed by the complex it appears blue (see Table.10.4) Hydrated copper ions absorb red light and thus appear blue.

Table. 13.4
Relationship between the Wavelength of Light absorbed and the Colour obsrved in some Coordination Entities

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of Coordination Entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Violet

In case of transition metal complexes the energy difference between two sets of *d*-orbitals is small. So the excitation of electron from t_{2g}orbital to e_g orbital involves absorption of low energy radiation and as a result the complex appears coloured. The complex $[Ti\ (H_2O)_6]^{3+}$ is having octahedral geometry. It has d^1configuration. It absorbs radiations in the green and yellow regions corresponding to wave length around $5000A^0$. This corresponds to energy 240 kJ ($\because$ E = $h\upsilon = \frac{hc}{\lambda}$, h = Planck's constant, c = velocity of light) This energy (equals to Δ_0) is required to cause promotion of electron from t_{2g} to e_g orbital. The solution of the complex looks purple which is the complementary colour to the absorbed colour.

Since the value of Δ_0 depends upon the nature of ligands, nature of ions and geometry of the complex formed, different coordination compounds absorb radiations from different regions of visible light and exhibit different colours, e.g. octadral $[Co\ (H_2O)_6]^{2+}$ absorbs in blue region and appears pink (red). Tetrahedral $[CoX_4]^{2-}$ absorb in red region and appears blue. $[Co(NH_3)_6]^{3+}$ absorbs in blue region and appears orange in solution.

Transition metal ions having completely filled orbitals or completed empty orbitals are colourless. So complexes of $Cu^+(d^{10})$, Zn^{2+} (d^{10}), Ag^+ (d^{10}), $Sc^{3+}(d^0)$, $Ti^{4+}(d^0)$ etc. are colourless.

Limitations of CFT (Crystal Field Theory)

(1) Anionic ligands are found at the low end of spectrochemical series inspite of the fact that they produce greatest splitting effect.

(2) It is not concerned with the covalent character of metal-ligand bond.

13.9 BONDING IN METAL CARBONYLS :

In metal carbonyls, a metal atom is directly linked to the carbon atom of a carbonyl group. Metal carbonyls possess simple structures, in which electrons forming OC → M bond are furnished by CO molecules. For this, metal atom in carbonyls is said to be in zero oxidation state. Basing on the number of metal atoms present, these may be (i) mononuclear carbonyls, $M(CO)_x$ and (ii) polynuclear carbonyls. $M_x(CO)_y$.

According to Valence Bond Theory, the structures of the carbonyls are explained on the basis of nature of hybridisation of atomic orbitals. For example, $Ni(CO)_4$ is tetrahedral, $Fe(CO)_5$ is trigonal bipyramidal and $Cr(CO)_6$ is octahedral.

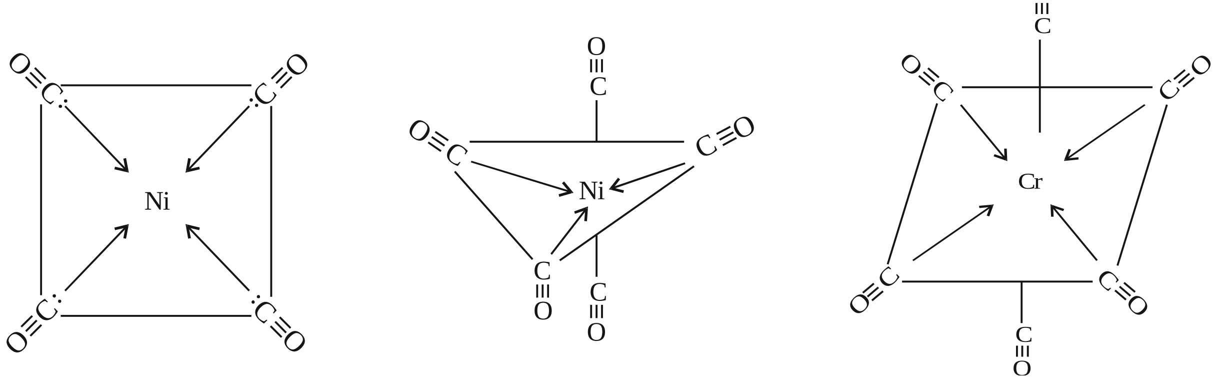


Fig.13.12 (a) $Ni(CO)_4$ **(b) $Fe(CO)_5$** **(c) $Cr(CO)_6$**

From the X-ray or electron diffraction method, it is found that the metal-carbon bonds are intermediate between the $M - C \equiv O$ and $M = C = O$ states, i.e. there is some double bond character in M – CO. Thus, it can be said that a M – C σ bond is formed along with M – C π bond. While the M – C σ bond involves the donation of lone pair of electrons on the carbonyl carbon atom to an empty metal orbital, the M – C π bond is formed by dative overlapping of a filled d-orbital of metal with empty antibonding p-orbital of the carbon atom.

$$\text{Metal} \underset{\text{dative } \sigma\text{bond}}{\overset{\text{dative } \pi \text{ bond}}{\rightleftarrows}} \text{carbon monoxide}$$

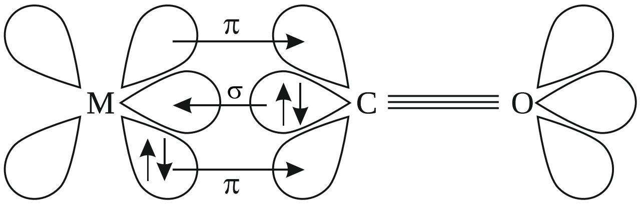


Fig. 13.13. M → C π bond and M ← C σ bond

13.10 STABILITY OF CO-ORDINATION COMPOUNDS :

While studying the stability of a coordination compound formed in solution, following stepwise addition of ligands to a metal ion is considered. Formation of the complex, ML_n is supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML \qquad : K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad : K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad : K_3 = \frac{[ML_3]}{[ML_2][L]}$$

\- -

\- -

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad : K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where K_1, K_2, K_3 .... K_n are referred to as stepwise stability constants and the overall stability constant, K is expressed as :

$$M + nL \rightleftharpoons ML_n \quad K = K_1K_2K_3..........K_n = \frac{ML_n}{[M][L]^n}$$

Greater the value of the overall stability constant, more will be the stability of the complex. The reciprocal of stability constant is called dissociation constant or instability constant (1/K).

The value of stability constant depends on the nature of the metal ion and the ligand. It is observed that, higher the charge density on the central metal ion more is the stability of its complexes, i.e. for a bigger value of $\frac{\text{charge}}{\text{radius of ion}}$, stability of its complex has a bigger value too. Again, more basic nature of a ligand also accounts for greater stability of the complex, as the donation of lone pairs of electrons by the ligands becomes easier.

13.11 IMPORTANCE OF COORDINATION COMPOUNDS :

1. In Qualitative analysis

The coordination compounds are of great importance and have wide range of applications. Since they are present in the mineral, plant and animal world they find extensive use in analytical chemistry, metallurgy and biological systems.

In qualitative analysis the detection and estimation of metal ions by chemical and instrumental methods of analysis are based on colour reactions with a number of chelating ligands resulting in the formation of coordination entities. Examples of such chelating ligands include EDTA, DMG etc.

2. Extraction of metals

Extraction processes of metals like silver and gold make use of complex formation. In presence of oxygen and water gold combines with cyanide to form the complex ion $[Au(CN)_2]^-$

in aqueous solution. By adding zinc to this solution, gold can be separated in the form of metal. Purification of metal can also be made through complex formation. For example, impure nickel is converted to $[Ni(CO)_4]$ which on decomposition yields pure nickel.

3. In Biological systems

We know that **chlorophyll** is very much necessary for the process of photosynthesis. It is a coordination compound of magnesium. The coordination compound of iron is **haemoglobin** which acts as an oxygen carrier. Vitamin B_{12} known as cyanocobalamine is an antipernicious anaemia factor. It is a coordination compound of cobalt. Similarly many enzymes coordinate with metal ions forming coordination compounds which are of great importance in biological systems.

13.12 ORGANOMETALLIC COMPOUNDS :

13.12.1 Introduction :

Compounds containing atleast one carbon-metal bond are called **organometallic compounds.** The first organometallic compound was prepared by Zessie in 1830 by the action of ethylene on a solution of potassium chloroplatinate (II). Quite a good number of such compounds have been synthesised and investigated during the last few years. Grignard reagent, R Mg X is a familiar example of organometallic compounds where R is an alkyl group. Other organometallic compounds include diethyl zinc $[Zn(C_2H_6)]$, teraethyl lead $[Pb\ (C_2H_5)_4]$, dibenzene chromium $[Cr(C_6H_6)_2]$, ferrocene $[Fe(C_5H_5)_2]$ and metal carbonyls.

13.12.2 Classification :

Organometallic compounds may be classified into three classes :

1. Sigma (σ) bonded complexes.
2. Pi (π) bonded complexes.
3. Complexes containing both σ - and π -bonding characteristics.

1. Sigma (σ) bonded complexes :

In these complexes, the metal atom and carbon atom of the ligand are joinedtogether with a sigma bond. Here, the ligand donates one electron and is therefore, called one electron donor. Examples are :

(i) Grignard reagent, R-Mg-X where R is an alkyl or aryl group and X is a halogen.

(ii) Dialkyl zinc, R_2Zn i.e. $(C_2H_5)_2$ Zn. Other similar compounds are $(CH_3)_4$ Sn, $(C_2H_5)_4$ Pb, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$, $(CH_3)_4Pb$ etc.

2. Pi (π) bonded organometallics:

Metals form compounds with alkenes, alkynes, benzene and other ring compounds in this type. In these complexes, the metal and ligand form a bond involving π - electrons of the ligand. Common examples are Zeise's salt, ferrocene and dibenzene chromium. They have the formula $K[PtCl_3(\eta^2—C_2H_4)]$, $Fe(\eta^5\text{-}C_5H_5)_2$, and $Cr(\eta^6\text{-}C_6H_6)_2$ respectively where prefixes η^2 (etc), η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are bound to the metal in the compound.

3. **Sigma (σ) and Pi (π) bonded organometallics :**

Metal carbonyls which are formed between metal and carbon monoxide belong to this class. These compounds possess both σ -and π -bonding. The oxidation state of the metal atoms in these compounds is **zero.** Carbonyls are mainly formed by the tranisitional metals of VI, VII & VIII groups. Carbonyls may be monomeric, bridged or polynuclear. Some common examples are tetracarbonyl nickel (0), $Ni(CO)_4$; Pentacarbonyl iron (0), $Fe(CO)_5$; hexacarbonyl chromium (0), $Cr(CO)_6$; and $Fe_2(CO)_9$.

13.12.3 Applications of Organometallic compounds :

Some important applications of organometallic compounds are mentioned below.

i. Tetraethyl lead (TEL) is used as an antiknock compound in gasoline.

ii. Silicones are used as polymers with unique properties.

iii. Grignard reagents and organoalkali are used in many organic synthesis.

iv. The extraction and purification of nickel is based on the formation of $Ni(CO)_4$.

v. Organometallic compounds are often used as homogeneous and heterogenous catalysts. Zeigler Natta catalyst [$TiCl_4$ and triethyl aluminium] acts as a catalyst in the polymerisation of ethylene to polythene.

CHAPTER (13) AT A GLANCE

1. **Double Salt —** Double salts are those molecular compounds which exist only in crystal lattices but breakdown into their constituent compounds when dissoved in water or any other solvent.

   Alum, $K_2SO_4 . Al_2(SO_4)_3 24H_2O$.

2. **Complex Compounds —** Complex compounds retain their identities even when dissoved in water or any other solvent and their properties are completely different from those of the constituents.

   Examples : $[Cu(NH_3)_4]SO_4$, $[Ag(NH_3)_2]Cl$.

3. **Ligands -** The ions or molecules bound to the central ion in the coordination compounds are called ligands.

4. **Coordination number -** The number of ligands attached to the central ion is known as coordination number of that ion.

5. **Coordination sphere -** The central ion bonded to the ligands constitutes the coordination sphere. It is written within square bracket.

6. **Unidentate, bidentate & polydentate ligands -** The ligands which can coordinate to the central ion through one, two and more than two donor atoms are known as monodentate, bidentate and polydentate ligands respectively.

7. **Chelates -** A bidentate or polydentate ligand may link to the central ion through two or more donor atoms forming a ring structure. The ligand is called a chelating ligand and the complex is called a chelate.

8. **Inner orbital or low spin or spin paired complex -** In the formation of octahedral complex if the inner 3*d* orbitals are used in hybridisation (d^2sp^3) the complex is known as inner orbital or low spin or spin paired complex.

9. **Outer orbital or high spin or spin free complex -** In the formation of octahedral complex if the outer 4*d* orbitals are used in hybridisation (sp^3d^2) the complex is known as outer orbital or high spin or spin free complex.

10. **Crystal field splitting -** The splitting of five degenerate *d*-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

11. **Spectrochemical series** - The ligands may be arranged in the increasing order of field strength produced by them in a series known as spectrochemical series.

12. **Geometrical or cis-trans isomerism -** Geometrical isomerism is due to ligands occupying different positions around the central ion. Ligand positions adjacent to one another is called **cis-isomer** and positions opposite to one another is called **trans-isomer.**

13. **Optical isomerism -** Optical isomers have identical chemical and physical properties and differ only in the direction in which they rotate the plane of polarised light. Those which rotate the plane to left are called **laevo** *(1)* and those which rotate the plane to right are called **dextro** *(d)*. These are mirror image isomers.

14. **Structural isomerism -** These include ionisation isomerism, hydrate isomerism, linkage isomerism, coordination isomerism, ligand isomerism, and coordination position isomerism.

15. **Organometallics -** Compounds containing atleast one carbon-metal bond are called organometallics. They are classified into three classes — (i) Sigma bonded complexes (ii) Pi-bonded complexes and (iii) Complexes containing both sigma and pi-bonding characteristics. These organometallics have several applications.

QUESTIONS

A. Short answer type question (3 marks each) :

1. What is the difference between molecular compound and complex compound ?
2. Define the terms : central ion, complex ion, ligand, coordination number.
3. Give the IUPAC names of the following compounds :

   $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^+$, $[Cr(H_2O)_4Cl_2]$, $K_2[PtCl_6]$, $[Fe(CN)_6]^{4-}$, $[Co(en)_2Cl_2]_2SO_4$, $[Cr(NH_3)_6]\ (NO_3)_3$, $Na_3\ [Co(NO_2)_6]$, $[Co(en)_2\ Cl(NO_2)]^+$, $[Pt(NH_3)Cl_5]^-$.
4. Write the formula of the following complexes :-

   Hexaamminenickel (II) chloride, hexaamminechromium (III)nitrate, potassium hexachloroplatinate (IV), trinitritoamminecobalt (III), potassium hexacyanoferrate (II), potassium hexacyanoferrate (III), potassium trioxalatoaluminate (III), Dichlorobis (ethylenediamine)-cobalt (III) sulphate, Ammonium tetrathiocyanatodiamminechromate (III), Potassium pentachloro monoammine platinate (IV).
5. Write notes on Werner's theory of coordination compounds.
6. Give some examples of molecular (non-ionic)complexes.
7. Give some examples of ionic complexes.
8. What is the symbol used before the bridging ligand while naming a complex ?
9. Give the order of naming the ligands.
10. What type of numeral is used to indicate oxidation state of central ion ? Write the structure of $Fe(CO)_5$.
11. Give examples of cis-trans isomerism exhibited by complexes of coordination number 4 and 6.
12. Give some examples of optical isomerism exhibited by complexes of coordination number 6.
13. What are primary and secondary valencies ?
14. How optical isomers are designated ?
15. (a) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ show __________ isomerism.

    (Ans: ionisation)

    (b) $KCl.MgCl_2.6H_2O$ is a _____________, but $K_4\ [Fe(CN)_6]$ is a ________.

    (Ans: double salt, complex compound)

    (c) $[Co(NH_3)_4Cl_2]Cl$ give _______ Cl^- ions in solution.

    (Ans: one)

    (d) Whether cis-trans isomerism is exhibited by $[Co(en)_2Cl_2]Cl$?

    (e) Whether $[Cr(en)_3Cl_3]$ exhibits optical isomerism or not ?

(f) Complexes of type MA_4B_2 can exist as _________ isomers.

(Ans: cis-trans)

(g) Write the possible isomers of the following compounds.

(i) $[Cr(en)_3]Cl_3$ (ii) $[Cr(en)_2Cl_2]Cl$.

(h) How many isomers are there for the complex $[Co(NH_3)_3Cl_3]$?

(i) Which type of square planar complexes show cis-trans isomerism ?

(j) Which type of octahedral complexes show geometrical isomerism ?

(k) Does $[Co(NH_3)_6]Cl_3$ show optical isomerism ?

(l) Give an example of two hydrate isomers.

(m) Give as example of two ionisation isomers.

(n) What do you understand by linkage isomerism of CNS^- ?

(o) Give an example of two coordination isomers.

(p) Draw all possible isomers of $[Cr (NH_3)_3Cl_3]$.

(q) Give one example of both ionisation and hydrate isomerism in single compound.

$[Co(NH_3)_4 (H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

(r) Draw the structure of triammine - 1, 2, 3 trichloroplatinum(IV)chloride.

(s) $[Rh(en)_3]$ $[IrCl_6]$ and $[Rh(en)_2Cl_2]$ $[Ir(en)Cl_4]$ are which type isomers ?

(t) How many chloride ions can be precipitated from an aqueous solution of $[Cr(py)_2 (H_2O)_2 Cl_2]Cl$ with $AgNO_3$?

(u) How a double salt can be distinguished from a complex salt ?

B. Short answer type questions (2 marks each) :

1. What is the coordination number of each ion in NaCl?

2. (i) Write the name of the compound :

$[Co(en)_2Cl_2]SO_4$

(ii) Write the formula of the compound :

‘Potassium pentachloro monoamine platinate (IV).

3. (i) What is the IUPAC name of the following compound.

$K_3[Fe(CN)_6]$

(ii) Write formula of the following :

Ammonium diamminetetrathiocyanato chromate (III)

4. Write the formula of the following complex :

Tris (ethylene diamine) cobalt (III) sulphate.

5. Write short notes on : Werner's theory of coordination compounds.

6. Write the name of the compound :

$[(C_2H_5)_5N]_2[ZnCl_4]$

C. Very short answer type questions (one mark each) :

1. Fill in the blanks :

(i) Ethylene diamine is an example of _____ ligand.

(ii) The IUPAC name of $Fe(CO)_5$ is _____.

(iii) Dimethyl glyoxime is used for the gravimetric estimation of _____ ion.

(iv) EDTA is a _____ ligand.

(v) $K_4[Fe(CN)_6]$ is a complex compound, but potash alum is a _____

(vi) One molecule of $[Pt(NH_3)_6]Cl_4$ gives _____ ions in solution and requires _____ of $AgNO_3$ for complete precipitation of chloride ions.

(vii) Geometrical isomerism is not observed in complexes of coordination number 4 of _____ geometry.

(viii) The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is _____

[**Answer :** (i) bidentate (ii) pentacaronyliron (0) (iii) Ni^{2+} (iv) hexadentate (v) double salt (vi) five, 4 molecules (vii) tetrahedral (viii) paramagnetism]

2. Match the following

1.	Double salt	(a) $[Co(NH_3)_3Cl_3]$
2.	Neutral molecule	(b) Hexadentate
3.	EDTA	(c) Bidentate
4.	$Ni(CO)_4$	(d) Paramagnetic
5.	$[Cr(NH_3)_6]^{3+}$	(e) $FeSO_4(NH_4)_2SO_4.6H_2O$
6.	Low spin complex	(f) $K_4[Fe(CN)_6]$
7.	Glycine	(g) Diamagnetic

[**Answer :** (1-e), (2,-a), (3-b), (4-g), (5-d), (6-f), (7-c)]

3. What type of isomers are the following

(a) $[(CO)_5MnSCN]$ and $[(CO)_5MnNCS]$

(b) $[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$

(c) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(d) $[Co(py)_2(H_2O)_2Cl_2]Cl$ and $[Co(py)_2(H_2O)Cl_3]H_2O$

[**Answer** : (a) Linkage, (b) Coordination, (c) Ionisation, (d) Hydrate

D. Long Answer type (7 marks each) :

1. (a) What are the postulates of Valence Bond Theory ?

   (b) Distinguish between inner and outer orbital complex with suitable examples.

2. Account for the following on the basis of Valence bond theory

   (a) $[Ni(CN)_4]^{2-}$ is diamagnetic and squareplanar.

   (b) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral.

3. Discuss in brief the Crystal Field theory. How does it differ from Valence Bond theory ? Explain the fact that $[CoF_6]^{3-}$ is paramagnetic whereas $[Co(NH_3)_6]^{3+}$ is diamagnetic although both are octahedral.

4. (a) Describe the bonding in $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ in terms of Valence Bond theory and Crystal Field theory.

   (b) Tetrahedral complexes do not show low spin configuration - Explain.

5. (a) Discuss briefly how Crystal Field theory explains the magnetic properties of complexes of transition metals.

   (b) Discuss the structure of following complexes on the basis of CFT.

   (i) $[Co(NH_3)_6]^{3+}$, (ii) $[Fe(CN)_6]^{4-}$.

❑❑❑

UNIT - X

HALOGENATED HYDROCARBONS (HALOALKANES AND HALOARENES)

CHAPTER - 14

HALOALKANES (ALKYL HALIDES)

14.1 INTRODUCTION :

When hydrogen atoms of an alkane are replaced by same number of halogen atoms the compound formed is called halogen derivative of alkane. These are synthetic products and not found in nature. Alkyl halides are the starting materials for the synthesis of a large variety of aliphatic compounds. The halogen derivatives of alkanes, alkenes and alkynes are known as alkyl halides (haloalkanes), alkenyl halides (haloalkenes) and alkynyl halides (haloalkynes) respectively.

14.2 CLASSIFICATION :

Halogenated compounds may be classified in several ways depending on the type of halogen atoms, number of halogen atoms and position of halogen atoms. Alkyl halides may be mono, di, tri and so an according to the number of halogen atoms replacing hydrogen atoms in an alkane. e.g. CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are mono, di, tri and tetrahalomethane respectively. Vinyl chloride ($CH_2=CH–Cl$) and ethynyl bromide ($CH \equiv C–Br$) are the monohalogen derivatives of unsaturated hydrocarbons.

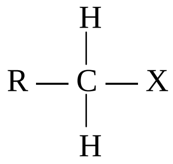
14.3 MONOHALOGEN DERIVATIVES OF ALKANES :

When only one hydrogen atom of an alkane is replaced by a halogen atom (X) where X=F, Cl, Br, I, the compound in called monohalogen derivative of the alkane, It has the general formula $C_nH_{2n+I}X$ and represented as R–X, where R=alkyl group and X = halogen atom.

In general, monohalogen derivatives are usually named as halides of the corresponding alkane and the homologous series is known as alkyl halides. They can be looked upon as the derivatives of halogen acids HF, HCl, HBr, HI in which the hydrogen atom of the acid has been replaced by alkyl group and can be called alkyl halides.

Monohalogen derivatives can be divided into three classes depending upon the attachment of halogen atom to a primary, secondary or tertiary carbon directly.

Primary halide :

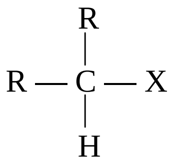


$R-\underset{H}{\overset{H}{C}}-X$

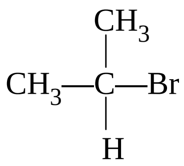
e.g $CH_3–CH_2–CH_2–Br$

(1- Bromopropane)

Secondary halide :



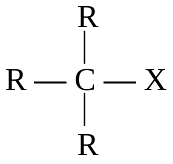
$R-\underset{H}{\overset{R}{C}}-X$



$CH_3-\underset{H}{\overset{CH_3}{C}}-Br$

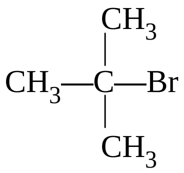
(2-Bromo propane)

Tertiary halide :



$R-\underset{R}{\overset{R}{C}}-X$

eg.



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$

(2-Bromo -2-methylpropane)

14.4 NOMENCLATURE :

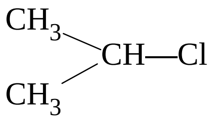
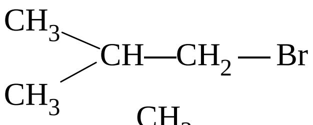
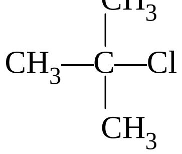
Common name to an alkyl halide in assigned by adding halide to the alkyl group .

Examples :

CH_3Cl	CH_3CH_2Br.	$CH_3CH_2CH_2I$
(Methyl chloride)	(Ethyl bromide)	(Propyl iodide)

According to the IUPAC system,, longest chain containing, the halogen atom is selected and the alkyl halide is named as the substitution product of the corresponding alkane and named as **haloalkanes**.

The common and IUPAC name of some alkyl halides are given below.

Formula	Common name	IUPAC name
CH_3Br	Methyl bromide	Bromomethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1–Fluoropropane
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-Cl$	*Isopropyl chloride	2–Chloropropane
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2-Br$	*Isobutyl bromide	1– Bromo - 2 - methylpropane
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$	*tert – Butyl chloride	2– Chloro-2-methylpropane

* ***According to the new IUPAC system, trivial or common system like isopropyl, tert. butyl etc. can also be used in IUPAC nomenclature.***

14.5 METHODS OF PREPARATION :

Alkyl halides can be prepared by the following methods.

1. From alkanes :

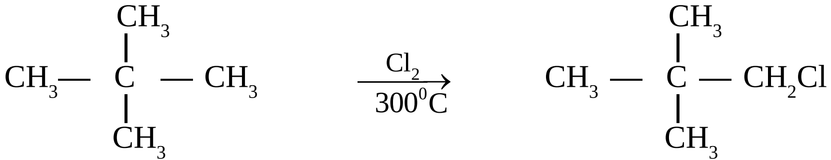
Alkyl halides can be prepared by the direct halogenation of lower alkanes in the gas phase, in diffused sunlight or at high temperature (400^0 C) or in the presence of catalyst such as $FeCl_3$, $FeBr_3$, $CuCl_2$ etc.

$$\underset{\text{Alkane}}{R-H} + X_2 \xrightarrow{h\nu} \underset{\text{Alkylhalide}}{RX} + HX$$

X = Cl or Br.

$$\underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{Cl_2} \underset{\text{Methylene chloride}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\text{Chloroform}}{CHCl_3} \xrightarrow{Cl_2} \underset{\text{Carbon tetrachloride}}{CCl_4}$$

It is not a suitable method, because a mixture of mono, di, tri and tetra halides are obtained.



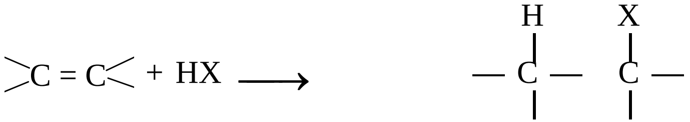
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow[300^0C]{Cl_2} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl$$

(neopentane) (neopentyl chloride)

Under the influence of heat or light, halogenation takes place through free radical mechanism

2. From alkenes :

Alkyl halide can be prepared by the addition of hydrogen halide HX(HX = HCl, HBr, HI) to alkene. The reaction takes place when gaseous halogen halide is passed through a solution of alkene in an inert solvent, in dark and at low temperature.



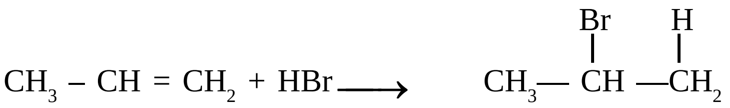
$$>C=C< + HX \longrightarrow -\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{X}{|}}{\underset{|}{C}}-$$

(Alkene) (Alkyl halide)

Addition of halogen acids to unsymmetrical alkenes follows Markownikoff's rule.

$$R-CH=CH_2 + HX \longrightarrow R-\overset{\overset{X}{|}}{CH}-\overset{\overset{H}{|}}{CH_2}$$

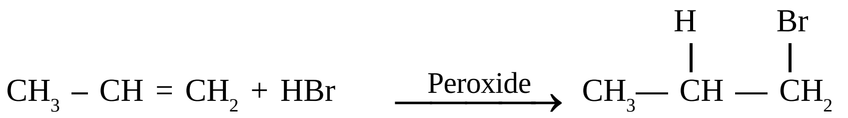
For example :



$$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-\overset{\overset{Br}{|}}{CH}-\overset{\overset{H}{|}}{CH_2}$$

(Prop - 1- ene) (2 - Bromopropane)

In the presence of peroxide, in gas phase and at high temperature the above reaction follows Anti-Markownikoff's rule.



$$CH_3-CH=CH_2+HBr\xrightarrow{\text{Peroxide}}CH_3-\overset{\overset{\large H}{|}}{CH}-\overset{\overset{\large Br}{|}}{CH_2}$$

(Prop - 1- ene) (2 - Bromopropane)

3. From Alcohols :

(i) By the action of halogen acids :

Alkyl bromides and iodides are prepared by the action of corrosponding halogen halide (HBr, HI) on the alcohol. Alkyl chlorides can be prepared by the action of concentrated HCl in the presence of **anhydrous zine chloride**.

$$R-OH+HX\xrightarrow{ZnCl_2}R-X+H_2O$$

(Alcohol) (Alkylhalide)

For example :

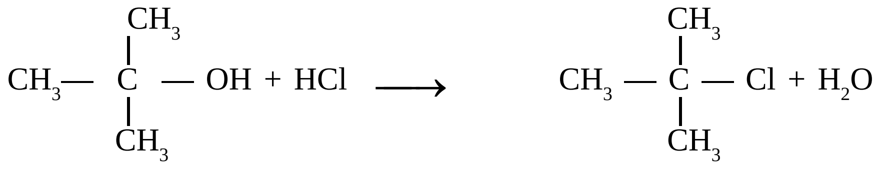
$$CH_3OH+HBr\xrightarrow{ZnCl_2}CH_3Br+H_2O$$

(Methylalcohol) (Methylbromide)

Order of reactivity of different alcohols in this reaction is

Tertiary > Secondary > Primary

Thus tertiary alcohol form tertiary alkyl chloride even in the absence of anhydrous $ZnCl_2$ in cold.



$$CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-OH+HCl\longrightarrow CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-Cl+H_2O$$

(tert-butyl alcohol) (tert-butyl chloride)

(ii) By the action of phosphorus halides :

Alkyl halides can be prepared by the action of phosphorus halides i.e. PX_5 or PX_3 on alcohols.

$$R-OH\xrightarrow{PX_5\text{ or }PX_3}R-X$$

For example :

$$CH_3-CH_2-OH+PCl_5\longrightarrow CH_3-CH_2-Cl+POCl_3+HCl$$

$$3\,CH_3-CH_2-OH+PCl_3\longrightarrow 3\,CH_3-CH_2-Cl+H_3PO_3$$

Methyl iodide and ethyl iodide can be prepared in the laboratory by this method. PI_3 is prepared *insitu* by the action of Red P and I_2 in corresponding alcohol.

$$P_4 + 6I_2 \xrightarrow{\text{RedP}} 4PI_3$$

$$3\,R - OH + PI_3 \longrightarrow 3R - I + H_3PO_3. \qquad (R = CH_3 \text{ or } C_2H_5)$$

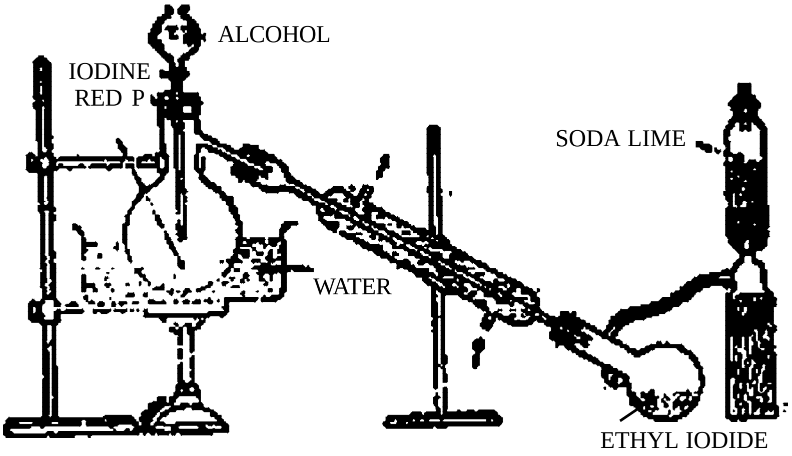


Fig. 14.1 Preparation of ethyl iodide.

(iii) By the action of thionyl chloride :

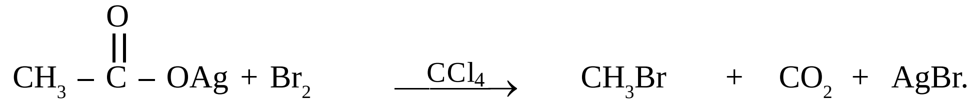
Alkyl chloride can be prepared by the action of thionyl chloride ($SOCl_2$) on alcohol in the presence of pyridine.

$$R - OH + SOCl_2 \xrightarrow{Py} R - Cl + SO_2 + HCl$$

$$CH_3 - CH_2 - OH + SOCl_2 \xrightarrow{Py} CH_3 - CH_2 - Cl + SO_2 + HCl$$

4. From monocarboxylic acid (Hunsdiecker Reaction)

When silver salt of a carboxylic acid is treated with chlorine or bromine in carbon tetrachloride solution, alkyl halides are obtained. This reaction is known as **Hunsdiecker reaction**.



$$CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - OAg + Br_2 \xrightarrow{CCl_4} CH_3Br + CO_2 + AgBr.$$

(Silver acetate) (Methyl bromide)

14.6 PROPERTIES :

(A) Physical Properties :

(1) **State :** Lower alkyl halides like methyl chloride, methyl bromide and ethyl chloride are gases while methyl iodide and rest of the lower members upto C_{18} are colourless liquids. Beyond C_{18} are odourless crystalline solids.

(2) **Colour change :** Alkyl iodides decompose even on exposure to light and therefore, they turn brown on standing due to the liberation of iodine.

$$2RI \longrightarrow R - R + I_2.$$

(3) **Solubility :** Alkyl halides are slightly polar, but they are insoluble in water. They are soluble in organic solvents like alcohol, ether, benzene etc.

This is because, alkyl halides fail to form hydrogen bonds with water and can not break the hydrogen bonds already existing between water molecules.

(4) **Density :** Alkyl bromide and iodides are heavier than water, while chlorides are lighter than water.

(5) **Melting Point and Boiling point :** Alkyl halides have boiling points higher than the corresponding hydrocarbons. In general, boiling points rise with the increase of molecular mass and decrease of branching of alkyl group. Boiling points of alkyl halides are in the order,

$$RI > RBr > RCl$$

Their high boiling points are due to two types of inter molecular forces, i.e. dipole-dipole attractions and van der Walls forces, which are stronger in them compared to parent hydrocarbons.

Examples :

(i)

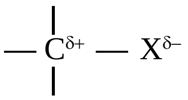
Compound :	CH_3Cl	CH_3CH_2Cl	$CH_3(CH_2)_2Cl$
b.p (K)	249	285.5	320

(ii)

Compound :	CH_3I	CH_3Br	CH_3Cl	CH_3F
b.p (K)	315	277	249	195

(B) Chemical Properties :

Since alkyl halides are polar compounds, the more electronegative halogen atom withdraws the shared pair of electrons of carbon-halogen covalent bond towards itself, thereby increasing the electron density around the halogen atoms and acquiring a partial negative charge. The carbon atom becomes electron deficient and acquires a partial positive charge.



$$-\overset{|}{\underset{|}{C}}{}^{\delta+}-X^{\delta-}$$

The polarity in carbon-halogen bond produces dipole moment. Some of the important chemical properties of alkyl halides are given below.

1. Reduction :

Alkyl halides when treated with reducing agents such as Zn – Cu couple and ethanol, Sn / HCl, $LiAlH_4$, hydrogen in the presence of Pd, sodium in ethanol, sodium amalgam and water, Zn / HCl etc. are converted into their corrosponding alkanes.

$$R - X + 2H \longrightarrow R - H + HX$$

Alkyl iodide may be reduced to alkane with HI and Red P at 150^0C.

$$R - I + HI \xrightarrow[150^0C]{\text{Red P.}} R - H + I_2$$

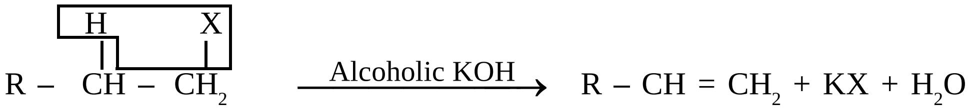
2. Elimination Reaction :

Alkyl halides undergo elimination reaction to form alkenes with the removal of a molecule of hydrogen halide. During dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms.

The order of elimination reaction is

Tertiary halides > Secondary halides > Primary halides.

Alkyl halides on boiling with alcoholic KOH produce alkenes.



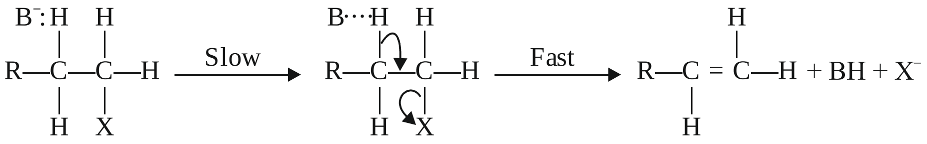
$$R - \overset{H}{CH} - \overset{X}{CH_2} \xrightarrow{\text{Alcoholic KOH}} R - CH = CH_2 + KX + H_2O$$

For example :

$$CH_3 - CH_2 - CH_2 - Br. \xrightarrow{\text{Alcoholic KOH}} CH_3 - CH = CH_2 + KBr + H_2O$$

(1 - Bromopropane) (Propene)

When approached by a strong base, haloalkane loses a proton from the β-carbon atom and halogen atom from ∝-carbon atom, which is often called as β-elimination.



Nucleophilic Substitution Reactions :

Substitution reaction involves replacement of one functional group by another. Here halogen (X) is replaced by another group (Y)

$$R - X + Y \longrightarrow R - Y + X$$

Electron rich reagents are called *nucleophilic reagents* and the substitution reaction with those reagents are called *nucleophilic substitution reaction*.

Here in case of alkyl halide, halide ion (X^-) is an extremely weak base. The reagents which are more basic than the halogen atoms can attack the positively charged carbon and can easily displace the halogens as halide ions.

Nucleophilic substitution reaction is abbreviated as S_N. According to the number of reacting species, participating in the rate determining step of a particular reaction, the S_N reaction maybe distinguished as S_N1, S_N2 , where 1 and 2 stands for unimolecular and bimolecular respectively.

A wide variety of organic compounds can be prepared by the nucleophilic substitution reaction in alkyl halides. Some of them are given below.

Mechanism : There are two mechanisms, through which this reaction is found to proceed. (i) S_N2 mechanism (ii) S_N1 mechanism.

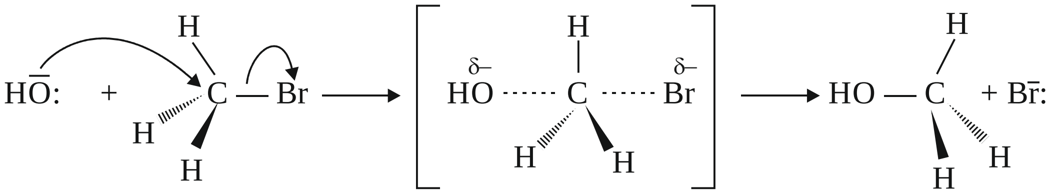
(i) **S_N2 mechanism :** In this case, the reaction involves both the substrate (alkylhalide) and the nucleophile in the rate determing step and follows a concerted mechanism where the departure of the leaving group is assisted by the incoming nucleophile.

Rate = k [alkyl halide] [nucleophile]

Example :

$$H\bar{O} + CH_3 - Br \longrightarrow CH_3 - OH + B\bar{r}:$$

In S_N2 reaction, the nucleophile attacks the substrate from the back side, i.e. the side opposite to the leaving group.



Reactants Transition state Products

As the nucleophile attacks from the backside, the configuration of the product relative to reactant is inverted, exactly like an umbrella in a gale. This change in configuration is called as 'inversion of configuration' or **Walden inversion**.

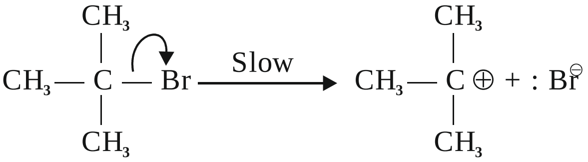
(ii) **S_N1 mechanism :** This type of reaction involves only the substrate (alkyl halide) in the rate determining step, where the bond between carbon and the leaving group breaks forming a carbocation.

Rate = k [alkyl halide]

Example : $(CH_3)_3\ C - Br + OH^- \rightarrow (CH_3)_3\ C - OH + Br^-$

S_N1 reaction takes place in two steps. The first step involves the ionization of C–Br bond to form a 3° carbocation intermediate.

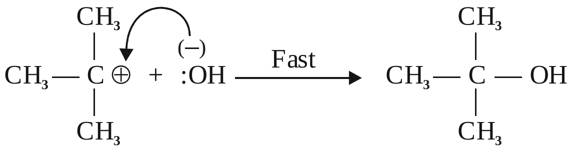
Step-1 :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow{Slow} CH_3-\underset{CH_3}{\overset{CH_3}{C}}\oplus + :Br^{\ominus}$$

(tert-Butyl bromide)

Step-2 : In the 2nd step, the carbocation is attacked by the nucleophile.



$$(CH_3)_3C^{\oplus} + \overset{(-)}{:OH} \xrightarrow{\text{Fast}} (CH_3)_3C-OH$$

tert-Butyl alcohol

Due to the high stability of tertiary carbocation, the order of reactivity for S_N1 reaction is :

Tertiary halide > Secondary halide > Primary halide

(a) Substitution by hydroxyl group :

Alkyl halides when treated with aqueous KOH or moist Ag_2O, are hydrolysed to alcohols

$$R - X + KOH\ (aq) \longrightarrow R - OH + KX$$

i.e. $CH_3 - CH_2 - Br + KOH(aq) \longrightarrow CH_3 - CH_2 - OH + KBr.$
(Ethylbromide) (Ethyl alcohol)

$CH_3Br + AgOH \longrightarrow CH_3OH + AgBr.$
(Methyl bromide) (moist silver oxide) (Methyl alcohol)

(b) Substitution by alkoxy group :

Alkyl halides on treatment with metal alkoxides (RO^-Na^+) produce ethers. This method of preparation of ethers is known as **Williamson synthesis**.

$R - X + R^1O^-Na^+ \longrightarrow R - O - R^1 + NaX$
(Alkyl halide) (Sodium alkoxide) (Ether)

$CH_3CH_2I + CH_3CH_2ONa \longrightarrow CH_3–CH_2–O–CH_2–CH_3+NaI.$
(Ethyl iodide) (Sodium ethoxide) (Diethyl ether)

The reaction of alkyl halide with dry silver oxide (Ag_2O) also results in the formation of an ether.

$$2RX + Ag_2O \longrightarrow R - O - R + 2AgX$$

$2CH_3Cl + Ag_2O \longrightarrow CH_3 - O - CH_3 + 2AgCl$
(Methyl chloride) (Silver oxide) (Dimethyl ether)

(c) Substitution by cyanide group :

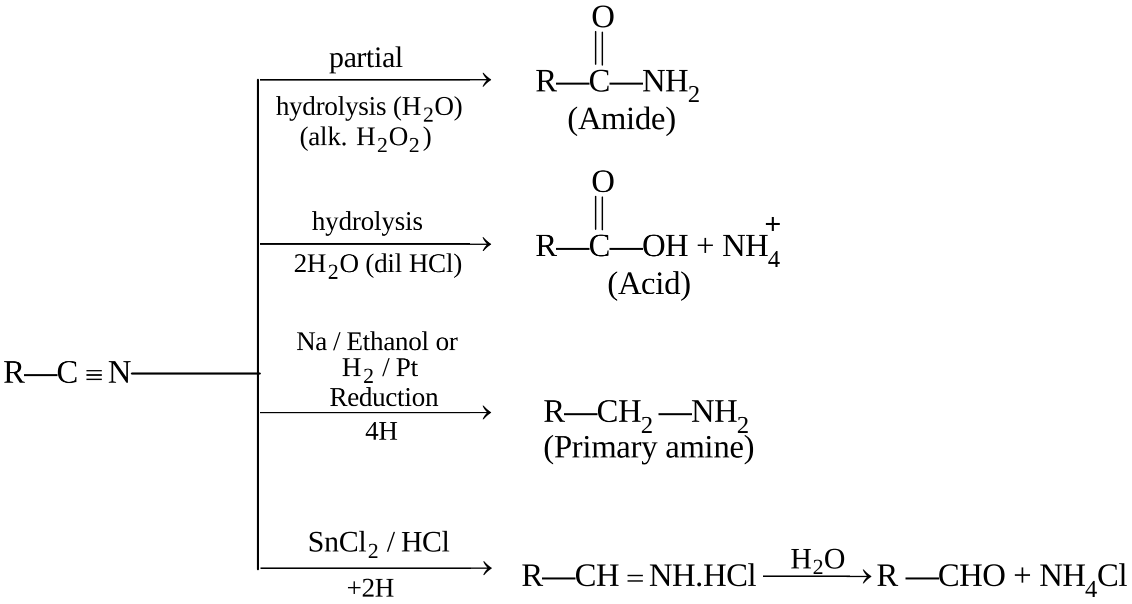
When alkyl halides are heated with aqueous or alcoholic KCN, alkyl cyanides are formed. This involves the nucleophilic attack of CN^- on alkyl halide.

$R - X + K^+CN^- \longrightarrow R - CN + KX$

Alkyl halide → Alkyl cyanide or acid nitrile

$CH_3 - CH_2 - I + KCN \longrightarrow CH_3 - CH_2 - CN + KI$

(Ethyliodide) → (Ethyl cyanide)



Since the conversion of an alkyl halide into alkyl cyanide, involves addition of one carbon atom into the molecule, it affords a means of ascending a homologous series i.e. the conversion of lower member into a higher member.

Substitution of isocyanide group :

Alkyl halides when treated with aqueous alcoholic silver cyanide, form alkyl isocyanides.

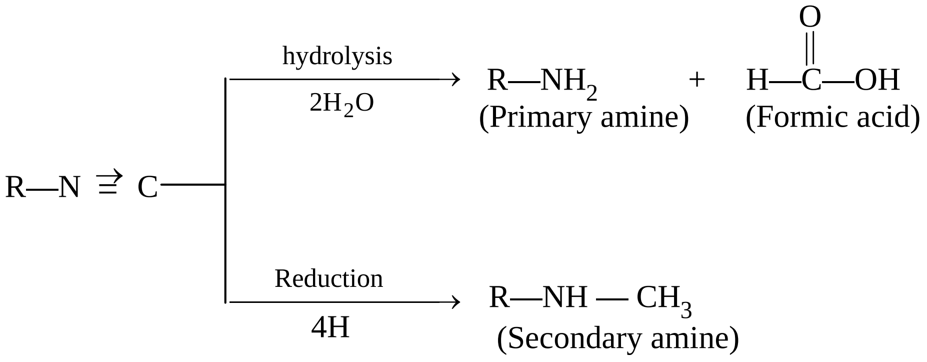
$R - X + AgCN \longrightarrow R - N \stackrel{\rightarrow}{=} C + AgX.$

(Alkyl halide) (silver cyanide) → (Alkyl isocyanide)

$CH_3 - CH_2 - I + AgCN \longrightarrow CH_3 - CH_2 - NC + AgI.$

(Ethyl iodide) → (Ethyl isocyanide)

Isocyanides on hydrolysis give primary amines and formic acid and on reduction give secondary amines.



(d) Substitution by nitro group :

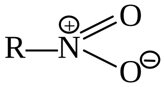
Alkyl halides when treated with alcoholic solution of silver nitrite, nitroalkanes are formed. When alkyl halides are treated with alcoholic solution of potassium nitrite (KNO_2), alkyl nitrites (ester) are formed.

$$R - X \quad + \quad AgNO_2 \longrightarrow \underset{\text{(Nitroalkane)}}{R - NO_2} \quad + \quad AgX$$

$$\underset{\text{(ethyl iodide)}}{C_2H_5\text{-}I} \quad + \quad AgNO_2 \longrightarrow \underset{\text{(Nitroethane)}}{C_2H_5 - NO_2} \quad + \quad AgI.$$

$$R - X + K - O - N = O \xrightarrow[\text{alc.soln}]{\text{Heat}} \underset{\text{(alkyl nitrite)}}{R - O - N = O} + KX$$

$$\underset{\text{(Ethyl bromide)}}{CH_3\ CH_2\ Br} + K - O - N = O \xrightarrow[\text{alc.soln}]{\text{Heat}} \underset{\text{(Ethyl nitrite)}}{CH_3CH_2 - O - N = O} + KBr$$

[Note : It must be remembered that reaction with alcoholic solution of $AgNO_2$ gives nitroalkane,  whereas alcoholic solution of KNO_2 gives an ester, nitrite, R–O–N = O. as the major product]

(e) Substitution by amino group :

Alkyl halides when treated with ethanolic ammonia under pressure, give primary amines.

$$\underset{\text{(Alkyl halide)}}{R - \boxed{X + H} - NH_{2(alc)}} \longrightarrow \underset{\text{(Primary amine)}}{R - NH_2 + HX}$$

$$CH_2 - CH_2 - I + NH_{3(alc)} \longrightarrow \underset{\text{(Ethylamine)}}{CH_3 - CH_2 - NH_2 + HI}$$

If excess of alkyl halide is used, the reaction continues to form a mixture of secondary amine, tertiary amine and finally quatenary ammonium salt.

$$C_2H_5I + C_2H_5NH_2 \longrightarrow \underset{\text{(Diethylamine)}}{(C_2H_5)_2\ NH + HI}$$

$$C_2H_5I + (C_2H_5)_2\ NH \longrightarrow \underset{\text{(triethylamine)}}{(C_2H_5)_3\ N + HI}$$

$$C_2H_5I + (C_2H_5)_3N \longrightarrow (C_2H_5)_4\ N^+I^-$$

(Tetraethyl ammonium iodide)

(Quaternary ammonum salt)

4. **Reactions with metals :** Alkyl halides react with a number of metals to form organometallic compounds.

(a) Reaction with magnesium :

Alkyl halides react with magnesium in dry ether solution to form Grignard reagents (alkyl magnesium halides)

$$R - X + Mg \xrightarrow{\text{dry Ether}} R - Mg - X$$

(Alkyl magnesium halide)

For example :

$$CH_3 - CH_2 - Br + Mg \xrightarrow{\text{dry Ether}} CH_3CH_2MgBr$$

(Ethyl bromide) (Ethyl magnesium bromide)

(b) Reaction with sodium :

Alkyl halides when heated with metallic sodium, in dry ether, higher alkanes are obtained. The above reaction in known as **Wurtz reaction.**

$$R - \boxed{X + 2Na + X} - R \xrightarrow[\text{heat}]{\text{dry ether}} R - R + 2NaX.$$

$$CH_3 - \boxed{I + 2Na + I} - CH_3 \xrightarrow[\text{heat}]{\text{dry ether}} CH_3 - CH_3 + 2NaI.$$

(Methyl iodide) (Ethane)

(c) Reaction with lead-sodium alloy :

Alkyl halides when treated with lead–sodium alloy, form tetraalkyllead.

For example :

$$4C_2H_5Cl + 4Pb(Na) \longrightarrow (C_2H_5)_4 Pb. + 4NaCl + 3 Pb.$$

Sodium– lead alloy Tetraethyl lead (TEL)

Tetraethyl lead (TEL) was used as an antiknocking compound in petrol. Due to air pollution by lead, TEL is no more used in petrol (unleaded petrol)

(5) Alkylation of Aromatic hydrocarbons :

Alkyl halide when treated with benzene in the presence of anhydrous aluminium chloride, alkyl benzenes are formed. This reaction is known as **Friedel Craft's reaction**.

$$R - X + C_6H_6 \xrightarrow{\text{Anh.AlCl}_3} C_6H_5 - R + HX$$

(Alkyl halide) (Benzene) (Alkyl benzene)

$$CH_3Cl + C_6H_6 \xrightarrow{\text{Anh.AlCl}_3} C_6H_5 - CH_3 + HCl$$

(Methyl chloride) (Benzene) (Methyl benzene or Toluene)

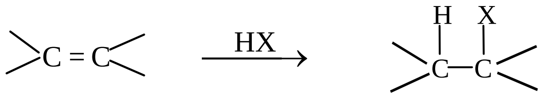
CHAPTER (14) AT A GLANCE - HALOALKANES

General molecular formula : R–X , X = F, Cl, Br or I

A. Preparation of alkyl halide

1. $R-H \xrightarrow[h\nu]{X_2} R-X+HX$

(Alkane)

2. 

(Alkene)

3. $R-OH \rightarrow$ (Alcohol)

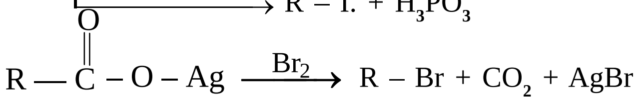
$\xrightarrow{HBr} R-Br+H_2O$

$\xrightarrow{HCl\,/\,ZnCl_2} R-Cl+H_2O$

$\xrightarrow{PX_5\,/\,PX_3} R-X$

$\xrightarrow{SOCl_2} R-Cl$

$\xrightarrow{\text{Red }P_4\,/\,I_2} R-I.+H_3PO_3$

4. 

$R-\overset{O}{\overset{\|}{C}}-O-Ag \xrightarrow{Br_2} R-Br+CO_2+AgBr$

(Silver salt of acid)

B. Properties of Alkyl halides :

$R-X \rightarrow$

$\xrightarrow{\text{Reduction}} R-H$ (Alkane)

$\xrightarrow{\text{Elimination Reaction (Alc.KOH)}}$ Alkene

$\xrightarrow{\text{Aqueous KOH.}} R-OH$ (Alcohol)

$\xrightarrow{\text{RONa or }Ag_2O\text{ moist}} R-O-R$ (Ether)

$\xrightarrow{KCN} R-C\equiv N$ (Alkyl cyanide)

$\xrightarrow{AgCN} R-N\rightleftarrows C$ (Alkyl isocyanide)

$\xrightarrow{AgNO_2} R-NO_2$ (Nitroalkane)

$\xrightarrow{KNO_2} R-O-N=O$ (Alkylnitrite)

$\xrightarrow{NH_3} R-NH_2$ (Primary amine)

$\xrightarrow{R'COOAg} R'-COOR$ (Ester)

$\xrightarrow{\text{Mg in dry ether}} R-Mg-X$ (Grignard reagent)

$\xrightarrow{\text{Na in dry ether}} R-R$ (Higher alkane)

$\xrightarrow{Pb(Na)} (R)_4Pb$ (tetraalkyl lead)

$\xrightarrow{C_6H_6\,/\,\text{Anh. }AlCl_3} C_6H_5-R$ (Alkyl benzene)

QUESTIONS

(A) Short Questions (One mark each)

1. In methyl chloride molecule there are – bonds.

   [4 sigma, 3 sigma and one pi, 2 sigma 2 pi; 3 sigma and 2 pi]
2. What happens when chloroform is boiled with aqueous solution of caustic potash ?
3. Write the name of the monomer of teflon.
4. What organic compound is obtained when ethyl bromide reacts with aqueous NaOH solution ?
5. Write the graphic formula of acid halide.

(B) Short Questions (two marks each)

1. What happens when methyl iodide in treated with metallic zinc ? [CHSE 1987 A]
2. Write with equation, what happens when ethyl iodide is boiled with aqueous alkali ?
3. How will you prepare ethyl amine from ethyl iodide ?
4. Give equation for the reaction of ethyl iodide with equeous and alcoholic potassium hydroxide.
5. What happens when ethyl bromide is treated with alcoholic KOH ?
6. What happens when methyl iodide reacts with sodium methoxide ?
7. What happens when ethyl iodide is heated with sodium in dry ethereal solution ? Give equation.
8. How can you get ethyl chloride from ethyl alcohol ? Give equation.
9. How would you distinguish between C_6H_5Cl and $C_6H_5CH_2Cl$?
10. Write all the possible structural formulae and give IUPAC names of the isomers of C_4H_9Br, $C_5H_{11}Br$ and C_3H_7Cl.
11. Write the reaction of preparing an alkyl chloride using sulphuryl chloride as halogenating agent.
12. Write balanced equation for the reaction of methyl iodide with AgOH, C_2H_5ONa, CH_3COOAg and $AgNO_2$.
13. Using bromoethane how will you obtain diethyl ether and ethyl amine ?
14. What happens when : (Give equations)
    - (i) Silver acetate is treated with bromine.
    - (ii) Ethyl alcohol reacts with iodine in the presence of caustic alkali.
15. (i) Ethyl alcohol is treated with PCl_5.
    - (ii) Ethyl iodide in treated with dry silver oxide.

(C) Short Questions (three marks each)

1. Complete the following equation :

   (i) $CH_3I + AgCN \longrightarrow$

   (ii) $CH_3I + NH_3 \longrightarrow$

   (iii) $CH_3CH_2CH_2Br + KOH\ (alc) \xrightarrow{\triangle}$ —— + —— + H_2O [CHSE, 2002 IR]

   (iv) $CH_3I + KOH(aq) \longrightarrow$

2. Explain why ?

   (i) Although alkyl halides are slightly polar, they are insoluble in water.

   (ii) Alkyl halides have higher boiling points than the corresponding hydrocarbons.

3. Explain why?

   For a given alkyl group, the order of boiling point is

   (i) RI > RBr > RCl > RF.

   (ii) For a given alkyl group, the order of reactivity is

   RI > RBr > RCl > RF.

4. Explain why?

   (i) Alkyl halides undergo nucleophilic substitution reaction.

   (ii) Dipole moment of carbon tetrachloride is zero.

   (iii) A small amount of alcohol is usually added to chloroform bottle.

5. Explain why?

   (i) Alkyl halide of lower alkanes when treated with metallic sodium give higher alkanes.

   (ii) Hydrogen atom of chloroform is definitely acidic but that of methane is not.

   (iii) An alkyl halide can be utilised for the synthesis of a desired aliphatic compound.

6. Identify A, B and C in the following reaction sequence.

   (i) $A \xrightarrow{PCl_5} B \xrightarrow{alc.KOH} C \xrightarrow{H_2/Ni} CH_3CH_2CH_3$

   (ii) $A \xrightarrow{KCN} B \xrightarrow{4H} CH_3CH_2CH_2NH_2$

   (iii) $A \xrightarrow{alc.KOH} B \xrightarrow{Cl_2} C \xrightarrow{AgOH} CH_2OH - CH_2OH$

   (iv) $C_2H_5OH \xrightarrow[\Delta]{conc.\ H_2SO_4} A \xrightarrow{Br_2} B \xrightarrow{alc.KOH} C.$

   (v) $C_2H_5I \xrightarrow{alc.KOH} A \xrightarrow{Br_2} B \xrightarrow{KCN} C.$

(D) Long Questions : (7 marks each)

1. Describe the general method (only one) of preparation of an alkyl halide. How does it react with ammonia, metallic sodium and dilute caustic potash.

2. Write notes on
   (a) Iodoform reaction
   (b) Williamson synthesis.
3. What are halogen derivatives ? How are they classified ?
4. How ethyl bromide is prepared from ethyl alcohol ?
   How will you obtain the following compounds from it ?
   (i) Ethane (ii) ethene (iii) ethyl methyl ether (iv) ethyl amine.
5. How will you obtain the ethyl bromide from ethylene ?
   How does ethyl bromide react with sodium, aqueous KOH, alcoholic KOH and silver nitrite ?
6. What are the main products formed, when ethyl bromide reacts with KCN, AgCN, KI in acetone, $AgNO_2$, KNO_2, aq.KOH and alcoholic KOH ? Give equations.
7. Explain with equation, how alkyl halide can be prepared from alcohols. What happens when the following substances react with ethyl chloride ?
   (a) CH_3ONa (b) Na (c) Alcoholic KOH

MULTIPLE CHOICE QUESTIONS

1. Ethyl iodide reacts with sodium ethoxide to produce
   (a) Butane (b) Acetic acid
   (c) Diethyl ether (d) Ethane
2. When alkyl halide is treated with alcoholic KOH, the compound formed is
   (a) Alkane (b) Alkene
   (c) Alcohol (d) Ether
3. Which of the following is known as freon :
   (a) CCl_2F_2 (b) $CHCl_3$
   (c) CH_2F_2 (d) CF_4.
4. Which of the following is optically active ?
   (a) CH_3CHCl_2 (b) $CH_3CH_2CHClCH_3$
   (c) CH_3CH_2Cl (d) CH_2ClCH_2Cl
5. Which of the following will not give iodoform reaction
   (a) Acetaldehyde (b) Acetone
   (c) Ethyl alcohol (d) Methyl alcohol.
6. Which of the following reaction provides an example of nucleophilic substitution of an alkyl halide (RX).
   (a) $RX + Mg \longrightarrow RMgX$ (b) $RX + 2H \longrightarrow RH + HX$
   (c) $RX + KOH \longrightarrow ROH + KX$ (d) $2RX + Na \longrightarrow R-R + 2NaX$

7. The reagent required to convert CH_3I to CH_4 is

(a) Zn – Cu couple and ethanol (b) Magnesium in ether.

(c) Sodium methoxide (d) Sodium in ether.

8. For a given alcohol the order of reactivity with halogen acid is

(a) HI > HCl > HBr. (b) HCl > HI > HBr

(c) HCl > HBr > HI (d) HI > HBr > HCl

9. The compound with zero dipole moment is

(a) CH_3Cl (b) CH_2Cl_2

(c) CCl_4 (d) $CHCl_3$

10. IUPAC name of the compound having formula $(CH_3)_3$ CCl is

(a) t-butyl chloride (b) Isobutyl chloride

(c) 2-Methyl - 2 - chloropropane (d) n-butyl chloride

11. Alkyl halides react with alcoholic KOH to give

(a) Alkene (b) Alkane

(c) Alcohol (d) ether.

12. CH_2Cl_2 is the formula of

(a) Methylene chloride (b) Methyl chloride

(c) Ethyl chloride (d) Dichloroethylene.

13. When ethylene dibromide reacts with alcoholic KOH we get,

(a) C_2H_4 (b) C_2H_2

(c) C_3H_6 (d) C_2H_6

14. Which of the following compound is used as refrigerant ?

(a) Chloroform (b) Carbon tetrachloride

(c) Dichlorodifluoromethane (d) Carbontetrafluoride

15. Which of the following is optically active

(a) CH_3CH_2OH (b) CH_2OH . CHOH .CH_2OH

(c) $CH_3CHOHC_2H_5$ (d) CCl_2F_2

ANSWERS TO MULTIPLE CHOICE QUESTIONS

1. (c), 2. (b), 3. (a), 4. (b), 5. (d), 6. (c),
7. (a) 8. (d), 9. (c), 10. (c), 11. (a), 12 (a),

13. (b), 14. (c) 15. (c).

* * *

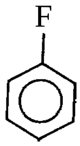
HALOARENES (ARYL HALIDES)

Aromatic halogen compounds are obtained by replacement of one or more hydrogen atoms of an aromatic hydrocarbon by an equal number of halogen atoms. These have been further classified into the following categories.

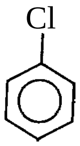
(i) Nuclear halogen derivatives : Halogen derivatives of aromatic hydrocarbons in which the halogen atom

(F, Cl, Br, or I) is directly attached to an aromatic ring are called aryl halides.

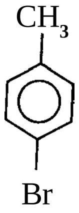
Their general formula is Ar-X where Ar (short name for aryl) represents a phenyl, a substituted phenyl, naphthyl, etc. Some examples of aryl halides are :



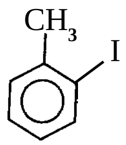
Fluorobenzene



Chlorobenzene

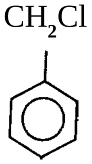


1-Bromo-4-methylbenzene
or 4-Bromotoluene
(*p*-Bromotoluene)



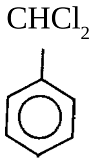
1-lodo-2methylbenzene
or 2-Iodotoluene
(*o*-lodotoluene)

(ii) Side chain halogen derivatives : ***Halogen derivatives of aromatic hydrocarbons in which the halogen atom is linked to one of the carbon atoms of the side chain carrying the aryl group are called arylalkyl (aralkyl) halides***. For example,



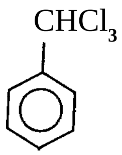
Benzylchloride

(1-Chloro-1-phenylmethane)



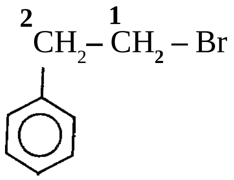
Benzal dichloride

(1,1-Dichloride- 1-phenylmethane)



Benzotrichloride

(1,1,1-Trichloro - 1-phenylmethane



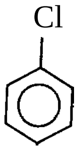
p-Phenylethyl bromide

(1-Bromo-2-phenylethane)

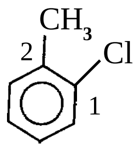
Like alkyl halides, arylalkyl halides are very reactive and thus undergo a number of substitution reactions. On the other hand, aryl halides are less reactive and thus undergo only a few substitution reactions that too, under drastic conditions.

14.7 NOMENCLATURE OF HALOGEN COMPOUNDS :

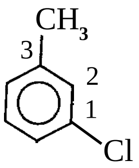
Haloarenes have the common as well as IUPAC names . For dihalogen derivatives, the prefixes *o*-, *m*-, *p*- are used in the common system but in the IUPAC system, numerical prefixes 1, 2, 1, 3 and 1, 4 are respectively used. In case the parent aromatic hydrocarbon carries a side chain or substituent, then the numbering of the carbon atoms of the ring begins with the substituent and in case the parent hydrocarbon is benzene, then the numbering begins with the halogen atom. However, polyhalogen derivatives do not have common names, but only have IUPAC names in which the positions of halogens are indicated by arabic numerals. For example,



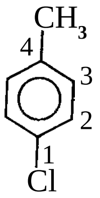
Chlorobenzene
(Chlorobenzene)



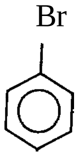
o-Chlorotoluene
(1-Chloro-2-methylbenzene
or 2-Chlorotoluene)



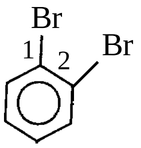
m-Chlorotolune
(1-Chloro-3-mehylbenzene
or 3- Chlorotoluene)



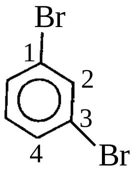
p-Chlorotoluene
(1-chloro-4-methyl-benzene
or 4-chlorotoluene)



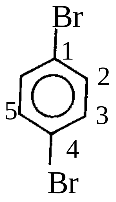
Bromobenzene
(Bromobenzene)



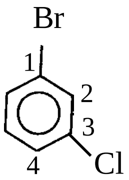
o-Dibromobenzene
(1,2,Dibromobenzene)



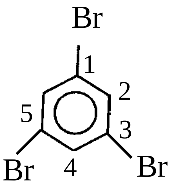
m-Dibromobenzene
(1,3-Dibromobenzene)



p-Dibromobenzene
(1,4-Dibromobenzene)



1-Bromo -3-chlorobenzene

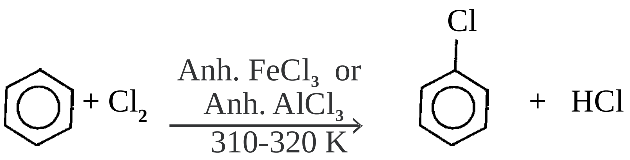


1,3,5 - Tribromobenzene

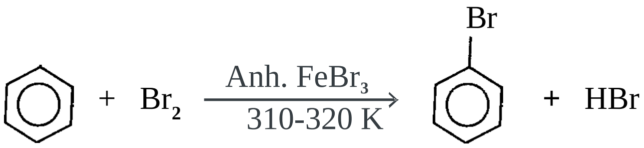
14.8 METHODS OF PREPARATION OF HALOARENES :

1. From aromatic hydrocarbons by direct halogenation.

(a) Nuclear halogenation : Chloroarenes (aryl chlorides) and bromoarenes (aryl bromides) can be easily prepared by direct chlorination or bromination of aromatic hydrocarbons. **The reaction is usually carried out at low temperature (310-320K), in the absence of sunlight and in the presence of a Lewis acid such as anhydrous ferric or aluminium halide as catalyst**.

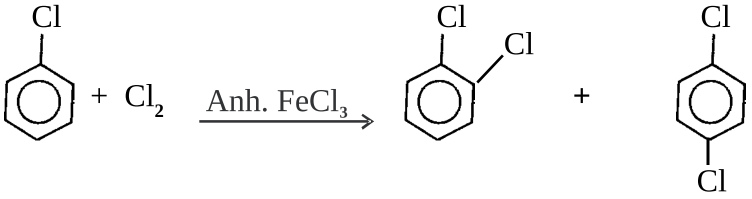


Chlorobenzene



Bromobenzene

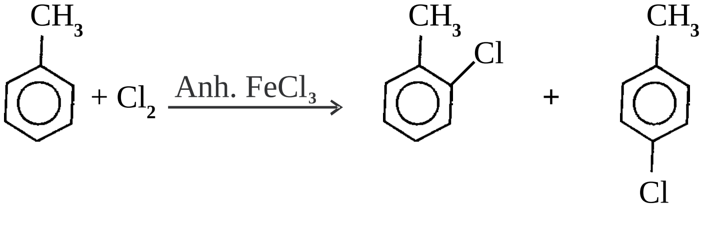
If excess of halogen is used - a second atom of halogen is introduced in the ring mainly at *o*- and *p*- positions with respect to the first since halogens are *o, p*- directing.



Chlorobenzene *o*-Dichlorobenzene (minor) *p*- Dichlorobenzene (major)

Similarly, further bromination with excess of bromine in presence of anhyd. $FeBr_3$ gives a mixture of *o*-dibromobenzene (minor) and *p*-dibromobenzene (major).

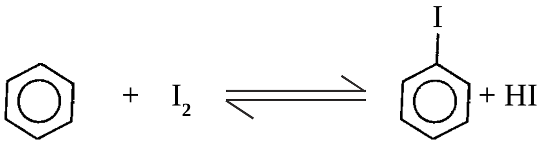
If toluene is used instead of benzene, a mixture of *o*- and *p*- chlorotoluene is obtained since CH_3 group is *o, p* - directing.



Toluene *o*-chlorotoluene (minor) *p*-chlorotoluene (major)

Similarly, bromination of toluene with Br_2 in presence of anhydrous $FeBr_3$ gives a mixture of *o*-bromotoluene (minor) and *p*-bromotoluene (major)

The direct iodination of aromatic hydrocarbons is not so useful since HI produced during the reaction, being a good reducing agent reduces the aryl iodide back to the aromatic hydrocarbon and iodine.



Benzene Iodine Iodobenzene

However, in the presence of oxiding agents such as nitric acid, iodic acid (HIO_3), mercuric oxide etc. the HI produced is either oxidised to iodine or eliminated as mercuric iodide and thus the reaction proceeds in the forward direction producing iodobenzene.

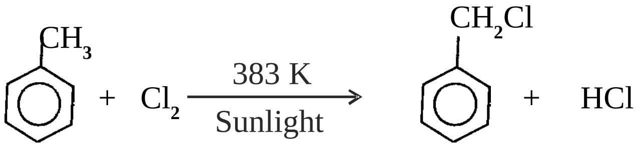
$$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

$$HgO + 2HI \longrightarrow HgI_2 + H_2O$$

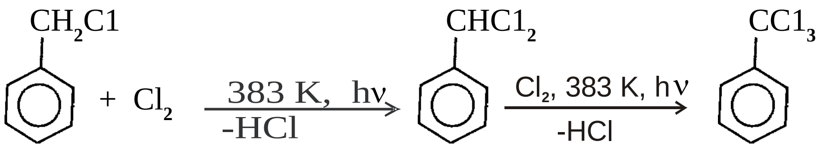
Fluoroarenes (aryl fluorides), however, cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is violent and cannot be easily controlled.

(b) Side chain halogenation : The most convenient method for the preparation of side chain substituted aryl halides or aralkyl halides is by the direct halogenation of a suitable arene. For example, when chlorine is passed through boiling toluene in presence of sunlight and absence of halogen carrier, phenylchloromethane (benzyl chloride) is formed.



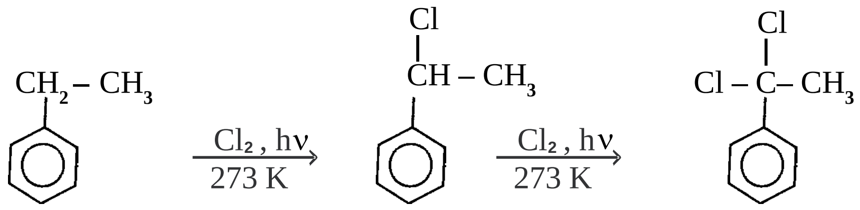
Toluene Benzyl chloride (Phenylchloromethane)

If Cl_2 is passed for a longer time, the initially formed benzyl chloride reacts further to form first benzal dichloride and then benzotrichloride.



Benzyl chloride Benzal dichloride Benzotrichloride

When the side chain is larger than a methyl group, side chain halogenation preferentially occurs at the benzylic carbon (i.e. carbon atom next to the benzene ring) and the process is called benzylic halogenation. For example,



1-chloro-1-phenylethane 1,1 - Dichloro - 1- phenylethane

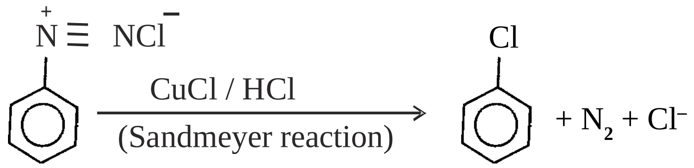
Instead of Cl_2, sulphuryl chloride (SO_2Cl_2) at 475 K in presence of light and traces of peroxide can also be used for benzylic halogenation of arenes. For example,

$$C_6H_5CH_3 + SO_2Cl_2 \xrightarrow[\text{traces of peroxide}]{\text{475 K, h}\nu} C_6H_5-CH_2Cl + SO_2 + HCl$$

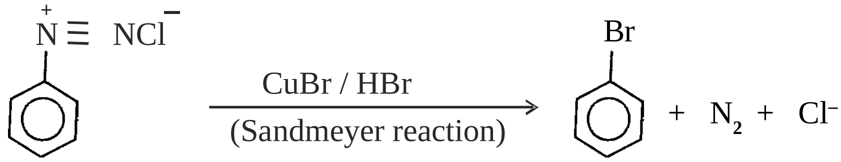
Toluene Benzyl chloride

2. From diazonium salts.

(i) By Sandmeyer reaction - Chloroarenes (aryl chlorides) and bromoarenes (aryl bromides) are easily prepared when the diazonium salts are treated with CuCl dissolved in HCl or CuBr dissolved in HBr. This reaction is called *Sandmeyer reaction*.

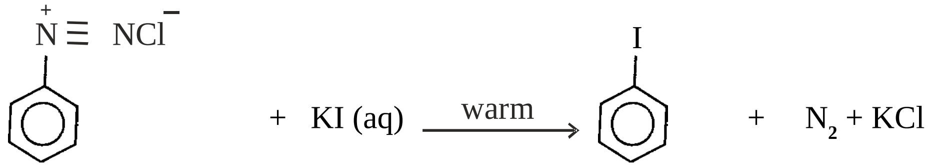


Benzene diazonium chloride



Benzenediazonium chloride Bromobenzene

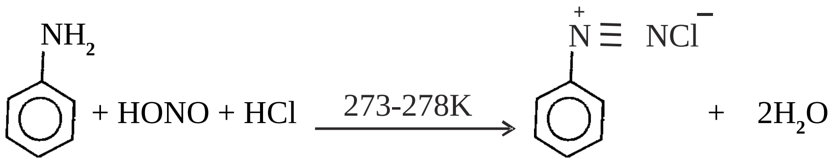
However, iodoarenes (aryl iodides) are prepared by simply warming the diazomium salt solution with aqueous KI solution.



Benzenediazonium chloride Iodobenzene

Benzenediazonium chloride needed for this purpose is obtained by treating aniline dissolved in dil. HCl with an aqueous solution of sodium nitrite at 273 – 278 K (0^0 - 5^0C).

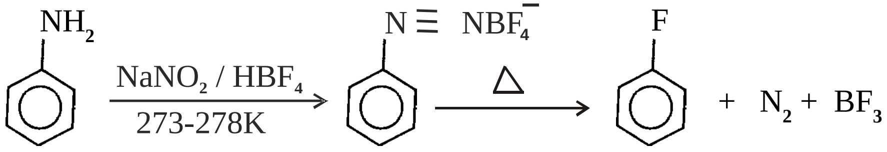
$$NaNO_2 + HCl\,(dil) \longrightarrow HONO + NaCl$$



Aniline

Benzenediazonium chloride

Fluoroarenes (aryl fluorides) are prepared by heating the corresponding diazonium tetrafluoroborate which, in turn are obtained by the diazotisation of suitable aromatic primary amine with aq $NaNO_2$ in presence of fluoroboric acid (HBF_4) at 273 – 278 K.

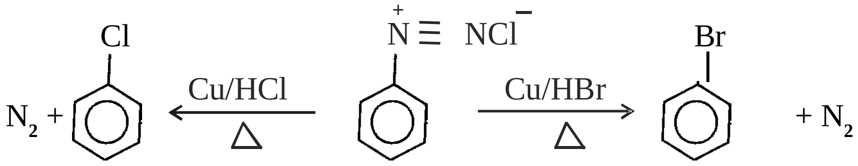


Aniline

Fluorobenzene Boron trifluoride

This reaction is called **Balz-Schiemann** reaction.

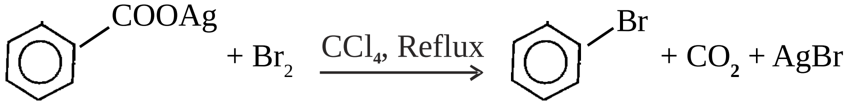
(ii) By Gattermann reaction - Haloarenes particularly chloro - and bromoarenes can also be prepared by Gattermann reaction. It is a modification of Sandmeyer reaction. In this reaction, a mixture of freshly prepared copper powder in the presence of corresponding halogen acid (HCl or HBr) is used instead of cuprous halide dissolved in the corresponding halogen acid (CuCl / HCl or CuBr / HBr) as used in Sandmeyer reaction. The yields are often around 40%.



Chlorobenzene

Bromobenzene

3. From silver salt of aromatic acids (Hunsdiecker reaction). Like alkyl bromides, aryl bromides can also be prepared by refluxing the silver salt of aromatic acids with bromine in boiling carbon tetrachloride.



Silver benzoate

Bromobenzene

4. Commercial preparation Chlorobenzene.

Chlorobenzene is prepared commercially by the **Raschig process**. In this process, a mixture of benzene vapours, air and hydrogen chloride is passed over heated cupric chloride.

$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2,\ \Delta} 2C_6H_5Cl + 2H_2O$$

14.9 PROPERTIES :

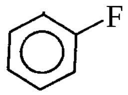
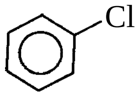
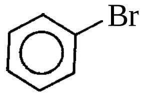
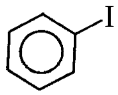
Physical Properties

1. Aryl halides are colourless oily liquids or relatively low melting point solids, having odour characteristic of aromatic compounds.

2. Because of their low polarity, they are insoluble in water but soluble in all common organic solvents such as ethanol and diethylether.

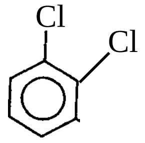
3. They have density greater than one.

4. For the same aryl group, the melting points, boiling points and densities rise gradually as we pass from fluoro to iodocompounds.

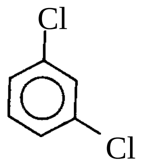
Haloalkanes				
M.P.^{0}C	–42	–45	–31	–30
B.P.^{0}C	85	132	156	188
Density (g/ml at 20^{0}C)	1.031	1.112	1.495	1.838

5. The boiling points of *o*-, *m*- and *p*- isomers are so close that these are difficult to separate by distillation. However, the melting point of a *p*-isomer is much higher than that of *o*- or *m*-isomer. This is so because the more symmetrical *p*-isomer fits more easily into a crystal lattice and the stronger intercrystalline forces result in a higher melting point.

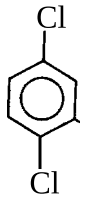
For example, the physical constnts of *o*-, *m*- and *p*- isomers of dichlorobenzene are



ortho



meta



para

	ortho	*meta*	*para*
BP^{o}C	179	172	175
MP^{o}C	–17	–26	–53

6. Since the strength of C – X bond decreases in the order C – F > C – Cl > C – Br > C – I, therefore, stability of the haloarenes having the same aryl group decreases from fluoride to the corresponding iodide.

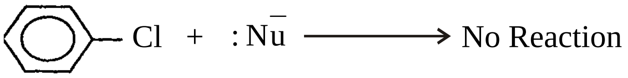
7. Many haloarenes show physiological activity and are used as insecticides (DDT)

CHEMICAL PROPERTIES

1. Nucleophilic substitution of aromatic halogen.

Halogens attached to an aromatic ring do not ordinarily undergo displacement (S_N1 or S_N2). Thus unlike alkyl halides, aryl halides do not react with nucleophilic reagents under normal laboratory conditions.

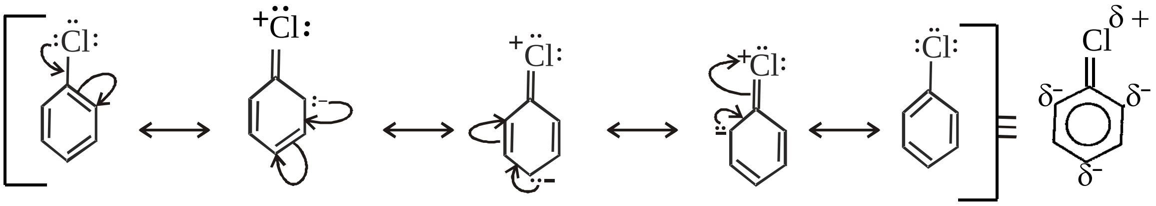
$$\underset{\text{methyl chloride}}{CH_3 - Cl} + :\overset{-}{Nu} \longrightarrow \underset{\text{Product}}{CH_3 - Nu} + Cl^-$$



Chlorobenzene

The following reasons can be attributed to account for the low reactivity of aryl halides.

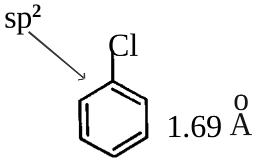
(i) **Resonance effect.** In haloarenes (e.g. chlorobenzene), the lone pairs of electrons on the halogen atom are delocalized on the benzene ring as shown below :

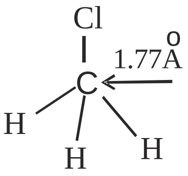


(a) As a result, C – Cl bond acquires some double bond character, i.e. Cl is attached to C by little more than a single pair of electrons. On the other hand, in case of alkyl halides (say methyl chloride) carbon is attached to chlorine by a pure single bond. Consequently, C – X bond in aryl halides is little stronger than in alkyl halides, and hence cannot be easily broken.

(b) As discussed above, aryl halides are stabilised by resonance but alkyl halides are not. Consequently, the energy of activation for the displacement of halogen from aryl halides is much greater than that from alkyl halides. Thus aryl halides are much less reactive than alkyl halides towards nucleophilic substitution reactions.

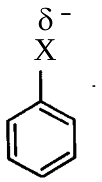
(ii) Difference in hybridization of carbon atom in C – X bond : In haloalkanes (e.g. methyl chloride), the halogen is attached to sp^3-hybridized carbon while in haloarenes the halogen is attached to sp^2-hybridized carbon. Since a sp^2- hybridized orbital is smaller in size as compared to sp^3 orbital of carbon, the C – Cl bond in chlorobenzene should be shorter and hence stronger than in methyl chloride. This has been confirmed by the X-ray analysis which shows that the C – Cl bond in chlorobenzene in 169 pm (1.69 Å)whereas in methyl chloride, it is 177pm (1.77 Å).



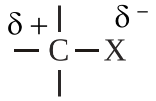


Thus, in chlorobenzene, C – Cl bond is stronger than in methyl chloride and hence difficult to break.

(iii) Polarity (or Nature) of the carbon-halogen bond. Another reason for the low reactivity of ary halides over alkyl halides is their lesser polar character.



Haloarene or arylhalide (C – X bond is less polar and hence X cannot be displaced easily by nucleophiles)

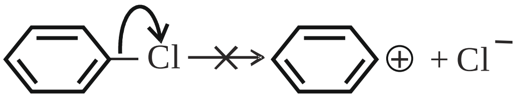


$$\overset{\delta+}{}\ -\overset{|}{\underset{|}{C}}-\overset{\delta-}{X}$$

Haloalkane or alkyl halide (C – X bond is more polar than in aryl halides and hence X can be easily displaced by nucleophiles)

The sp^2-hybrid carbon due to greater s-character is more electronegative than a sp^3 -hybrid carbon. Therefore, the sp^2-hybrid carbon of C – X bond in aryl halides has less tendency to release electrons to halogen than in sp^3 – hybrid carbon in alkyl halides. As a result, the C – X bond in aryl halides is less polar than in alkyl halides. This is supported by the observation that the dipole moment of chlorobenzene is just 1.69 D as compared to the dipole moment of methyl chloride, i.e. 1.86 D. Consequently, the halogen atom present in aryl halides cannot be easily displaced by nucleophiles.

(iv) Instability of phenyl cation. In haloarenes the phenyl cation formed as a result of self-ionization is not stabilized by resonance because the sp^2-hybridized orbital of carbon having the +ve charge is perpendicular to the p-orbitals of the phenyl ring. Therefore, these cations are not formed and aryl halide do not undergo nucleophilic substitution reactions easily.

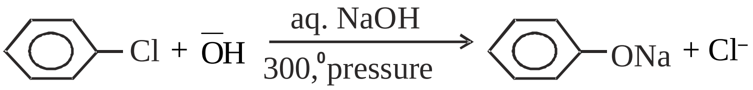


Chlorobenzene Phenyl cation

(v) Electronic repulsions. Since arene halides are electron rich molecules due to the presence of π-bonds, they repel the electron rich nucleophiles from attacking them.

For the reasons stated above, the substitution of halogen in aryl halides by S_N1 mechanism is considerably more difficult than with alkyl halides. S_N2 reactions are not possible because the usual backside approach of the nucleophile is blocked by the aromatic ring in aryl halides. Hence, simple aryl halides are ordinarily inert to most of the nucleophiles.

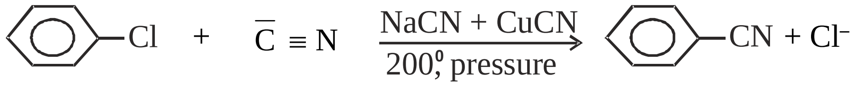
However, at sufficiently high temperature and pressure with nucleophiles e.g. hydroxide, cyanide ion or ammonia, nucleophilic substitution can be carried out.



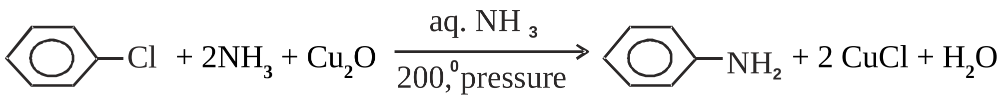
Chlorobenzene Sodium phenoxide

Phenol

(This reaction forms the basis of **Dow process** for the manufacture of phenol.)



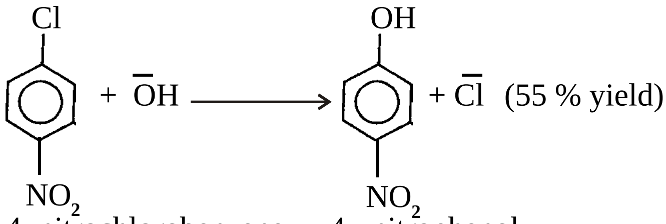
Phenyl cyanide



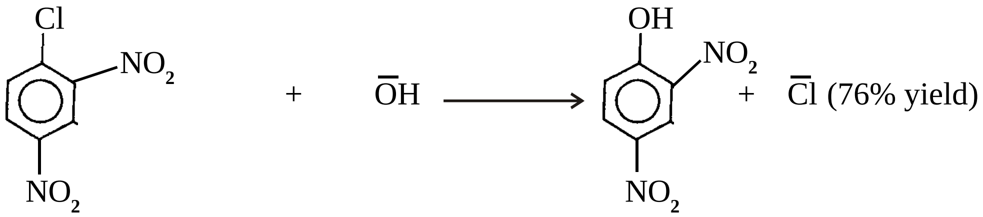
aniline

These reactions are used for the manufacture of the above derivatives. Because of the high temperature and pressure required, they are unsuitable as laboratory methods of preparation.

Aryl halides undergo nucleophilic displacement with increasing readiness if a strongly electron attracting group (– NO_2, – C ≡ N) is present in the 2-position (ortho) or in 4-position (para).

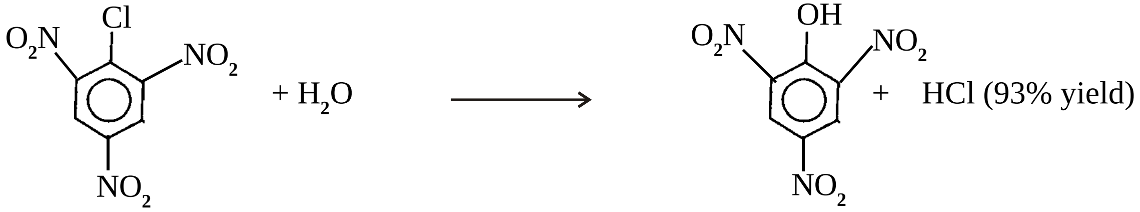


4- nitrochlorobenzene 4 - nitrophenol



2,4 - dinitrochlorobenzene 2,4-dinitrophenol

When three nitro groups are placed in 2,4 and 6- positions to a halogen, the reactivity of the latter is greatly increased and is comparable to that of alkyl halides.

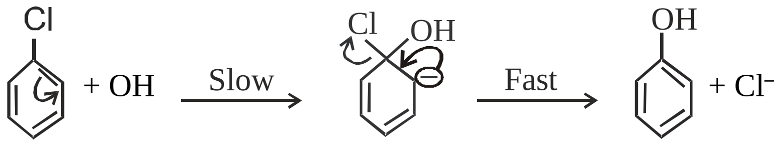


2,4,6-Trinitrochlorobenzene (Picryl chloride)

2,4,6 - Trinitrophenol (Picric acid)

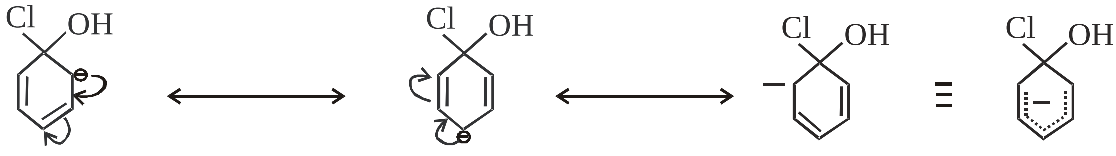
MECHANISM

The preparation of phenol from chlorobenzene illustrate the reaction mechanisms of the nucleophilic substitution of aryl halides. The reaction is believed to take place in two steps. In first step a carbanion is formed by the nucleophilic attack of $\overline{O}H$ on the carbon carrying the chlorine. This is a slow and rate determining step. In the second step which is fast, the halogen leaves the carbanion and phenol is formed.



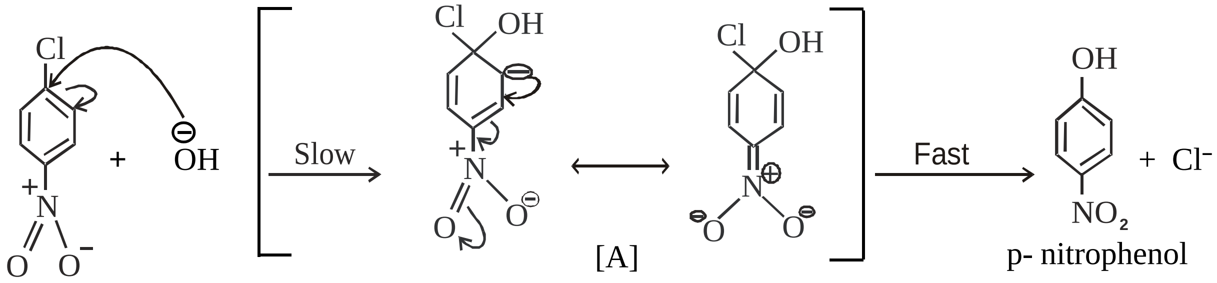
Chlorobenzene Carbanion intermediate Phenol

The carbanion is stable as it could be represented as the resonance hybrid of the following canonical forms.



Resonance hybrid

It will be noticed that the carbanion has small negative charges in ortho and para positions. An electron - attracting group such as – NO_2 group if present in ortho or para position to chlorine, spreads the negative charge to the oxygen atom of the –NO_2 group through resonance.



[A]

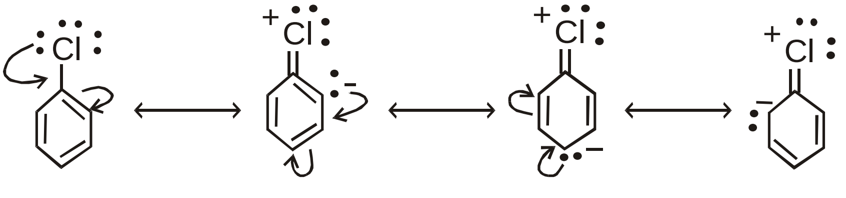
p- nitrophenol

Thus the carbanion (A) is more stable than in case of hydrolysis of chlorobenzene because of greater dispersion of the negative charge and the presence of – NO_2 group in para position. Similar dispersion of the negative charge of the carbanion is also felt when the –NO_2 group is in ortho position.

Hence the nucleophilic substitution with ortho and para nitrochlorobenzene is facilitated.

2. Electrophilic substitution reactions :

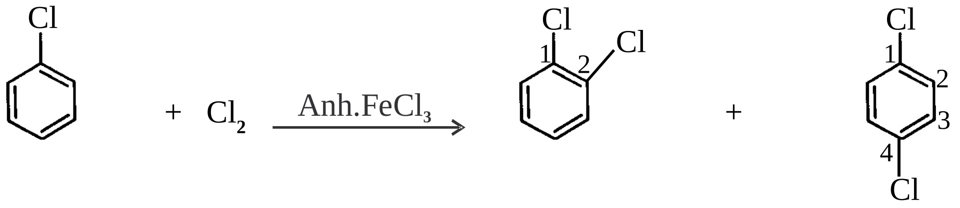
Haloarenes undergo the usual electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel - Craft reactions. Halogen atom is **slightly deactivating** and ***o, p* - directing**. Therefore, further substitution occurs at *o* - and *p* - positions with respect to the halogen atom. The *o*- and *p*-directing influence of the halogen atom can be easily understood if we consider the resonance structure of chlorobenzene. Chlorobenzene is to be regarded as resonance hybrid of the four contributing forms shown below.



I II III IV

In structures, II, III or IV , there is negative charge either at *o* – or *p*- positions. In other words, because of resonance, the electron density increases more at *o* - and *p*-positions than at *m*-positions. Therefore, further electrophilic substitution in haloarenes occurs at *o* - and *p*- positions. However, because of steric hindrance at the *o*-position, the *p*-product usually predominates over the *o*-product. Further, the halogen atoms because of its –I effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and under drastic conditions as compared to those in benzene.

(i) Halogenation

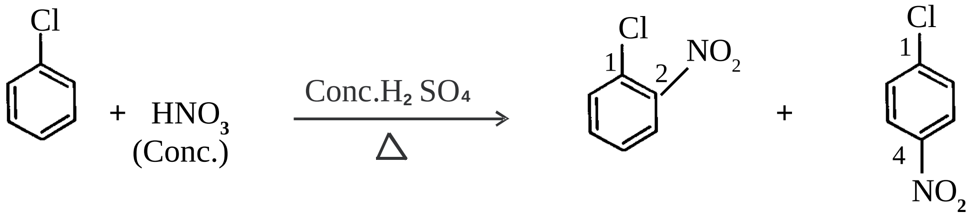


Chlorobenzene

1,2-Dichlorobenzene
(*o*-Dichlorobenzene)
(minor)

1,4-Dichlorobenzene
(*p*-Dichlorobenzene
(major)

(ii) Nitration

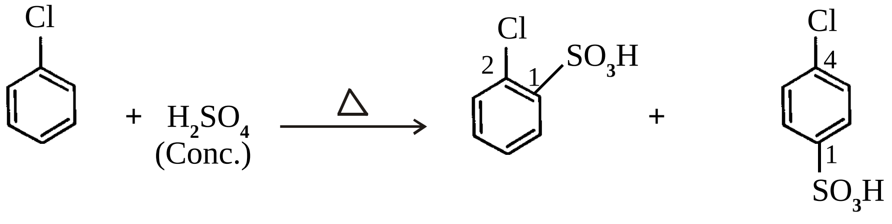


Chlorobenzene

1-Chloro-2-nitrobenzene
(*o*-Chloronitrobenzene)
(minor)

1-Chloro-4-nitrobenzene
(*p*-Chloronitrobenzene)
(major)

(iii) Sulphonation

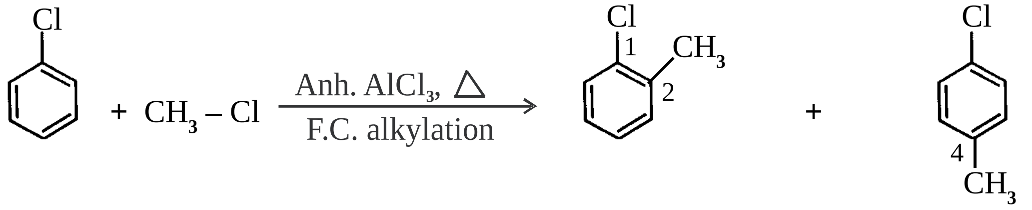


Chlorobenzene

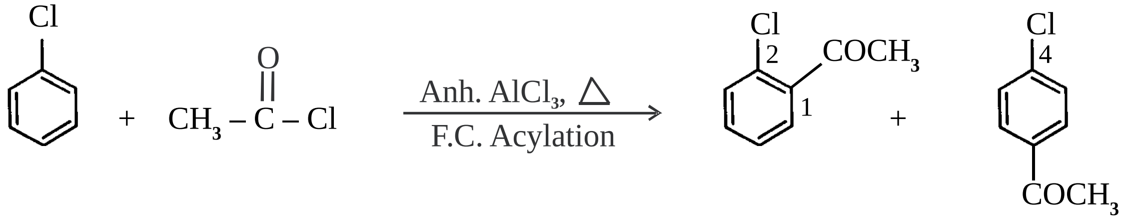
2-Chlorobenzene
sulphonic acid
(minor)

4-Chlorobenzene
sulphonic acid
(major)

(iv) Friedel-Crafts reaction



Chlorobenzene 1-Chloro-2-methylbenzene (*o*-Chlorotoluene) (minor) 1-Chloro-4-methylbenzene (*p*-Chlorotoluene) (major)



Chlorobenzene acetyl chloride 2-Chloroacetophenone (*o*-Chloroacetophenone) (minor) 4-Chloroacetophenone (*p*-Chloroacetophenone) (major)

3. Miscellaneous reactions

Besides these nucleophilic and electrophilic substitution reactions, haloarenes undergo a number of other reactions as described below :

(i) Reaction with sodium (a) Wurtz-Fittig reaction. Haloarenes when treated with an ethereal solution of an alkyl halide in presence of sodium, form alkyl derivatives of benzene. This reaction is called *Wurtz-Fittig reaction*

Bromobenzene Ethyl bromide Ethylbenzene

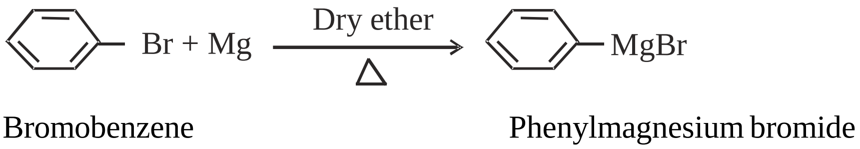
(b) **Fittig reaction** : When only haloarenes are treated with sodium, diaryls are produced. This reaction is called *Fittig reaction.*

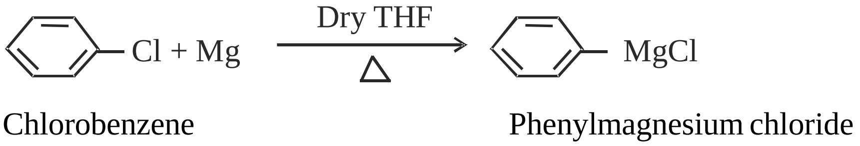
Chlorobenzene Chlorobenzene Diphenyl

(ii) Reaction with copper powder - (Ullmann biaryl synthesis.) When an iodoarene is heated with copper powder in a sealed tube, diaryl is formed. This is called *Ullmann biaryl synthesis*.

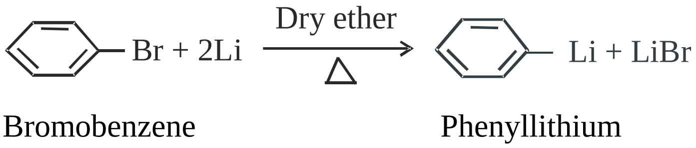
Iodobenzene Iodobenzene Diphenyl

(iii) Reaction with magnesium. Bromo-and iodoarenes form Grignard reagents when their ethereal solution is treated with magnesium turnings. Chloroarenes form Grignard reagents only if the reaction is carried out in dry tetrahydrofuran (THF) as solvent.

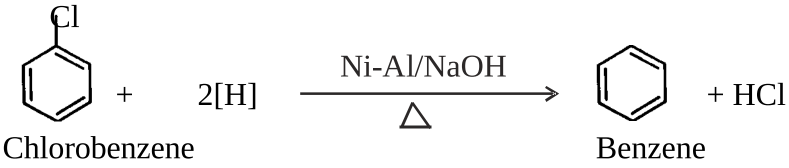




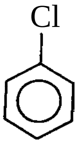
(iv) Reaction with lithium. Bromo- and iodoarenes also react with lithium metal in presence of dry ether to form the corresponding organometallic compounds. For example,



(v) Reduction : Haloarenes can be converted into the corresponding arenes by reduction with nickel-aluminium alloy in presence of alkali.



14.10 CHLOROBENZENE, Phenyl chloride, C_6H_5Cl,



Preparation

The preparation and the industrial preparation of chlorobenzene have been discussed in 16.2.

Properties

Chlorobenzene is a colourless, pleasant smelling liquid, b.p. 132^{0}C. It is insoluble in water, ethanol and ether. It is heavier than water, density 1.112 g/ml at 20^{0}C. It is steam-volatile.

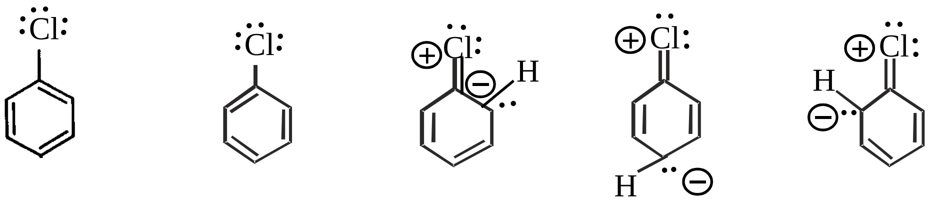
Interpretation of its reactivity. The low reactivity of chlorobenzene towards nucleophilic substitution as compared to alkyl halides is mainly attributed to two factors.

(a) delocalisation of electrons by resonance, and

(b) difference in the nature of C – X bond (sp^{3}C – **X** and sp^{2}C – **X** bonds)

(a) Let us look first at the resonance interpretation.

Chlorobenzene is considered to be a hybrid of not only the two Kekule structures I & II, but also of three structures, III, IV and V, in which the chlorine is joined to carbon by a double bond. In III, IV and V chlorine bears a positive charge and the **ortho** or **para** positions of the ring bear a negative charge.

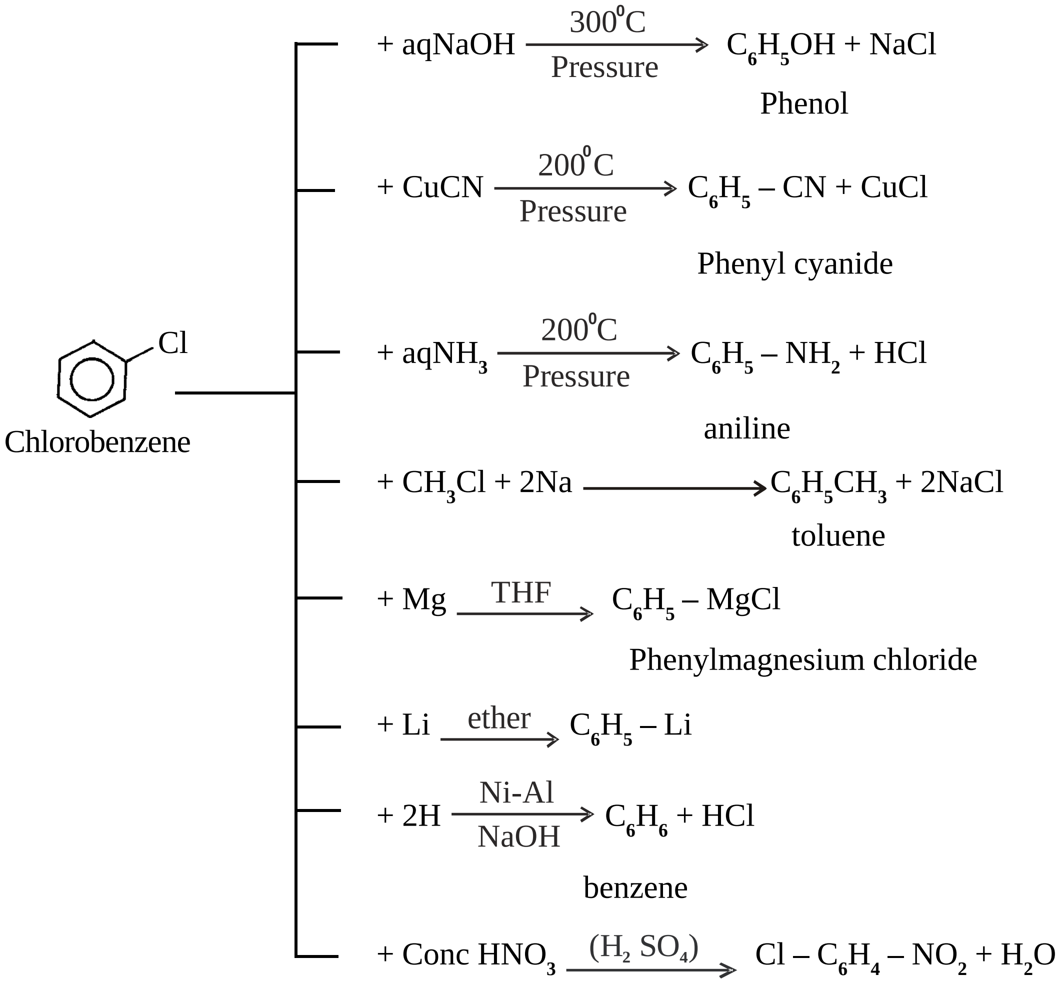


I II III IV V

Contribution from III, IV and V stabilizes the chlorobenzene molecule and gives double-bond character to the carbon chlorine bond. Carbon and chlorine are thus held together by something more than a single pair of electrons, and the carbon chlorine bond is stronger than if it were a pure single bond. Moreover the chlorobenzene molecule is stabilised by the contribution of all the resonating structures I to V and thus slow down the reactivity of the aryl halide.

(b) An alternative interpretation i.e. considering the nature of C – X bond is simple. In alkyl halides the carbon holding halogen is sp^3-hybridised. In aryl halides carbon is sp^2-hybridised, the bond to halogen is shorter and stronger and the molecule is more stable and accounts for its low reactivity.

Chlorobenzene gives all the reactions characterstic of aryl halides.



Chlorobenzene

$$+ \text{aqNaOH} \xrightarrow[\text{Pressure}]{300^0C} C_6H_5OH + NaCl$$

Phenol

$$+ CuCN \xrightarrow[\text{Pressure}]{200^0C} C_6H_5 - CN + CuCl$$

Phenyl cyanide

$$+ \text{aq}NH_3 \xrightarrow[\text{Pressure}]{200^0C} C_6H_5 - NH_2 + HCl$$

aniline

$$+ CH_3Cl + 2Na \longrightarrow C_6H_5CH_3 + 2NaCl$$

toluene

$$+ Mg \xrightarrow{\text{THF}} C_6H_5 - MgCl$$

Phenylmagnesium chloride

$$+ Li \xrightarrow{\text{ether}} C_6H_5 - Li$$

$$+ 2H \xrightarrow[\text{NaOH}]{\text{Ni-Al}} C_6H_6 + HCl$$

benzene

$$+ \text{Conc } HNO_3 \xrightarrow{(H_2SO_4)} Cl - C_6H_4 - NO_2 + H_2O$$

o- & *p* - nitrochlorobenzene

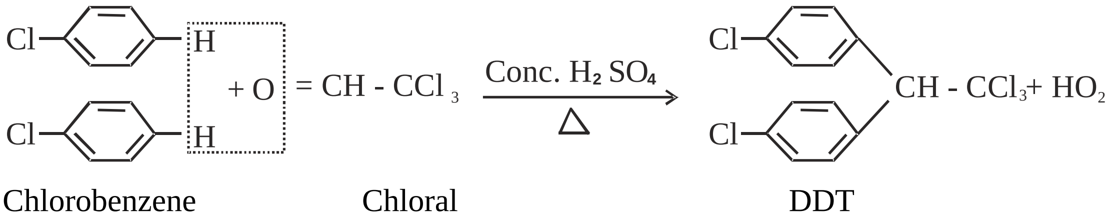
Uses : Chlorobenzene is used in the manufacture of phenol, aniline and DDT.

14.11 POLYHALOGEN COMPOUNDS :

1. DDT, 2, 2-di (p-chlorophenyl)-1, 1, 1 - trichloroethane

DDT was first prepared in 1873, but it was not until 1939 that Paul Muller, at Geigy pharmaceutical in Switzerland, discovered the effectiveness of DDT as an insecticide. **Paul Muller** was awarded the Nobel Prize in medicine and physiology in 1948 for this discovery.

Preparation : It is prepared by heating chlorobenzene with chloral (trichloroacetaldehyde) in presence of conc. H_2SO_4.

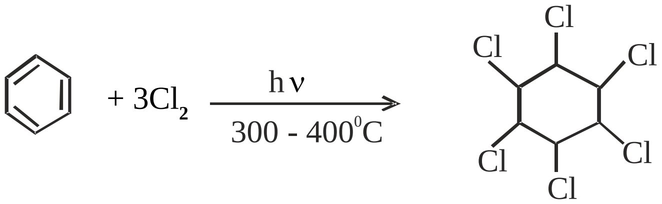


Uses : DDT is a cheap but powerful insecticide. It is widely used for sugarcane and fodder crops and to kill mosquitoes and other insects. It is particularly very effective against Anopheles mosquitoes which spread malaria and lice that carry typhus. Through its use, malaria has virtually been eliminated from India and large part of the world.

Tragic side effects : The use of DDT increased enormously on a worldwide basis after World War II. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT and DDT was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility further increased the problems. DDT is not completely biodegradable, i.e. it is not very rapidly metabolized by animals. Instead, it gets deposited and stored in fatty tissues. If this ingestion continues at a steady rate, DDT builds up within the animal over time. This affects the reproductive system of animals. Because of these tragic side effects, the use of DDT was banned in USA in 1973. However, in India and in many other Asian countries, DDT is still being widely used due to the non-availability of any other cheaper insecticide.

2. Benzene Hexachloride :

In the presence of sunlight or ultraviolet light, chlorine and bromine (but not iodine), add to benzene to give crystalline hexachlorides and hexabromides, $C_6H_6Cl_6$ and $C_6H_6 Br_6$.



benzene hexachloride

Benzene hexachloride is known by the commercial name BHC or 666, derived from its formula $C_6H_6Cl_6$. As we look at its structure, this is also named as 1,2,3,4,5,6 - hexachlorocyclohexane, and can theoretically exist in nine stereoisomeric forms due to different arrangement of H and Cl on opposite sides of the plane of the benzene ring. Seven of these have been isolated from the mixture obtained by the above procedure. The insecticidal properties are due to one of the isomers i.e. γ-isomer which is called **Gammaxane** or **Lindane**. It is very stable and acts more quickly than DDT.

3. Trichloromethane or Chloroform, $CHCl_3$

Chloroform was discovered by Leibig in 1831 and finds its use as a solvent for fats, waxes, alkaloids, rubber, resins, iodine etc. Previously it was used as anaesthetic but due to its harmful effects, has been replaced by less toxic, safer anaesthetics such as ether. Now-a-days, chloroform is used for the production of freon refrigerant R-22.

Chloroform is prepared by distilling ethyl alcohol or acetone with bleaching powder and water.

(i) Alcohol is first oxidised to acetaldehyde by chlorine, obtained from bleaching powder.

$$CH_3CH_2OH + O \longrightarrow CH_3CHO + H_2O$$

(ii) Acetaldehyde, now reacts with chlorine forming trichloro acetaldehyde, called **chloral**.

$$CH_3CHO + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

(iii) Chloral, then gets hydrolysed by calcium hydroxide.

$$2\,CCl_3CHO + Ca\,(OH)_2 \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2\,CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

4. Tetrachloromethane or carbon tetrachloride, CCl_4

It is the most useful tetrahalogen derivative of methane. Earlier, carbon tetrachloride was used in industries as a cleaning agent and in the homes, as a spot remover and fire extinguisher under the name **pyrene**. It is now used as a solvent for fats, oils, waxes and greases, resins, iodine etc. Now. it finds its use in the production of refrigerants and propellants for aerosol cans.

CCl_4 is prepared by the process of chlorination of methane which involves heating of methane with excess of chlorine at 400°C

$$CH_4 + 4\,Cl_2 \xrightarrow{400°C} CCl_4 + 4\,HCl$$

Chloroform can be preapred from carbon tetrachloride by reduction with moist iron fillings.

$$CCl_4 + 2H \xrightarrow{Fe\,/\,H_2O} CHCl_3 + HCl$$

5. Freons :

The chlorofluoro derivatives of methane and ethane are collectively called freons. Freons are named on the basis of number of fluorine atoms present in these compounds.

e.g. CF_4 (Freon-14), CF_3Cl (Freon - 13), CF_2Cl_2 (Freon-12) and $CFCl_3$ (Freon - 11)

The most important and useful freon is Freon-12, which is most widely used refrigerant. Freon-12 is manufactured from carbon tetrachloride by treating it with antimony trifluoride in presence of a catalyst, $SbCl_5$ (Swarts Reaction)

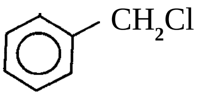
$$3CCl_4 + 2\,SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon - 12}}{3\,CCl_2F_2} + 2\,SbCl_3$$

Freon is an odourless, non-corrosive, non-toxic gas, which is stable at high temperatures and pressures. Its b.p is – 29.8°C and can be easily liquified by applying pressure at room temperature for which it is widely used as refrigerant in refrigerators and air conditioners. Most freons are responsible for destruction of the ozone layer in stratosphere.

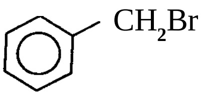
14.12 ARALKYL HALIDES :

These compounds, in fact, could be regarded as aryl-substituted alkyl halides. They have halogen atoms present in the side-chain and are also often referred to as **side-chain halogen derivatives**.

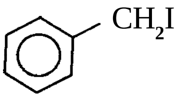
The structure of simple aralkyl halides are given below.



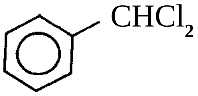
benzyl chloride



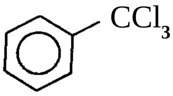
benzyl bromide



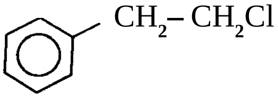
benzyl iodide



benzalchloride

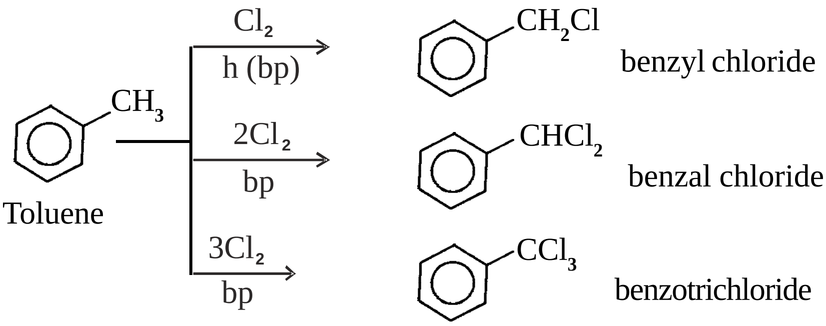


benzotrichloride



β-chloroethylbenzene

The simple aralkyl halides are mostly derived from toluene.



The aralkyl halides are mostly used as intermediates in organic synthesis.

CHAPTER (14) AT A GLANCE-HALOARENES

1. Haloarenes are halogen derivatives of arenes. They may be nuclear halogen derivatives e.g. Ar – X or side -chain halogen derivatives, e.g. Ar – $(CH_2)_n$ – X, where X = halogen and n = no. of CH_2 groups.

2. **Methods of Preparation :**

(i) **Electrophilic substitution reaction**

Nuclear halogen derivatives are usually prepared from arenes by direct halogenation at low temperature in presence of anhydrous $AlCl_3$ or $FeCl_3$ or $FeBr_3$ and in absence of sunlight.

$$\text{Ar – H} \xrightarrow[\text{Anh.}AlCl_3 \text{ or Anh. }FeCl_3 \text{ or Anh.}FeBr_3]{X} \text{Ar – X}, \qquad X = \text{Cl or Br}$$

$$\text{Ar – H} \xrightarrow[HNO_3 \text{ or } HIO_3 \text{ or HgO}]{I_2} \text{Ar – I}$$

Side-chain halogenation is carried out in presence of sunlight and in the absence of halogen carriers.

$$R – CH_3 \xrightarrow[h\nu]{X_2} R – CH_2 – X \text{ or } R – CHX_2 \text{ or } R – CX_3 \text{ depending on the amount of } X_2.$$

(ii)

$$\left.\begin{array}{l} Ar\text{-}\overset{+}{N}\equiv N\,\bar{X} \xrightarrow{CuCl/HCl} Ar\text{ - }Cl \\ Ar\text{-}\overset{+}{N}\equiv N\,\bar{X} \xrightarrow{CuBr/HBr} Ar\text{ - }Br \end{array}\right\} \textbf{Sandmeyer reaction}$$

$$Ar\text{-}\overset{+}{N}\equiv N\,\bar{X} \xrightarrow[\text{Warm}]{\text{aq.KI}} Ar\text{ - }I$$

$$Ar\text{-}\overset{+}{N}\equiv N\,\bar{X} \xrightarrow[0^0\text{-}5^0C]{NaNO_2/HBF_4} \xrightarrow{\Delta} Ar\text{ - }F \qquad \textbf{Balz-Schiemann reaction}$$

$$Ar\text{-}\overset{+}{N}\equiv N\,\bar{X} \xrightarrow[\Delta]{Cu/HX} Ar\text{ - }X,\ X = \text{Cl or Br} \qquad \textbf{Gattermann reaction}$$

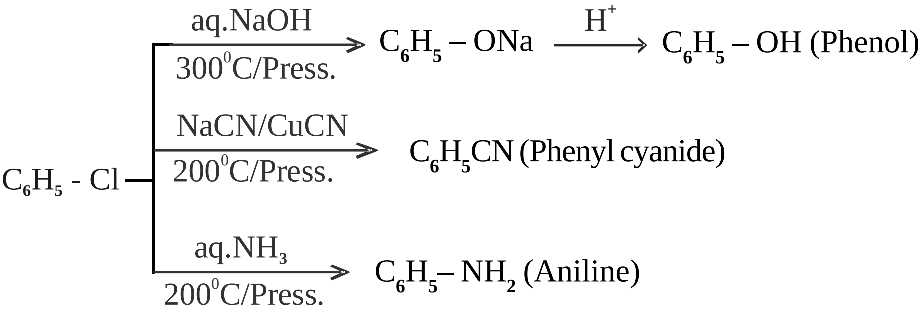
(iii) $Ar – COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} Ar – Br$ **Hunsdiecker reaction**

(iv) **Industrial method for chlorobenzene, Raschig process.**

$$2C_6H_6 + 2HCl + O_2 \xrightarrow[\Delta]{CuCl_2} 2C_6H_5Cl + 2H_2O$$

3. Chemical proporties

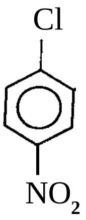
(i) Nucleophilic substitution under drastic conditions.



$$C_6H_5 - Cl \xrightarrow[300^0C/Press.]{aq.NaOH} C_6H_5 - ONa \xrightarrow{H^+} C_6H_5 - OH \text{ (Phenol)}$$

$$C_6H_5 - Cl \xrightarrow[200^0C/Press.]{NaCN/CuCN} C_6H_5CN \text{ (Phenyl cyanide)}$$

$$C_6H_5 - Cl \xrightarrow[200^0C/Press.]{aq.NH_3} C_6H_5 - NH_2 \text{ (Aniline)}$$



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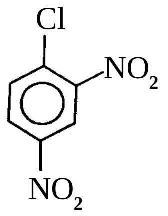
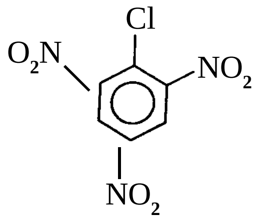


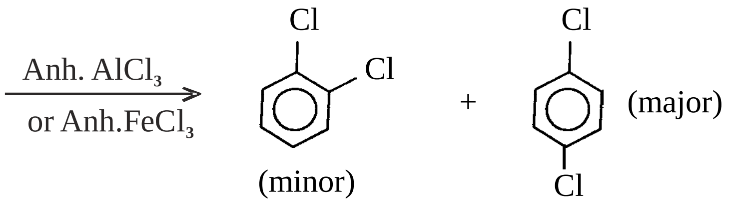
and



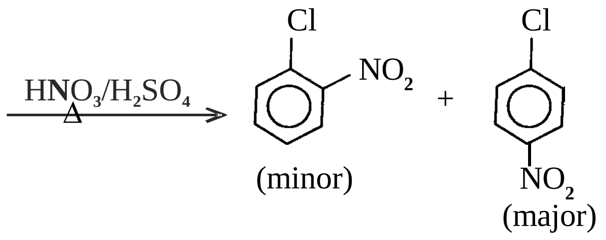
readily undergo nucleophilic displacement reaction with $\overset{\ominus}{OH}$ giving the corresponding phenols (–Cl is replaced by – OH)

(ii) **Electrophilic substitution reaction under ordinary conditions.**

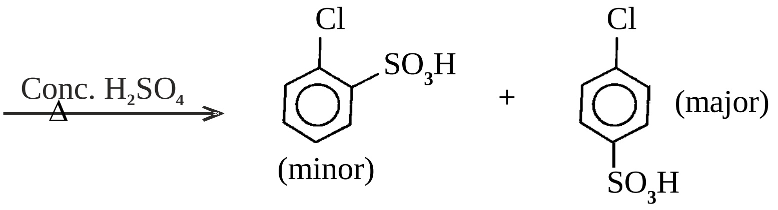
(a) **Halogenation** : Ar – Cl



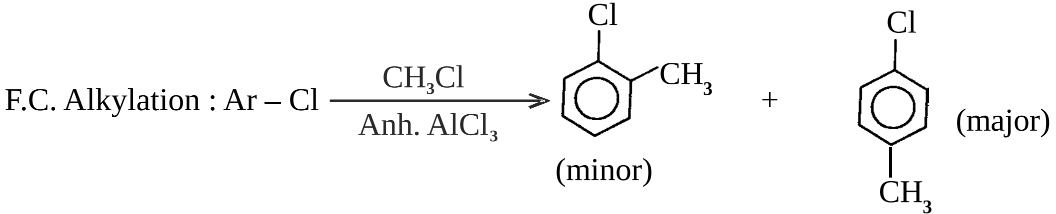
(b) **Nitration :** Ar – Cl

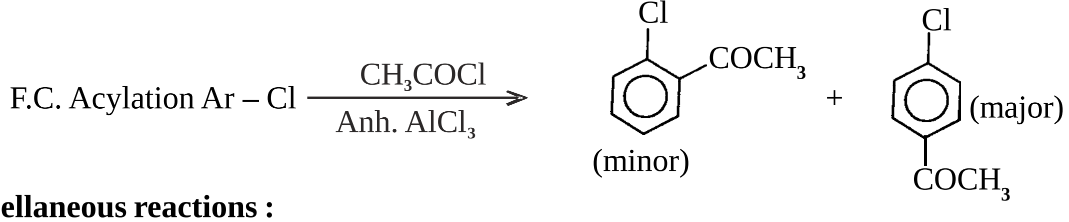


(c) **Sulphonation :** Ar – Cl



(d) **Friedel Crafts reaction :**





(iii) **Miscellaneous reactions :**

$$2C_6H_5Cl \xrightarrow[\text{Dry ether}]{2Na,\ \Delta} \underset{\text{(Diphenyl)}}{C_6H_5 - C_6H_5}$$ **Fittig reaction**

$$C_6H_5Cl + C_2H_5Cl \xrightarrow[\Delta]{2Na\ /\ \text{Dry ether}} \underset{\text{(ethyl benzene)}}{C_6H_5 - CH_2 - CH_3}$$ **Wurtz - Fittig reaction**

$$2C_6H_5\text{–}I + 2Cu \xrightarrow{\Delta} C_6H_5 - C_6H_5$$ **Ullmann biaryl synthesis**

$C_6H_5 - X + Mg \xrightarrow[\Delta]{\text{Dry THF}} C_6H_5Mg - X$ (Phenyl magnesium halide, a **Grignard reagent**)

$C_6H_5 - X + Li \xrightarrow[\Delta]{\text{dry ether}} C_6H_5 - Li$ (Phenyl lithium)

$C_6H_5 - Cl \xrightarrow[\Delta,\ \text{Reduction}]{\text{Ni-Al/NaOH}} C_6H_6$ (Benzene)

4. Chlorobenzene can be prepared according to the general methods of preparation [2(i), (ii) & (iv)] and is used for the preparation of phenol, aniline and DDT, a powerful insecticide.

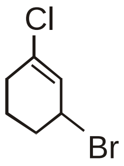
5. Aralkyl halides are side chain halogen derivatives and the simple one is prepared from toluene by direct halogenation in presence of sunlight and a trace of peroxide and in the absence of halogen carrier.

$$C_6H_5\text{–}CH_3 \xrightarrow[\text{BP}]{Cl_2,\ h\nu} C_6H_5 - CH_2 - Cl + C_6H_5\ CH\ Cl_2 + C_6H_5CCl_3.$$

6. Benzene hexachloride (BHC) is an insecticide obtained under the trade name **Gammaxane** or **Lindane.** Chlorine adds up to benzene in presence of U.V. light forming BHC. The γ-isomer of this compound is actually active and is called **Lindane.**

QUESTIONS

I. Multiple Choice Questions

1. The IUPAC name of the compound  is :

   (a) 2-bromo-6-chlorocyclohex-1-ene

   (b) 6-bromo-2-chlorocyclohexene

   (c) 3- bromo - 1- chlorocyclohexene

   (d) 1-bromo-3-chlorocyclohexene

2. Flurobenzene (C_6H_5F) can be prepared in the laboratory

   (a) by heating phenol with HF and KF

   (b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

   (c) by direct fluorination of benzene with F_2 gas

   (d) by reacting bromobenzene with NaF solution

3. Which of the following has highest melting point ?

   (a) Chlorobenzene (b) *o*-Dichlorobenzene

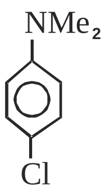
   (c) *m*-Dichlorobenzene (d) *p*-Dichlorobenzene

4. Chlorobenzene on treatment with sodium in dry ether gives diphenyl. The name of the reaction is

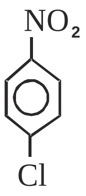
   (a) Fittig reaction (b) Wurtz-Fittig reaction

   (c) Sandmeyer reaction (d) Gattermann reaction

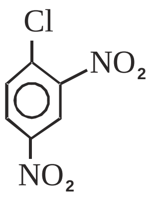
5. Order of reactivity towards nucleophilic substitution reaction of the compounds



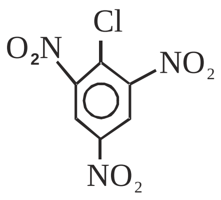
(i)



(ii)



(iii)



(iv)

   (a) i > ii > iii > iv (b) ii > i > iii > iv

   (c) iv > iii > ii > i (d) iii > iv > ii > i

6. Which of the following is not an exmaple of Wurtz - Fittig reaction ?

   (a) $C_6H_5CH_2Cl + CH_3Cl \xrightarrow{\text{Na/ether}}$

(b) $C_6H_5CH_2Cl + C_6H_5Cl \xrightarrow{Na/ether}$

(c) $C_6H_5Cl + CH_3Cl \xrightarrow{Na/ether}$

(d) None of the above

7. The bromination of ethylbenzene in presence of sunlight will preferentially yield,

(a) 1-bromo - 1 - phenylethane

(b) 2-bromo - 1 - phenylethane

(c) *p*-bromophenylethane

(d) *o* - bromophenylethane

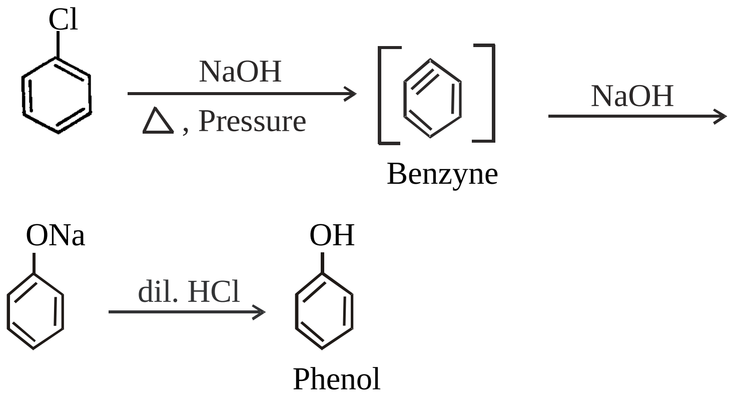
[Note : During side chain halogenation, benzylic hydrogen is preferentally substituted]

Answer : 1 (a), 2. (b), 3. (d), 4. (a), 5. (c), 6. (a), 7. (a)

II. Fill in the blnaks (One mark each)

1. Formation of phenol from chlorobenzene is an example of ______ aromatic substitution and occurs through ______ intermediate.
2. The reaction of *p*-nitrochlorobenzene with sodium methoxide to form *p*-nitroanisole occurs by ______ reaction.
3. Preparation of chlorobenzene from benzenediazonium chloride with cuprous chloride and aq. HCl is known as ______ reaction.
4. Chlorobenzene reacts with ______ in presence of conc. H_2SO_4 to form D.D.T.
5. Iodobenzene on heating with copper powder forms diphenyl. The reaction is called ______

Answer : 1. nucleophilic, benzyne



2. bimolecular aromatic nucleophilic substitution

3. Sandmeyer reaction

4. Chloral (CCl_3CHO)

5. diphenyl, Ullmann biaryl synthesis

Short Answer questinos (Two marks) :

1. Write the structure of the following aryl halogen compounds

   (i) *p*-Bromochlorobenzene

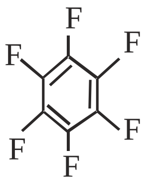
   (ii) Perfluorobenzene

   (iii) Benzyl chloride

   (iv) Benzal chloride

   (v) Benzotrichloride

   (vi) D.D.T

   [Hint. (ii) Perfluorobenzene structure ]

2. How can the following conversions be carried out ?

   (i) Toluene to benzylalcohol

   (ii) Benzene to biphenyl

   (iii) Benzene to 4-bromonitrobenzene

   (iv) Aniline to chlorobenzene

3. Explain the following :

   (i) Chlorine present in chlorobenzene is ortho and para directing

   (ii) Aryl halides are extremely less reactive towards nucleophilic substitution

   (iii) Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

   (iv) Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

Short answer questions (Three marks) :

1. Write the structural formulae of all possible isomers of aromatic compounds having the molecular formula C_7H_7 Cl.

2. How will you synthesise phenylacetic acid from toluene ?

   [Hint : Use the following steps :

   (i) Cl_2/uv, (ii) Mg/ether, (iii) CO_2 and (iv) H_2O / H^+

   or, (i) Cl_2/ uν, (ii) KCN (iii) hydrolysis

3. How will you distinguish between benzyl bromide and p-bromotoluene ?

   [Hint : Benzyl bromide forms a preciptitate of AgBr with alcoholic $AgNO_3$ solution. *p*-bromotoluene does not react]

Long Questions (7 marks) :

1. Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides ? How can the reactivity of aryl halides be enhanced ?
2. Discuss the resonating structures of chlorobenzne. How do you account for double bond character of C-Cl bond ? Describe the industrial method of preparation of chlorobenzene.
3. Describe the preparation and properties of chlorobenzene.
4. Give the mechanism of nucleophilic substitution in aryl halides.
5. Give a general account for the preparation and chemical properties of aryl halides.
6. Discuss the mechanism of formation of phenol from chlorobenzene by reaction with aqueous sodium hydroxide at high temperature and pressure. How can you distinguish *o*-chlorotoluene from benzyl chloride ?
7. What is the product formed when
   (i) Chlorobenzene reacts with chloral in the presence of conc. sulphuric acid.
   (ii) Bromobenzne reacts with nitric acid in the presence of sulphuric acid.
8. Write notes on :
   (i) Wurtz - Fittig reaction
   (ii) Ullmann reaction
   (iii) DDT
9. Write notes on :
   (i) Freons
   (ii) Chloroform

❑❑❑

UNIT - XI

ALCOHOLS, PHENOLS AND ETHERS

INTRODUCTION :

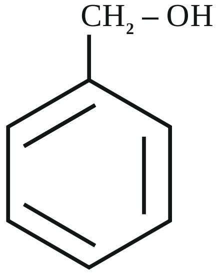
Alcohols and phenols are formed when a hydrogen atom in aliphatic hydrocarbon and aromatic hydrocarbon is replaced by –OH group respectively.

$$\underset{\text{Alkane}}{R-H} \xrightarrow[+OH]{-H} \underset{\text{Alcohol}}{R-OH} \quad ; \quad \underset{\text{Benzene}}{C_6H_5H} \xrightarrow[+OH]{-H} \underset{\text{Phenol}}{C_6H_5-OH}$$

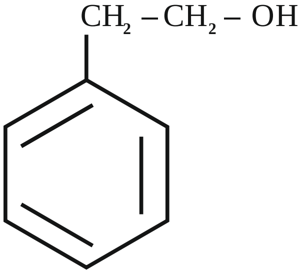
In alcohols the – OH group is directly attached to the carbon atom of an aliphatic system. Thus, **alcohols are the hydroxyl derivatives of aliphatic hydrocarbons**.

In phenols the –OH group is directly attached to carbon atom of an aromatic system. **Phenols are the hydroxy derivatives of aromatic hydrocarbons in which the hydroxyl group is directly attached to the carbon atom of the aromatic ring**.

Hydroxy derivatives in which the hydroxyl group is present in the side chain of an aromatic hydrocarbon is called **aromatic alcohols**. For example,



Phenylmethanol
(or benzyl alcohol)



2 - Phenylethanol

In benzylic alcohols, the – OH group is attached to carbon next to an aromatic ring, e.g. benzyl alcohol.

In aliphatic or benzylic alcohols the hydroxyl group is attached to a **sp^3–hybridised carbon atom**. In aromatic system the hydroxyl group is attached to a **sp^2–hybridised carbon atom** and phenols thus obtained are **quite stable**, whereas, in aliphatic alcohols when the hydroxyl group is attached to sp^2–hybridised carbon atom, the resultant alcohol is **unstable**. For example vinyl alcohol, $CH_2 = CH-OH$ is unstable.

The substitution of a hydrogen atom in a hydrocarbon by an **alkoxy** (OR) or aryloxy (OAr) group yields a class of compounds known as **ethers**. Ethers are also regarded as alkyl or aryl derivatives of alcohols i.e. H of OH is replaced by alkyl or aryl group.

$$\mathrm{R-H \xrightarrow[+OH]{-H} \underset{Ether}{R-O-R'}} \quad ; \quad \mathrm{Ar-H \xrightarrow[+OH]{-H} \underset{Ether}{Ar-O-R'}}$$

$$\mathrm{Ar-H \xrightarrow[+OAr]{-H} \underset{Ether}{Ar-O-Ar}} \quad ; \quad \mathrm{\underset{Alcohol}{R-OH} \xrightarrow[+R']{-H} \underset{Ether}{R-O-R'}}$$

R or R′ may be alkyl or aryl (Ar) group, same or different.

Ethers may also be regarded as dialkyl or diaryl derivative of water, both H of water is replaced by alkyl or aryl group.

$$\mathrm{\underset{Water}{H-O-H} \longrightarrow \underset{\substack{Alcohol\\or\\Phenol}}{R-O-H} \longrightarrow \underset{Ether}{R-O-R}}$$

Functional group of ether is OR, where R is alkyl or aryl group.

In this unit chemistry of three classes of compounds, namely alcohols, phenols, and ethers are discussed in different chapters.

CHAPTER - 15

ALCOHOLS

15.1 INTRODUCTION :

Alcohols may be defined as the hydroxyl derivatives of hydrocarbon.

$$\underset{\text{Hydrocarbon}}{R\text{–}H} \xrightarrow[+(-OH)]{-H} \underset{\text{Alcohol}}{R - OH}$$

The hydroxyl group is the functional group of all alcohols. When the functional group is directly attached to aliphatic hydrocarbon chain, it is called an **alcohol**. But, if the functional group is directly attached to aromatic ring, it is called a **phenol**. The alcoholic –OH group is neutral towards litmus, whereas phenolic –OH group is acidic in character.

15.2 CLASSIFICATION OF ALCOHOLS :

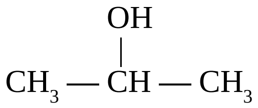
All alcohols can be broadly classified into two categories, i.e, aliphatic alcohols and aromatic alcohols.

(i) **Aliphatic alcohols :** In aliphatic alcohols, the hydroxyl group is directly attached to aliphatic hydrocarbon chain.

For example,

CH_3OH
Methanol
(Methyl alcohol)

C_2H_5OH
Ethanol
(Ethyl alcohol)

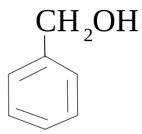


$$CH_3 - \underset{}{\overset{\displaystyle OH}{\overset{|}{C}H}} - CH_3$$

Propan-2-ol
(Isopropyl alcohol)

(ii) **Aromatic alcohols :** In aromatic alcohols, the hydroxyl group is directly attached to the side chain of an aromatic hydrocarbon.

For example,

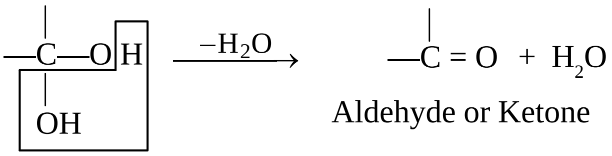


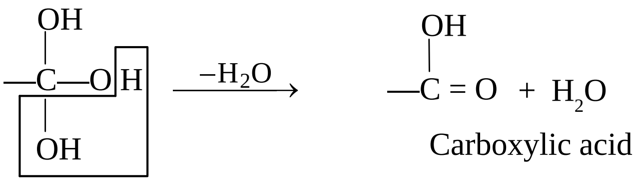
(Benzyl alcohol)

Alcohols can further be classified as monohydric, dihydric, trihydric and polyhydric alcohols, depending upon the number of the hydroxyl groups present in the molecules. If the molecules contain one, two or three hydroxyl group, they are termed as monohydric, dihydric or trihydric alcohols respectively. If their molecules contain four or more hydroxyl groups, they are called polyhydric alcohols.

Monohydric alcohols (Alkanol)	**Dihydric alcohols (Alkane diols)**	**Trihydric alcohols (Alkane triols)**	**Polyhydric alcohols**
CH_3OH Methyl alcohol (Methanol) C_2H_5OH Ethyl alcohol (Ethanol)	$CH_2—OH$ | $CH_2—OH$ Ethylene glycol (Ethane - 1,2 - diol)	$CH_2—OH$ | $CH—OH$ | $CH_2—OH$ Glycerol or Glycerine (Propane-1,2,3- triol)	$CH_2—OH$ | $(CH—OH)_4$ | $CH_2—OH$ Sorbitol

Note : If two or more hydroxy groups are attached to the same carbon atom, the molecule will be unstable. It will immediately lose water to form an aldyhyde or ketone or a carboxylic acid.



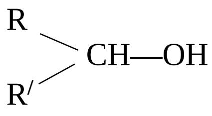


15.3 MONOHYDRIC ALCOHOLS :

The general formula of monohydric alcohols is $C_nH_{2n+1}OH$ or $C_n H_{2n+2} O$ or R — OH. Monohydric alcohols are further classified as primary, secondary, and tertiary alcohols according as the hydroxyl (–OH) group is attached to a primary, a secondary or a tertiary carbon atom respectively.

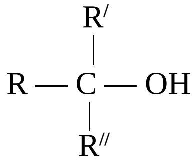
(i) Primary alcohol : $R — CH_2 — OH$ or $R — OH$

(ii) Secondary alcohol :



$$\left.\begin{matrix}R\\R'\end{matrix}\right\rangle CH—OH$$

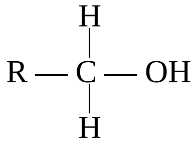
(iii) Tertiary alcohol :



$$\begin{array}{c} R' \\ | \\ R - C - OH \\ | \\ R'' \end{array}$$

Here, R' and R'' represent the same or different alkyl groups.

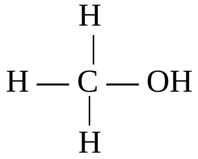
(i) **Primary alcohol :** In a primary alcohol, one alkyl group is attached to the saturated carbon atom containing the hydroxyl group. It is represented by the general formula,



$$\begin{array}{c} H \\ | \\ R - C - OH \\ | \\ H \end{array}$$

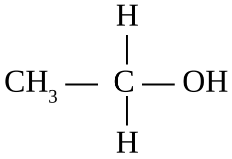
Here, 'R' is any alkyl group or a hydrogen atom. Thus, a primary alcohol should contain a $-CH_2OH$ group.

Examples :



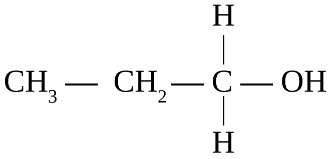
$$\begin{array}{c} H \\ | \\ H - C - OH \\ | \\ H \end{array}$$

Methyl alcohol
or Methanol



$$\begin{array}{c} H \\ | \\ CH_3 - C - OH \\ | \\ H \end{array}$$

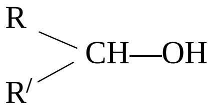
Ethyl alcohol
or Ethanol



$$\begin{array}{c} H \\ | \\ CH_3 - CH_2 - C - OH \\ | \\ H \end{array}$$

n-Propyl alcohol
or Propanol

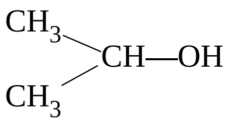
(ii) **Secondary alcohol :** In a secondary alcohol, two alkyl groups are attached to the saturated carbon atom containing the hydroxyl group. It is represented by the general formula,



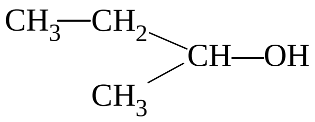
Here, R and R' may be same or different alkyl groups.

Thus, secondary alcohol should contain $>CH-OH$ group.

Examples :

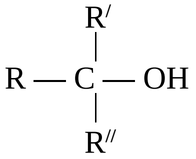


Isopropyl alcohol
or Propan-2-ol



sec-butyl alcohol
or Butan-2-ol

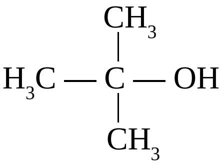
(iii) **Tertiary alcohol :** In a tertiary alcohol, three alkyl groups are attached to the saturated carbon atom containing the hydroxyl group. It is represented by the general formula,



$$\begin{array}{c} R' \\ | \\ R - C - OH \\ | \\ R'' \end{array}$$

Here, R, R' and R'' may represent the same or different alkyl groups.

Example :



$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

tertiary butyl alcohol

or

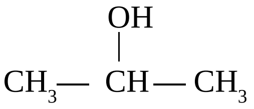
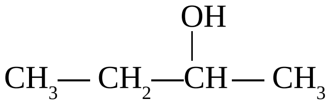
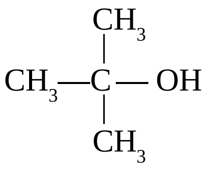
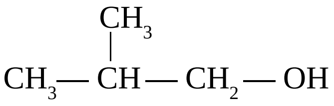
2- Methylpropan -2- ol

Thus, tertiary alcohol should contain $-\underset{|}{\overset{|}{C}}-OH$ group.

15.4 NOMENCLATURE OF MONOHYDRIC ALCOHOLS :

In the common system, alcohols are named as alkyl alcohols. In IUPAC system, the names of saturated alcohols are derived from the corresponding alkanes by replacing 'e' of an alkane by 'ol' . In IUPAC system, alcohols are named as alkanols.

$$\text{Alkane} \xrightarrow[+\,\text{ol}]{-\text{e}} \text{Alkanol}$$

Structural formula **$C_nH_{2n+2}O$**	**Common name** **Alkyl alcohol**	**IUPAC name** **Alkanol**
CH_3OH	Methyl alcohol	Methanol
$CH_3—CH_2—OH$	Ethyl alcohol	Ethanol
$CH_3—CH_2—CH_2—OH$	n-propyl alcohol	Propan - 1 - ol
 $CH_3-\overset{OH}{\overset{\mid}{CH}}-CH_3$	Isopropyl alcohol	Propan - 2 - ol
$CH_3—CH_2—CH_2—CH_2—OH$	n-Butyl alcohol	Butan - 1 - ol
 $CH_3-CH_2-\overset{OH}{\overset{\mid}{CH}}-CH_3$	sec-butyl alcohol	Butan - 2 - ol
 $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{\mid}{\overset{\mid}{C}}}}-OH$	tert-butyl alcohol	2- Methylpropan -2- ol
 $CH_3-\overset{CH_3}{\overset{\mid}{CH}}-CH_2-OH$	Isobutyl alcohol	2- Methylpropan -1- ol

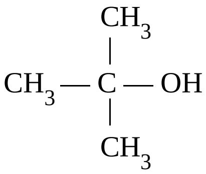
Besides these systems, there is another system of naming of alcohols in which CH_3OH is called **carbinol** and other alcohols are considered as alkyl derivatives of carbinol. However, this carbinol system of nomenclature is not preferred now.

CH_3OH

Carbinol

CH_3-CH_2-OH

Methylcarbinol



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

Trimethylcarbinol

15.5 ISOMERISM IN ALCOHOLS :

Higher aliphatic alcohols exhibit three types of structural isomerism along with stereoisomerism.

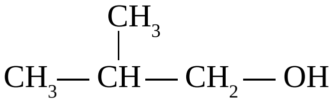
(a) **Chain Isomerism :** All alcohols are the derivatives of alkanes. Therefore, they exhibit chain isomerism due to the presence of different types of carbon chains.

For example, C_4H_9OH has the follwing chain isomers.

(i) $CH_3-CH_2-CH_2-CH_2-OH$

n – Butyl alcohol

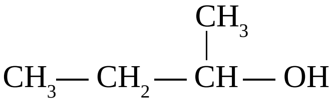
(ii)



$CH_3-\overset{CH_3}{CH}-CH_2-OH$

Isobutyl alcohol

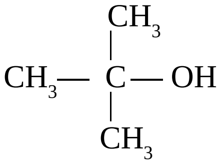
(iii)



$CH_3-CH_2-\overset{CH_3}{CH}-OH$

see-butyl alcohol

(iv)



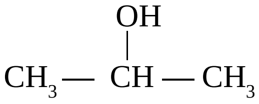
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

tert-butyl alcohol

(b) **Position Isomerism :** This isomerism is due to the different positions of –OH group in the same carbon chain. For example, C_3H_7OH has two position isomers.

(i) $CH_3-CH_2-CH_2-OH$

Propan - 1 - ol



$CH_3-\overset{OH}{CH}-CH_3$

Propan - 2 - ol

(c) **Functional Isomerism :** This isomerism is due to the difference in the functional group. For example, C_2H_6O represents dimethyl ether and ethyl alcohol, which have different functional groups.

CH_3-CH_2-OH

Ethyl alcohol

CH_3-O-CH_3

Dimethyl ether

Thus, ethyl alcohol and dimethyl ether are *functional isomers.*

(d) **Stereoisomerism :** Higher alcohols exhibit optical isomerism, due to the presence of asymmetric carbon atom. For example, butan-2-ol can give two optical isomers.

$H_3C-\overset{\overset{\Large C_2H_5}{|}}{\underset{\underset{\Large H}{|}}{C}}-OH$ (*d*-Butan - 2 - ol)

$HO-\overset{\overset{\Large H_5C_2}{|}}{\underset{\underset{\Large H}{|}}{C}}-CH_3$ (*l* - Butan - 2 - ol)

15.6 GENERAL METHODS OF PREPARATION :

Monohydric alcohols can be prepared by the following general methods.

1. By the hydrolysis of alkyl halides :

When alkyl halides are boiled with aqueous solution of sodium or potassium hydroxide, alcohols result.

$$\underset{\text{(Alkyl halide)}}{R\text{–}X} + KOH_{(aq)} \xrightarrow{\text{heat}} \underset{\text{(Alcohol)}}{R\text{–}OH} + KX$$

$$\underset{\text{(Ethyl bromide)}}{C_2H_5\text{–}Br} + KOH_{(aq)} \xrightarrow{\text{heat}} \underset{\text{(Ethyl alcohol)}}{C_2H_5\text{– }OH} + KBr$$

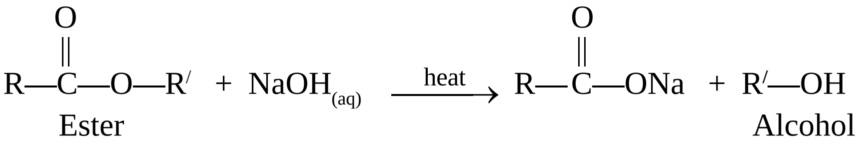
In this reaction, small amount of ether is also formed along with alcohol. But, when KOH is replaced by mild alkali, such as moist Ag_2O ($Ag_2O + H_2O$), alcohol is obtained in better yield.

$$\underset{\text{(Ethyl bromide)}}{C_2H_5Br} + AgOH \xrightarrow{\text{heat}} \underset{\text{(Ethyl alcohol)}}{C_2H_5 - OH} + AgBr$$

The order of reactivity of alkyl halides towards hydrolysis is RI > R –Br > RCl.

2. By hydrolysis of esters :

When esters are boiled with aqueous solution of sodium or potassium hydroxide, alcohols result along with the salt of the carboxylic acid. This process is called **saponification**.



$$\underset{\text{Ester}}{R-\overset{\overset{\large O}{\|}}{C}-O-R'} + NaOH_{(aq)} \xrightarrow{\text{heat}} R-\overset{\overset{\large O}{\|}}{C}-ONa + \underset{\text{Alcohol}}{R'-OH}$$

$$CH_3COOC_2H_5 + NaOH_{(aq)} \xrightarrow{\text{heat}} CH_3COONa + C_2H_5OH$$

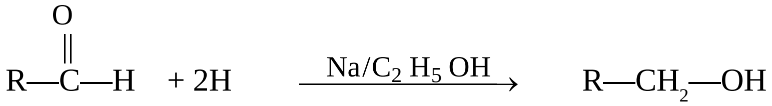
Hydrolysis of esters can also be carried out in the presence of a dilute mineral acid as a catalyst. In this case, alcohol and carboxylic acid are produced.

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{\text{dil. HCl}} CH_3COOH + C_2H_5OH$$

3. By reduction of aldyhydes and ketones :

Carbonyl compounds, such as aldehydes and ketones can easily be reduced to alcohols. The commonly used reducing agents are (i) hydrogen in the presence of a catalyst, such as finely divided Ni, Pt or Pd. (ii) nascent hydrogen obtained by the action of sodium in ethanol and (iii) complex metal hydrides, such as sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAIH_4$).

Aldehydes and ketones can be reduced by sodium in ethanol to give primary and secondary alcohols respectively. This process is otherwise known as **Bouveault - Blanc reduction**. A tertiary alcohol can not be obtained by this method.

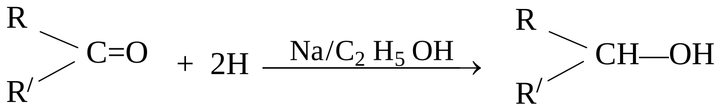


$$R—\overset{\overset{\large O}{||}}{C}—H + 2H \xrightarrow{Na/C_2H_5OH} R—CH_2—OH$$

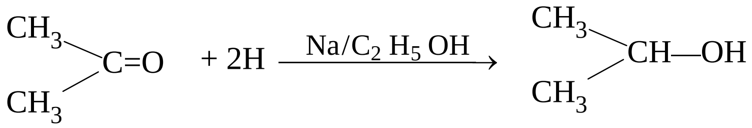
(Aldehyde) (1^0– Alcohol)

$$CH_3—CHO + 2H \xrightarrow{Na/C_2H_5OH} CH_3—CH_2—OH$$

(Acetaldehyde) (Ethanol)



(Ketone) (2^{0}Alcohol)

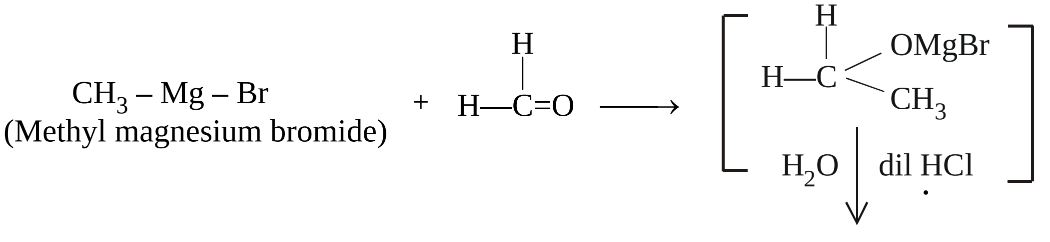


(Isopropyl alcohol)

4. By the action of Grignard reagents on aldehydes and ketones :

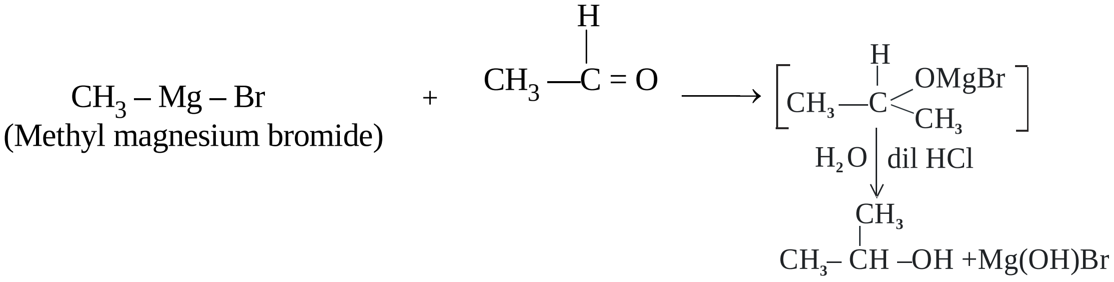
Grignard reagents (R - Mg - X) can be prepared by the addition of alkyl halides to magnesium, suspended in dry ether ($R - X + Mg \rightarrow R - Mg - X$). Grignard reagents react with aldehydes and ketones in the presence of dry ether to give addition products. These addition products on hydrolysis with dilute mineral acids (dil. HCl or dil H_2SO_4) produce alcohols. All the three types of alcohols can be prepared by this method.

(a) Primary alcohols are obtained by the action of Grignard reagent with formaldehyde.



$$\underset{\text{(Methyl magnesium bromide)}}{CH_3 – Mg – Br} + H—\overset{\overset{\large H}{|}}{C}=O \longrightarrow \left[H—\overset{\overset{\large H}{|}}{C}\begin{matrix} OMgBr \\ CH_3 \end{matrix} \right] \xrightarrow{H_2O \,|\, \text{dil HCl}} \underset{\text{(Ethanol)}}{CH_3– CH_2– OH} + Mg(OH)Br$$

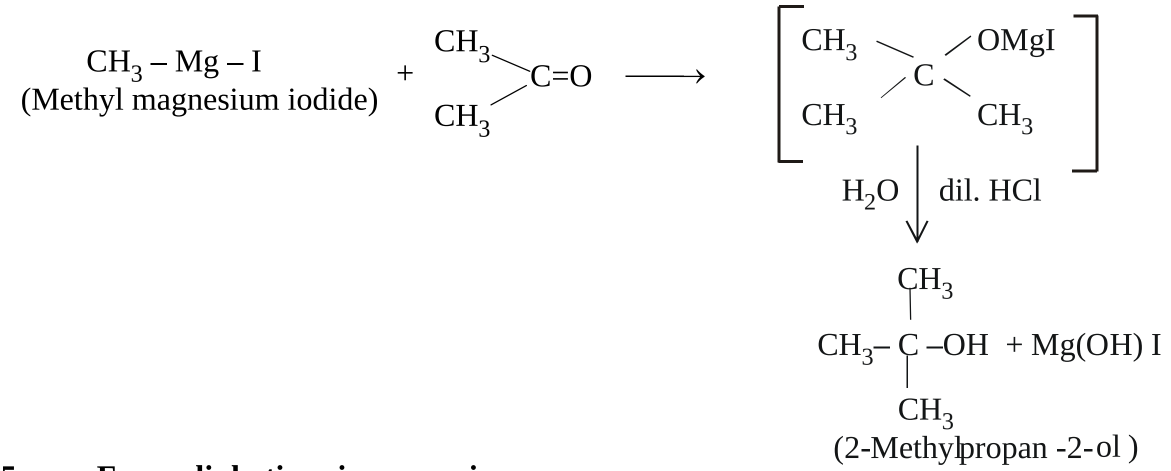
(b) Secondary alcohols are obtained by treating the Grignard reagent with aldehyde other than formaldehyde.



$$\underset{\text{(Methyl magnesium bromide)}}{CH_3 – Mg – Br} + CH_3—\overset{\overset{\large H}{|}}{C} = O \longrightarrow \left[CH_3—\overset{\overset{\large H}{|}}{C}\begin{matrix} OMgBr \\ CH_3 \end{matrix} \right] \xrightarrow{H_2O \,|\, \text{dil HCl}} CH_3– \overset{\overset{\large CH_3}{|}}{CH} –OH + Mg(OH)Br$$

(Propan-2-ol)

(c) Tertiary alcohols are obtained by the action of Grignard reagent with ketones.



5. From aliphatic primary amines :

When aliphatic primary amines (except CH_3NH_2) are treated with a cold solution of sodium nitrite and dilute hydrochloric acid, primary alcohols are produced. The nitrous acid, prepared by the reaction of sodium nitrite and dilute HCl reacts with the 1^0-amine.

$$NaNO_2 + \text{dil. HCl} \longrightarrow HNO_2 + NaCl$$

$$\underset{(1^0\text{-amine})}{R — NH_2 + HNO_2} \longrightarrow \underset{(1^0\text{ - alcohol})}{R — OH} + N_2\uparrow + H_2O$$

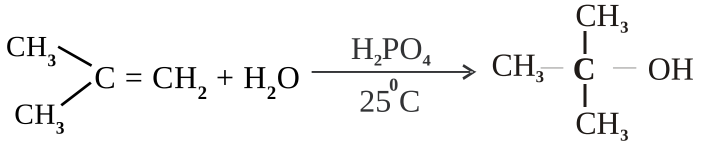
$$\underset{\text{(Ethyl amine)}}{CH_3 — CH_2 — NH_2 + HNO_2} \longrightarrow \underset{\text{(ethyl alcohol)}}{CH_3 — CH_2 — OH} + N_2\uparrow + H_2O$$

6. Addition of water (Hydration)

Alkenes undergo acid-catalysed addition of water to form alcohols. The method is used to prepare ethanol industrially. The commonly used acids are sulphuric acid and phoshoric acid.

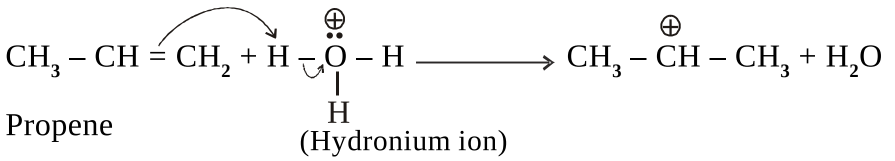
The reaction follows Markownikoff's rule

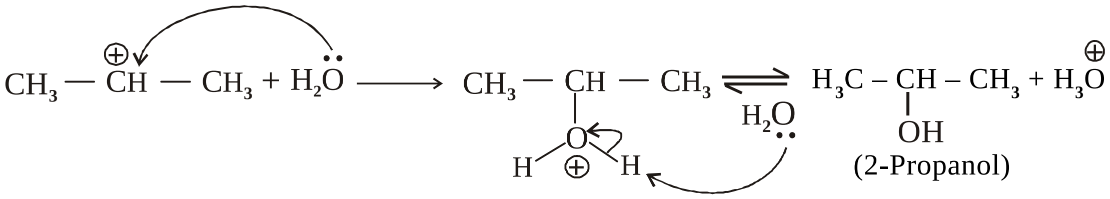
$$\underset{\text{(Ethene)}}{CH_2 = CH_2} + H_2O \xrightarrow[300^0C]{H_3PO_4} CH_3CH_2OH \text{ (ethanol)}$$



2-Methylpropene (tert. Butyl alcohol)

Acid transfers the proton to alkene is usually the solvated hydronium ion. Water itself is too weak to transfer the proton to the alkene. So acid - catalyst is essential





7. Hydroboration - Oxidation

Alkenes undergo hydroboration with the reagent diborane $(BH_3)_2$ to produce trialkyl boron R_3B which on subsequent oxidation with H_2O_2 in presence of alkali NaOH yields alcohol (1^0)

$$\underset{\text{Diborane}}{(BH_3)_2} \xrightarrow{CH_2=CH_2} CH_3\,CH_2\,BH_2 \xrightarrow{CH_2=CH_2} (CH_3\,CH_2)_2\,BH \xrightarrow{CH_2=CH_2} \underset{\text{Triethylboron}}{(CH_3\,CH_2)_3B}$$

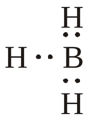
$$\underset{\text{Triethylboron}}{(CH_3CH_2)_3\,B} + \underset{\text{hydrogen peroxide}}{3H_2O_2} \xrightarrow{OH^-} \underset{\text{Ethyl alcohol}}{3CH_3\,CH_2OH} + \underset{\text{Boric acid}}{B\,(OH)_3}$$

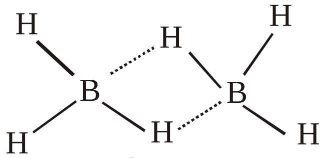
Diborane is a toxic gas prepared by the reaction of sodium borohydride and boron trifluoride.

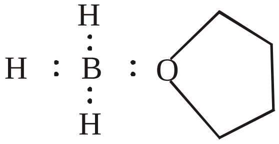
$3NaBH_4 + 4BF_3 \rightarrow 2B_2\,H_6 + 3NaBF_4$

Diborane is the dimer of hypothetical BH_3 (Borane)

Tetrahydrofuran is used as the solvent in the hydroboration reaction in which diborane exists as monomer forming a complex.

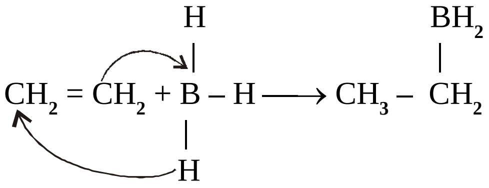

Borane

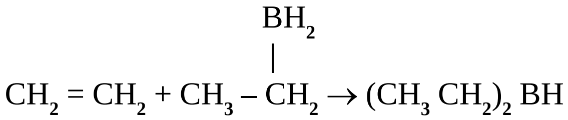

Diborane


Borane - tetrahydrofuran complex

Borane undergoes rapid and quantitative reaction with alkene to form organoboranes (R_3B). The overall reaction is the result of three separate steps.

Step (i)





Step (ii) $CH_2 = CH_2 + CH_3 - \overset{\overset{BH_2}{|}}{CH_2} \rightarrow (CH_3\,CH_2)_2\,BH$

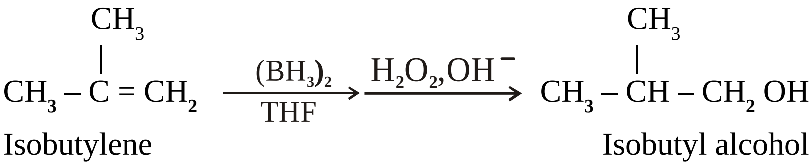
Step (iii) $CH_2 = CH_2 + (CH_3CH_2)_2\,BH \rightarrow (CH_3\,CH_2)_3\,B.$
Triethyl borane
(An organo borane)

Other examples

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} \xrightarrow[THF]{(BH_3)_2} \xrightarrow{H_2O_2, OH^-} \underset{\text{n - propylalcohol}}{CH_3 - CH_2 - CH_2 - OH}$$

$$CH_3-CH_2-CH=CH_2 \xrightarrow[THF]{(BH_3)_2} \xrightarrow{H_2O_2, OH^-} CH_3-CH_2-CH_2-CH_2-OH$$

1- Butene n-Butylalcohol



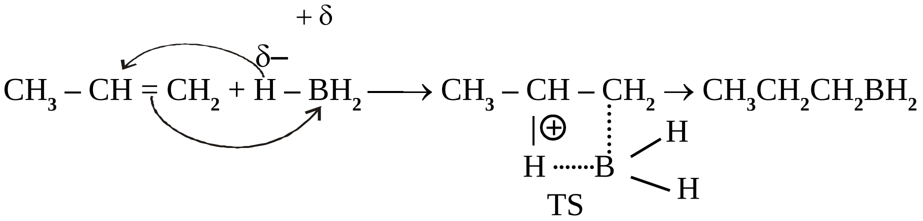
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[THF]{(BH_3)_2} \xrightarrow{H_2O_2, OH^-} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH$$

Isobutylene Isobutyl alcohol

Mechanism

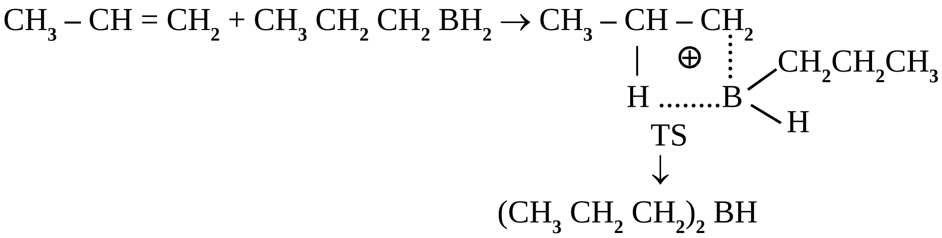
A four centred transition state is formed prior to the formation of organoborane. Hydroboration is thus a cis-addition.

Step I



$$CH_3-CH=CH_2+\overset{+\delta}{H}-\overset{\delta-}{BH_2} \longrightarrow CH_3-CH-CH_2 \rightarrow CH_3CH_2CH_2BH_2$$

TS



$$CH_3-CH=CH_2+CH_3CH_2CH_2BH_2 \rightarrow CH_3-CH-CH_2$$

TS

$$\downarrow$$

$$(CH_3CH_2CH_2)_2BH$$

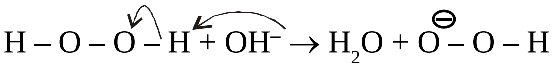
$$CH_3-CH=CH_2+(CH_3CH_2CH_2)_2BH \rightarrow (CH_3CH_2CH_2)_3B$$

Tripropyl borane

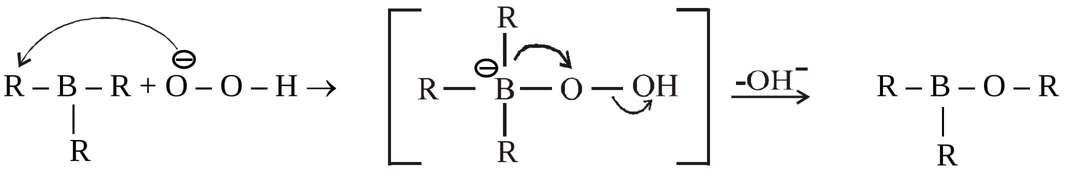
(R_3B) say

Step II

Trialkyl borane is oxidised with H_2O_2 in presence of NaOH to form alcohol.

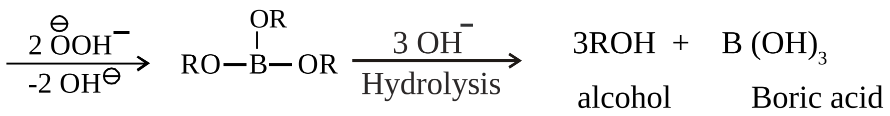


$$H-O-O-H+OH^- \rightarrow H_2O+\overset{\ominus}{O}-O-H$$



$$R-\underset{\underset{R}{|}}{B}-R+\overset{\ominus}{O}-O-H \rightarrow \left[R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{\overset{\ominus}{B}}}-O-OH\right] \xrightarrow{-OH^-} R-\underset{\underset{R}{|}}{B}-O-R$$

1,2-shift of R



$$\xrightarrow[-2\,OH^{\ominus}]{2\,\overset{\ominus}{O}OH^-} RO-\overset{\overset{OR}{|}}{B}-OR \xrightarrow[Hydrolysis]{3\,OH^-} 3ROH + B(OH)_3$$

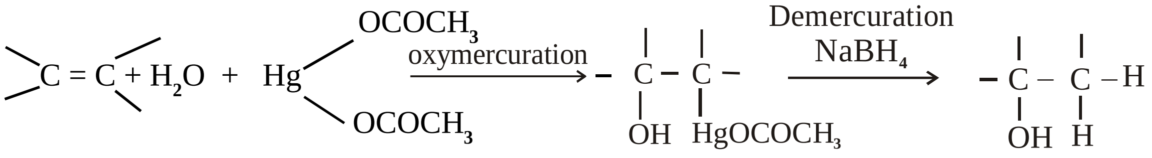
alcohol Boric acid

Hence, in case of propene, the product is $CH_3CH_2CH_2OH$ (n-propylalcohol).

The hydroboration – oxidation process gives products corresponding to anti - Markownikoff addition of water to C = C bond.

(8) Oxymercuration - demercuration

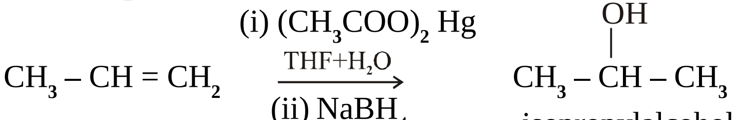
Alkenes react with mercuric acetate in presence of water to form hydroxy mercurial compounds which on subsequent reduction yield alcohols.



The first stage in oxymercuration which involves the addition of –OH and – HgO $COCH_3$ to C=C bond. The second stage is demercuration is which – $HgOCOCH_3$ is replaced by – H. The over all result amounts to hydration of alkene. The process is very fast and the yield is over 90%. At room temperature alkene is added to an aqueous solution of mercuric acetate diluted with solvent tetrahydrofuran.

Oxymercuration - demercuration is highly regioselective and produces alcohols corresponding to Markownikoff's addition of H_2O to C = C bond.

For example,



$$CH_3-CH=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } (CH_3COO)_2Hg,\ THF+H_2O} CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_3$$

isopropylalcohol

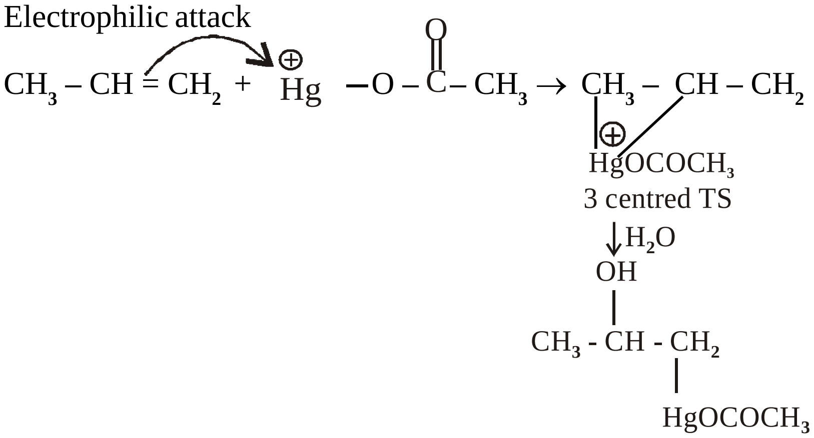
Mechanism

Step (I) Alkene when treated with mercuric acetate in presence of H_2O and THF forms hydroxy alkyl mercurial compound. A three centred transition state is formed as intermediate.

Dissociation of mercuric acetate :-

$$Hg(O_2CCH_3)_2 \rightleftarrows {}^{+}Hg\,O_2C.CH_3 + \overset{\ominus}{O}_2\,CCH_3$$

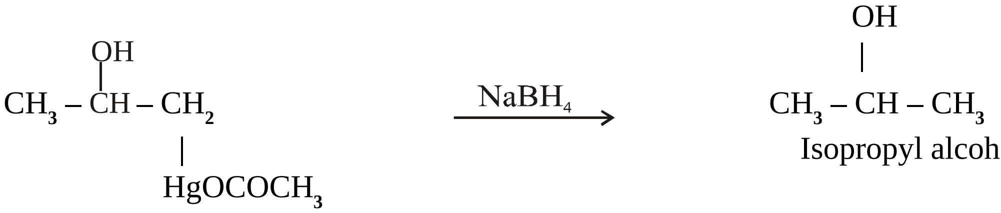
Electrophilic attack



(Organomercuric compound)

Step II

The hydroxy alkyl mercurial compound on reduction with $NaBH_4$ produces 2^0 alcohol.



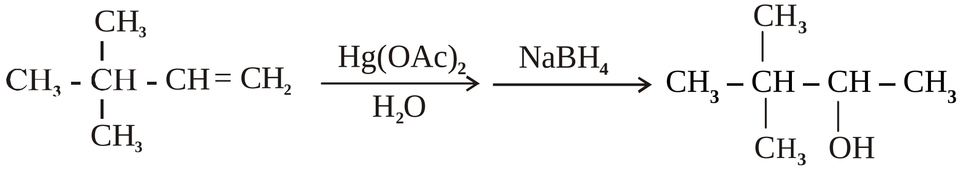
$$CH_3-\overset{OH}{\overset{|}{C}H}-\underset{HgOCOCH_3}{\underset{|}{CH_2}} \xrightarrow{NaBH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$$

Isopropyl alcohol

Other examples

1. 

1- methyl cyclopentene 1- methyl cyclopentanol

2. 

$$CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-CH=CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-\underset{OH}{CH}-CH_3$$

3, 3- dimethylbutan-2-ol

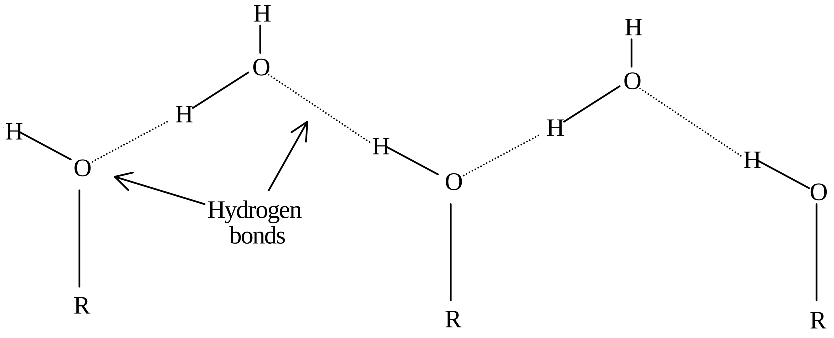
15.7 PROPERTIES :

(A) Physical Properties :

1. **Physical state :** At ordinary temperature, the lower members of alcohols are colourless volatile liquids having distinct odour and burning taste.

2. **Solubility :** The first three members are completely miscible in water. The solubility decreases rapidly with increase in the molecular mass. The higher members are completely insoluble in water but are soluble in organic solvents like benzene, ether etc.

   The solubility of lower members of alcohols in water is only due to the formation of hydrogen bonding between alcohol and water molecules.

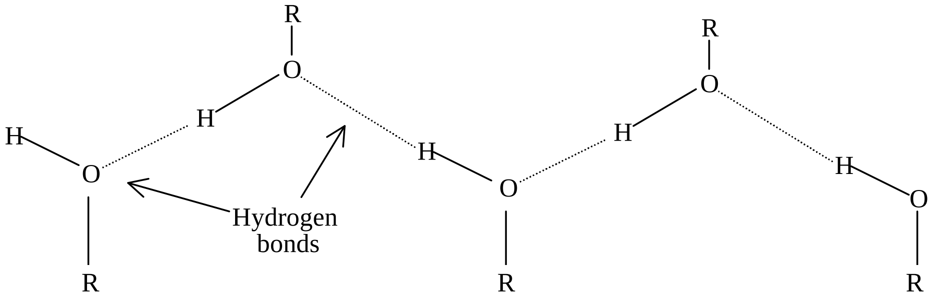


The increase in the molecular mass of the alcohol increases the size of the non-polar part of the hydrocarbon. As a result of which, it resists the formation of hydrogen bonding with water molecules and hence the solubility in water decreases.

Amongst isomeric alcohols, the solubility in water increases with branching of the chain. It is because, the surface area of the non-polar part in the molecule decreases. As for example, n-butyl alcohol is least soluble in water while tert -butyl alcohol is highly soluble.

3. **Boiling points :** The boiling points of alcohols are much higher that those of hydrocarbons, ethers and haloalkanes of comparable molecular masses. This arises due to the intermolecular

hydrogen bonding in alcohols. Due to the intermolecular hydrogen bonding, alcohols exist as associated molecules rather that discrete molecules. Thus, large amount of energy is required to break these bonds.



Compounds :	$CH_3–CH_2–OH$ Ethanol	$CH_3–O–CH_3$ Methoxymethane	CH_3Cl Chloromethane	$CH_3-CH_2-CH_3$ Propane
Mol. mass :	46	46	50.5	44
Boiling point :	351K	297K	249K	231K

Amongst the isomeric alcohols, the boiling points follow the order;

Primary > Secondary > Tertiary

For example, among n-butyl alcohol, sec-butyl alcohol and tert - butyl alcohol, the boiling point of n-butyl alcohol is more.

Alcohol :	n-Butyl alcohol	sec-butyl alcohol	tert-butyl alcohol
Boiling point :	391K	372.5K	356 K

This can be explained on the fact that branching decreases the surface area which in turn decreases intermolecular forces of attraction. Hence, boiling point becomes low. However, with the increase in molecular mass boiling points of alcohols increase regularly.

4. **Physiological effect :** Alcohols are toxic in nature when taken internally. Amongst all alcohols, ethyl alcohol is least toxic. Methyl alcohol, in turn, is quite toxic. Drinking methyl alcohol may cause blindness or death.

(B) Chemical properties :

The chemical properties of alcohols are mainly due to their functional group, i.e. hydroxyl (– OH) group. The chemical reactivity of alcohols can be calssified as follows.

1. Reactions involving replacement of hydrogen atom of the hydroxyl group (cleavage of oxygen- hydrogen bond)
2. Reactions invloving replacement of the hydroxyl group (cleavage of carbon-oxygen bond)
3. Reactions involving both alkyl group and hydroxyl group.

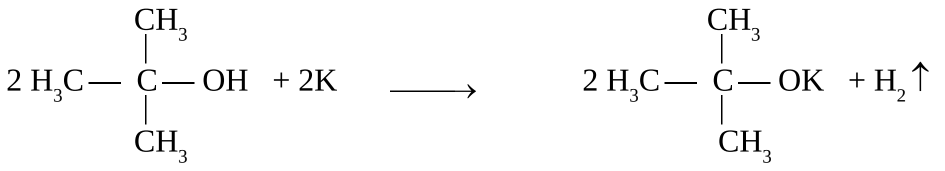
1. Reaction involving the cleavage of oxygen- hydrogen bond :

(i) **Reaction with alkali metals :** Alcohols react with alkali metals like Li, Na, K to form metal alkoxides with the liberation of hydrogen gas.

$$\underset{\text{Alcohol}}{2R-OH} + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2\,RONa} + H_2\uparrow$$

$$\underset{\text{Methanol}}{2CH_3OH} + 2Na \longrightarrow \underset{\text{Sodium methoxide}}{2\,CH_3ONa} + H_2\uparrow$$

$$\underset{\text{Ethanol}}{2\,C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2\,C_2H_5ONa} + H_2\uparrow$$



$$2\,H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH + 2K \longrightarrow 2\,H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OK + H_2\uparrow$$

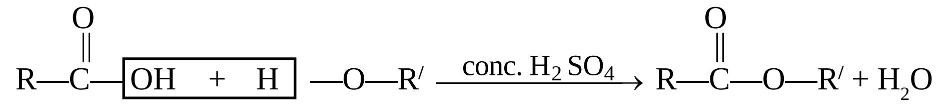
tert-butyl alcohol Potassium t-butoxide

In this reaction, the order of reactivity is

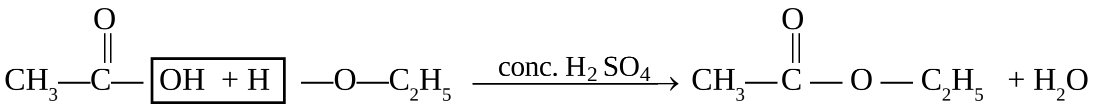
primary alcohol > sec - alcohol > tert. - alcohol.

(ii) Reaction with carboxylic acids :

Alcohols react with carboxylic acids in presence of conc. H_2SO_4, which acts as catalyst to form esters. This reaction is known as **esterification** reaction.



$$\underset{\text{(carboxylic acid)}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-}\boxed{OH\ +\ H}\underset{\text{(alcohol)}}{-O-R'} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(ester)}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-O-R'} + H_2O$$



$$\underset{\text{(acetic acid)}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-}\boxed{OH\ +H}\underset{\text{(ethyl alcohol)}}{-O-C_2H_5} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(ethyl acetate)}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5} + H_2O$$

(iii) Reaction with inorganic acids :

Alcohols react with inorganic acids like, HCl, H_2SO_4 etc. forming the corresponding alkyl halide, alkyl hydrogen sulphate respectively.

$$R-OH + HCl \xrightarrow{\text{Anh.}ZnCl_2} R-Cl + H_2O$$

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + HCl \xrightarrow{\text{Anh.}ZnCl_2} \underset{\text{(ethyl chloride)}}{C_2H_5-Cl} + H_2O$$

The order of reactivity of alcohols is as follows; $3^0 > 2^0 > 1^0$

Ethyl alcohol when treated with equimolar amount of conc H_2SO_4 at 100^0C, forms the corresponding inorganic ester ($C_2H_5HSO_4$)

$$C_2H_5 — OH + H_2SO_4 \longrightarrow C_2H_5 — HSO_4 + H_2O$$

When ethyl alcohol is taken in excess at 140^0C, diethyl ether is formed.

$$C_2H_5 — HSO_4 \quad + \quad HO\,C_2H_5$$

$$\downarrow$$

$$C_2H_5 — O — C_2H_5 + H_2SO_4$$

On the other hand, when conc. H_2SO_4 is taken in excess at 160^0C, ethylene is formed.

$$C_2H_5 — HSO_4 \xrightarrow[160^0C]{\Delta} \underset{\text{(ethylene)}}{C_2H_4} + H_2SO_4$$

2. Reaction involving the cleavage of carbon-oxygen bond :

(i) Reaction with phosphorus halides :

With PCl_5 : Alcohols react with PCl_5 to form the corresponding alkyl chlorides, phosphoryl chloride and HCl.

$$\underset{\text{Alcohol}}{R — OH} + PCl_5 \longrightarrow \underset{\text{alkyl chloride}}{R — Cl} + \underset{\text{phosphoryl chloride}}{POCl_3} + HCl\uparrow$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{ethyl chloride}}{C_2H_5 — Cl} + POCl_3 + HCl\uparrow$$

With PCl_3 : Alcohols react with PCl_3 to form the corresponding alkyl chlorides, and phosphorus acid.

$$\underset{\text{Alcohol}}{3\,R — OH} + PCl_3 \longrightarrow \underset{\text{alkyl chloride}}{3R — Cl} + \underset{\text{phosphorous acid}}{H_3PO_3}$$

$$\underset{\text{Ethyl alcohol}}{3\,C_2H_3OH} + PCl_3 \longrightarrow \underset{\text{ethyl chloride}}{3\,C_2H_5 — Cl} + H_3PO_3$$

(ii) Action of thionyl chloride ($SOCl_2$) :

Alcohols react with thionyl chloride in the presence of pyridine (a base) to form the corresponding alkyl chloride, SO_2 gas and HCl gas.

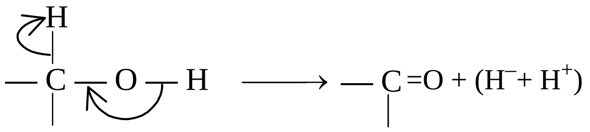
$$\underset{\text{Alcohol}}{R — OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Alkyl chloride}}{R — Cl} + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5\,OH} + \underset{\text{Thionyl chloride)}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + SO_2\uparrow + HCl\uparrow$$

3. Reactions involving both alkyl and hydroxyl groups :

(i) Oxidation of alcohols :

The process of oxidation involves the removal of hydrogen. In the oxidation of alcohols, hydrogen is removed from the carbon atom to which the functional group is directly linked (α-hydrogen atom) and also from the functional group. As a result of which a carbonyl group is produced.



$$-\overset{H}{\underset{|}{C}}-O-H \longrightarrow -\underset{|}{C}{=}O + (H^- + H^+)$$

$$(H^+ + H^-) + [O] \longrightarrow H_2O$$

Thus, the process of oxidation involves the breaking of a carbon -hydrogen and oxygen - hydrogen bond. Here, a carbonyl compound is formed along with hydrogen gas. But in the presence of solution of oxidising agents, it produces water in place of hydrogen gas.

The reagents commonly used for the oxidation of alcohols are,

(a) sodium or potassium dichromate solution and conc. sulphuric acid,

(b) alkaline solutions of potassium permanganate.

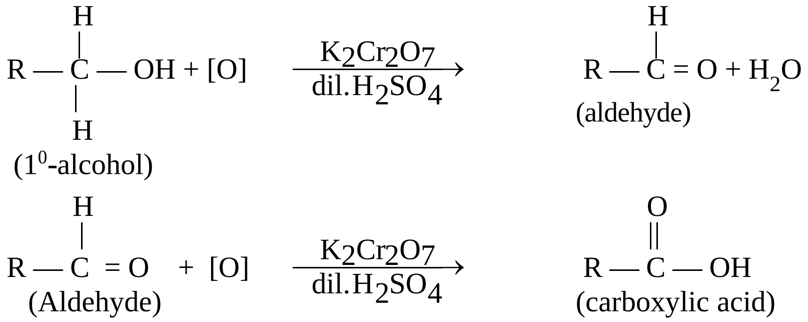
(c) conc. nitric acid and

(d) heated metal catalyst, such as silver and copper.

The products of oxidation depend on the type of alcohol used and also on the nature of oxidising agent.

(a) Oxidation of primary alcohols :

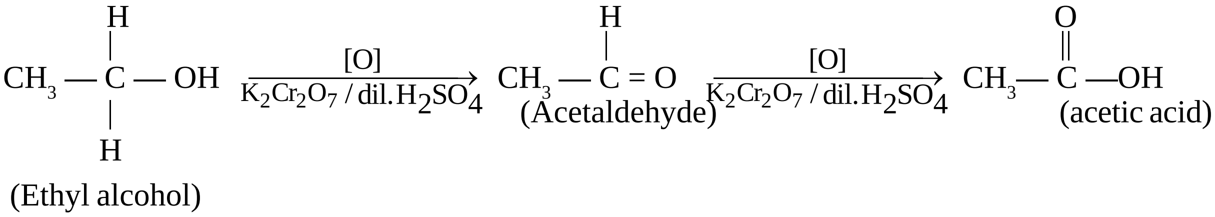
A primary alcohol is first oxidised to an aldehyde, having the same number of carbon atoms as the parent alcohol when treated with acidified potassium dichromate solution. Since the aldehyde formed also contains an α – hydrogen atom, it can readily be oxidised to carboxylic acid, having same number of carbon atoms as the parent alcohol.



$$\underset{(1^0\text{-alcohol})}{R-\overset{H}{\underset{H}{C}}-OH} + [O] \xrightarrow[\text{dil.}H_2SO_4]{K_2Cr_2O_7} \underset{(\text{aldehyde})}{R-\overset{H}{C}{=}O} + H_2O$$

$$\underset{(\text{Aldehyde})}{R-\overset{H}{C}{=}O} + [O] \xrightarrow[\text{dil.}H_2SO_4]{K_2Cr_2O_7} \underset{(\text{carboxylic acid})}{R-\overset{O}{\overset{\|}{C}}-OH}$$

Thus, ethyl alcohol when treated with acidified potassium dichromate solution, is first oxidised to acetaldehyde and then to acetic acid.



$$CH_3-\underset{H}{\overset{H}{C}}-OH \xrightarrow[K_2Cr_2O_7\,/\,dil.H_2SO_4]{[O]} \underset{\text{(Acetaldehyde)}}{CH_3-\overset{H}{C}=O} \xrightarrow[K_2Cr_2O_7\,/\,dil.H_2SO_4]{[O]} \underset{\text{(acetic acid)}}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

(Ethyl alcohol)

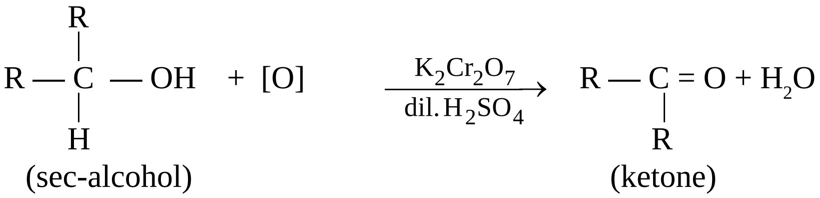
However, oxidation of 1^0-alcohol with potassium permanganate converts it directly to carboxylic acid.

$$R-CH_2-OH \xrightarrow[KMnO_4]{[O]} R-COOH$$

$$\underset{\text{(Ethyl alcohol)}}{CH_3-CH_2-OH} \xrightarrow[KMnO_4]{[O]} \underset{\text{(acetic acid)}}{CH_3\,COOH}$$

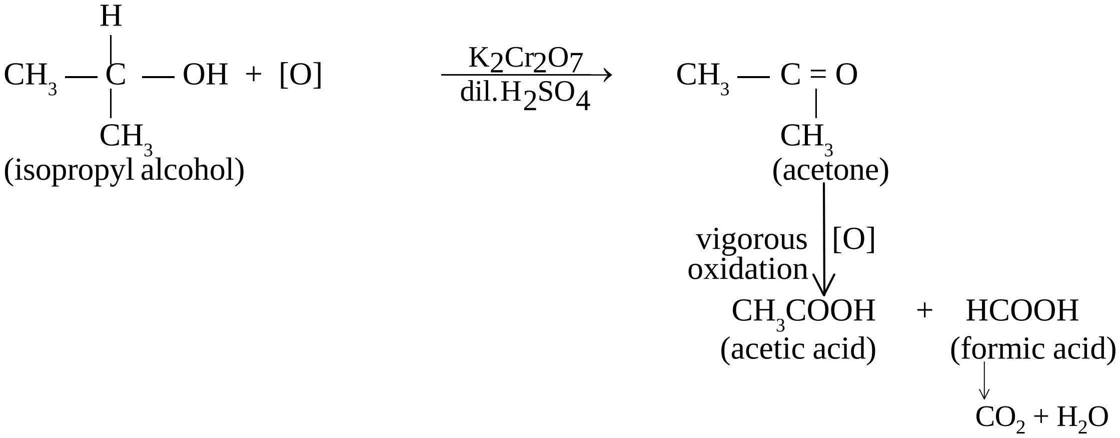
(b) Oxidation of secondary alcohols :

A secondary alcohol when treated with acidfied potassium dichromate solution, is oxidised to a ketone, having same number of carbon atoms as the parent alcohol.



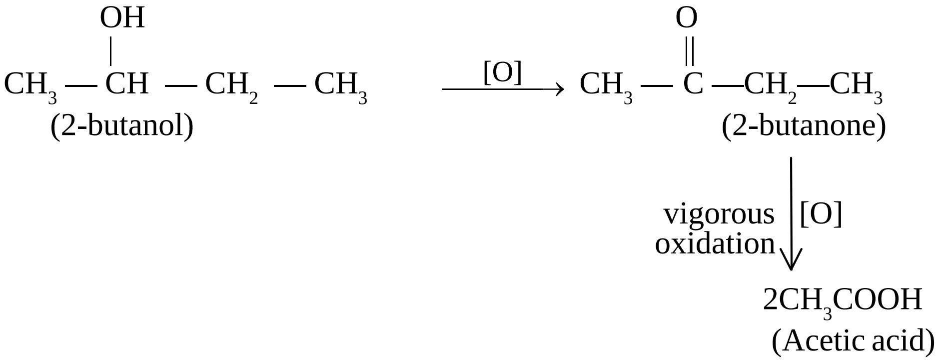
$$\underset{\text{(sec-alcohol)}}{R-\underset{H}{\overset{R}{C}}-OH} + [O] \xrightarrow[dil.H_2SO_4]{K_2Cr_2O_7} \underset{\text{(ketone)}}{R-\underset{R}{C}=O} + H_2O$$

Since the ketone formed has no oxidisable α — hydrogen atom, ordinarily it does not undergo further oxidation. However, on vigorous oxidation, the ketone formed is further oxidised and gives a mixture of lower carboxylic acids.



$$\underset{\text{(isopropyl alcohol)}}{CH_3-\underset{CH_3}{\overset{H}{C}}-OH} + [O] \xrightarrow[dil.H_2SO_4]{K_2Cr_2O_7} \underset{\text{(acetone)}}{CH_3-\underset{CH_3}{C}=O}$$

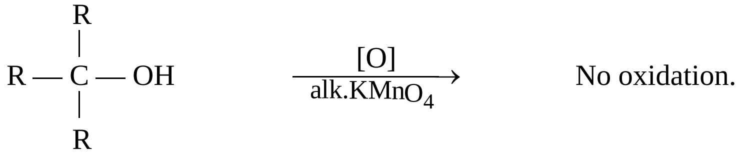
$$\xrightarrow[\text{vigorous oxidation}]{[O]} \underset{\text{(acetic acid)}}{CH_3COOH} + \underset{\text{(formic acid)}}{HCOOH} \rightarrow CO_2 + H_2O$$



$$\underset{\text{(2-butanol)}}{CH_3-\overset{OH}{CH}-CH_2-CH_3} \xrightarrow{[O]} \underset{\text{(2-butanone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3} \xrightarrow[\text{vigorous oxidation}]{[O]} \underset{\text{(Acetic acid)}}{2CH_3COOH}$$

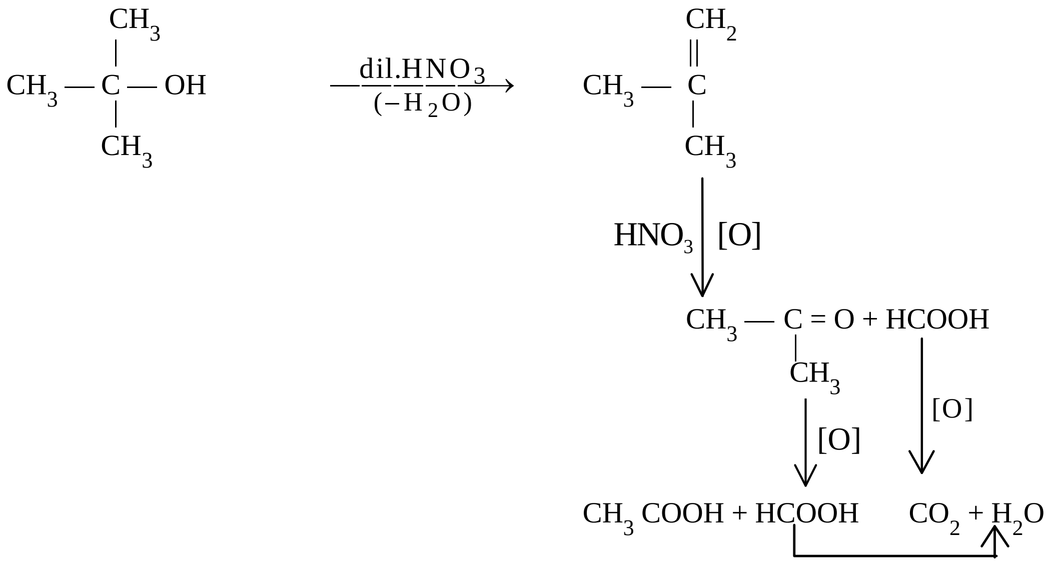
(c) Oxidation of tertiary alcohols :

Tertiary alcohols do not contain α — hydrogen atoms. Hence, it is resistant to oxidation in alkaline solution.



$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-OH \xrightarrow[\text{alk.}KMnO_4]{[O]} \text{No oxidation.}$$

However, on drastic oxidation, tertiary alcohol is oxidised to give a ketone and lower carboxylic acid, when treated with hot acid oxidising agents. Thus, tert-butyl alcohol when treated with dil HNO_3, is oxidised to acetone and formic acid. The initial step of oxidation involves the dehydration of alcohol to alkene, which is then oxidised.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[(-H_2O)]{\text{dil.}HNO_3} CH_3-\overset{\overset{\displaystyle CH_2}{||}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \xrightarrow[{[O]}]{HNO_3} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=O + HCOOH$$

$$\xrightarrow{[O]} CH_3COOH + HCOOH \qquad HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

Here acetone formed is further oxidised to acetic acid and formic acid. Similarly, formic acid formed is further oxidised to CO_2 and H_2O.

(ii) Catalytic dehydrogenation :

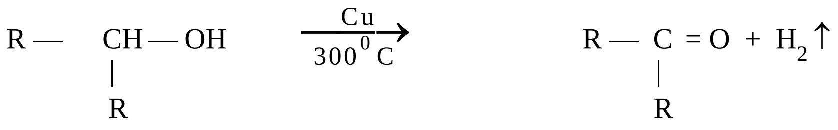
Alcohols are oxidised in presence of heated metal catalyst such as Cu or Ag. In this case, oxidation of alcohols involves the removal of a hydrogen molecule or dehydrogenation. Thus, when vapours of three types of alcohols are passed over heated copper at 300°C, primary, secondary and tertiary alcohols are oxidised to give different products. Depending on the products formed, the three types of alcohols can be easily distinguished.

(a) When vapours of primary alcohol is passed over heated reduced copper catalyst at 300°C, the alcohol is dehydrogenated to give an aldehyde.

$$\underset{(1^0\text{- alcohol})}{R-CH_2-OH} \xrightarrow[300^0C]{Cu} \underset{(\text{aldehyde})}{R-CHO} + H_2\uparrow$$

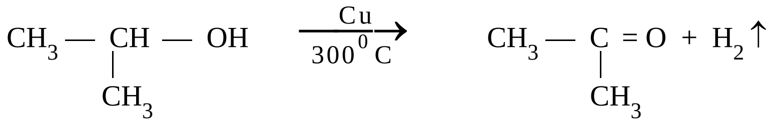
$$\underset{(\text{Ethyl alcohol})}{CH_3-CH_2-OH} \xrightarrow[300^0C]{Cu} \underset{(\text{acetaldehyde})}{CH_3CHO} + H_2\uparrow$$

(b) When vapours of secondary alcohol is passed over heated reduced copper catalyst at 300^0C, the alcohol is dehydrogenated to give a ketone.



$$R-\underset{\substack{|\\ R}}{CH}-OH \xrightarrow[300^0C]{Cu} R-\underset{\substack{|\\ R}}{C}=O + H_2\uparrow$$

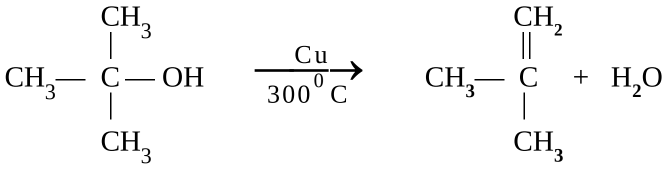
(2^0- alcohol) (ketone)



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-OH \xrightarrow[300^0C]{Cu} CH_3-\underset{\substack{|\\ CH_3}}{C}=O + H_2\uparrow$$

(Isopropyl alcohol) (acetone)

(c) But the tertiary alcohol is not dehydrogenated. Rather it is dehydrated to form an alkene, when passed over heated reduced copper catalyst at 300^0C.



$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-OH \xrightarrow[300^0C]{Cu} CH_3-\overset{\substack{CH_2\\ ||}}{\underset{\substack{|\\ CH_3}}{C}} + H_2O$$

(t-butyl alcohol) (2- methylpropene)

15.8 DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS :

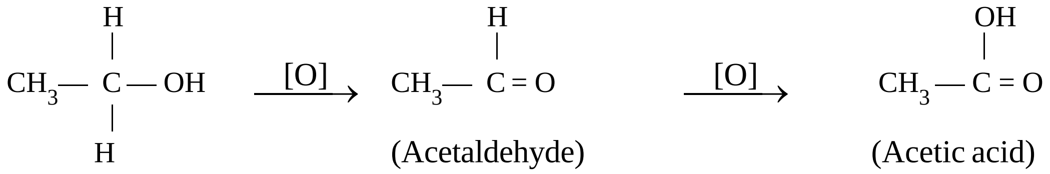
The following methods are used to distinguish primary, secondary and tertiary alcohols.

1. Oxidation method :

Primary, secondary and tertiary alcohols on oxidation produce different types of products. Basing on the products formed, three types of alcohols can be distinguished.

(i) A primary alcohol on oxidation first gives an aldehyde, which on further oxidation gives a carboxylic acid. Here, both the oxidation products contain the same number of carbon atoms as the parent alcohol.

For example, ethyl alcohol on oxidation first gives acetaldehyde, which on further oxidation gives acetic acid.



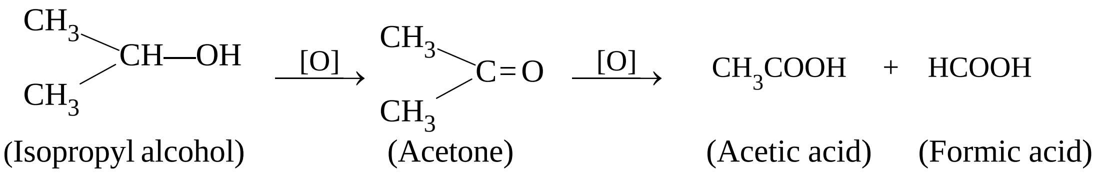
$$CH_3-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}-OH \xrightarrow{[O]} CH_3-\overset{\substack{H\\ |}}{C}=O \xrightarrow{[O]} CH_3-\overset{\substack{OH\\ |}}{C}=O$$

(Acetaldehyde) (Acetic acid)

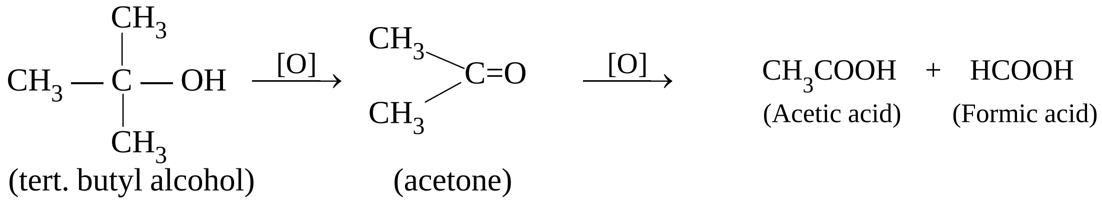
(Ethyl alcohol)

(ii) A secondary alcohol on oxidation first gives a ketone, having same number of carbon atoms as the parent alcohol. Since ketone does not contain α - hydrogen atom, it can not undergo further oxidation. But on vigorous oxidation, that is, on prolonged action of hot oxidising agents, ketone can be oxidised to give a mixture of carboxylic acids, each containing less number of carbon atoms than the parent alcohol.

For example, isopropyl alcohol on oxidation first gives acetone, which on vigorous oxidation gives a mixture of acetic acid and formic acid.



(iii) A tertiary alcohol can not be oxidised in presence of neutral or alkaline solution. But it is readily oxidised by an acid oxidising agent to give a mixture of ketone and carboxylic acid, each containing less number of carbon atoms than the parent alcohol.



2. Catalytic dehydrogenation method :

In this method, the vapours of the given alcohol is passed over reduced copper at 300^{0}C and the products obtained are identified. Here a primary alcohol on dehydrogenation produces an aldehyde, whereas a secondary alcohol produces a ketone. But under the same condition, a tertiary alcohol is not dehydrogenated, rather it is dehydrated to produce an alkene. The method is summarised as follows :

$$1^0\text{ - alcohol} \xrightarrow[300^0\text{C}]{\text{Cu}} \text{Aldehyde} + H_2$$

$$2^0\text{ - alcohol} \xrightarrow[300^0\text{C}]{\text{Cu}} \text{Ketone} + H_2$$

$$3^0\text{ - alcohol} \xrightarrow[300^0\text{C}]{\text{Cu}} \text{Alkene} + H_2$$

3. Lucas Test :

This test consists of reactions of the different types of alcohols with Lucas reagent, which is an equimolar mixture of conc.HCl and anhydrous $ZnCl_2$ at room temperature. On reaction, coresponding alkyl chlorides are formed, which being insoluble appears as turbidity in the solution.

$$\underset{\text{(Alcohol)}}{R - OH} + \text{Conc. HCl} \xrightarrow{\text{Anh.}ZnCl_2} \underset{\substack{\text{Alkyl chloride}\\\text{(turbidity)}}}{R - Cl} + H_2O$$

The alcohols are differentiated from each other on the basis of time required for the appearance of turbidity.

(i) 3^0 - alcohol $\xrightarrow[\text{anh. }ZnCl_2]{\text{conc.HCl}}$ Turbidity appears immediately.

(ii) 2^0 - alcohol $\xrightarrow[\text{anh. }ZnCl_2]{\text{conc.HCl}}$ Turbidity appears after five minutes.

(iii) 1^0 - alcohol $\xrightarrow[\text{anh. }ZnCl_2]{\text{conc.HCl}}$ No turbidity appears even after several hours.However, turbidity appears on heating.

4. Victor Meyer's Test :

This test is performed as follows :

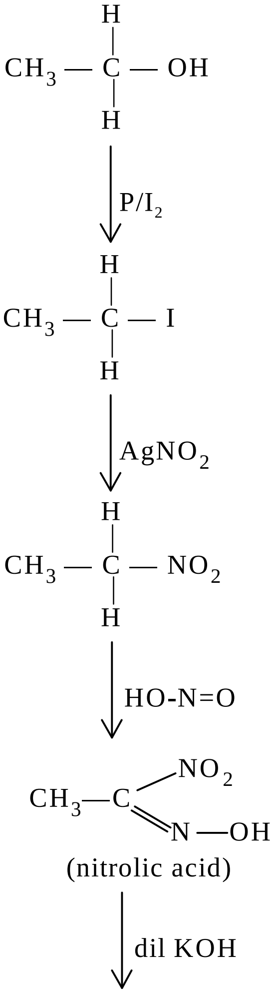
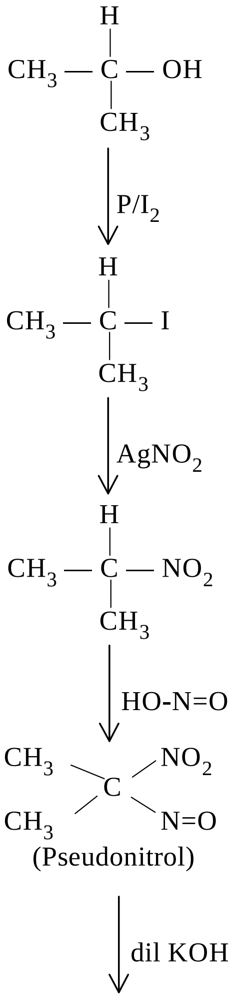
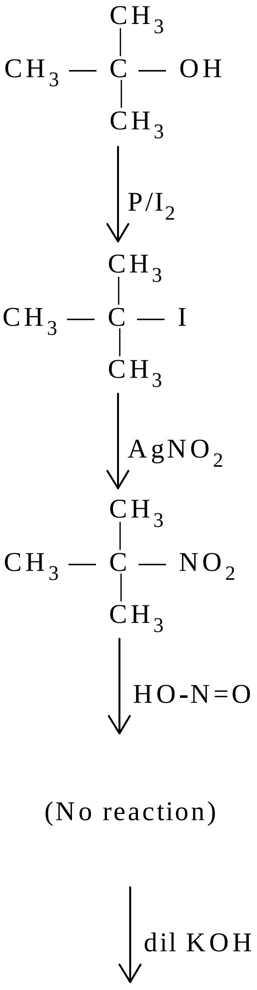
(i) The given alcohol is converted to the corresponding alkyl iodide by treating with red phosphorus and iodine.

(ii) Then the alkyl iodide obtained is treated with silver nitrite ($AgNO_2$) in order to get the corresponding nitroalkane.

(iii) The nitroalkane obtained is then treated with nitrous acid ($NaNO_2$ + dil H_2SO_4).

(iv) Finally, the resultant solution is made alkaline with aqueous KOH or NaOH.

If the resultant solution becomes blood red colour by performing the above tests, then the alcohol is primary. If the solution become blue in colour, the alcohol is secondary and if a colourless solution is obtained it is tertiary alcohol.

 Blood red colour	 Blue colour	 Colourless

15.9 TESTS FOR ALCOHOLIC –OH GROUP :

In order to detect the presence of alcoholic group in an unknown organic compound, the following tests may be performed.

(i) When a piece of sodium metal is added into a flask containing dry alcohol, hydrogen gas is evolved.

$$2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$$

(ii) Similary, if PCl_5 or acetyl chloride is added HCl gas is obtained with liberation of heat.

$$R\,OH + PCl_5 \longrightarrow R - Cl + POCl_3 + HCl\uparrow + \text{heat}$$

(iii) **Treatment of of the dry compound with acetyl chloride (CH_3COCl).** CH_3COCl reacts with a compound containing a hydroxyl group with the evolution of HCl gas and the production of an ester.

$$CH_3O\boxed{H + Cl}\,OCCH_3 \longrightarrow \underset{\text{Methyl acetate}}{CH_3COOCH_3} + HCl$$

(iv) **Ceric Ammonium Nitrate Test.** This is the most delicate and sensitive test. When a few drops of an organic compound containing OH group is added to the aqueous solution of ceric ammonium nitrate which is orange, the colour changes to red.

$$\underset{\text{(Orange)}}{(NH_4)_2Ce(NO_3)_6} + 2ROH \longrightarrow \underset{\text{(Red)}}{Ce(NO_3)_4(ROH)_2} + 2NH_4NO_3$$

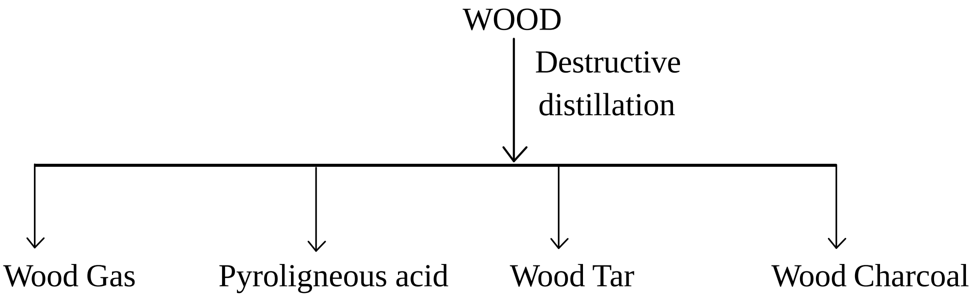
15.10 MANUFACTURE OF METHYL ALCOHOL FROM DESTRUCTIVE DISTILLATION OF WOOD :

Methyl alcohol can be commercially manufactured by the destructive distillation of wood.

Principle : The principle involved in this process is heating of wood at about 400^{0}C in the absence of air. The heating of wood at high temperature in iron retorts in absence of air is known as **destructive distillation** of wood.

Main products of distillation :

The main products of destructive distillation of wood are illustrated below.



(i) Wood Gas : It consists of CH_4, C_2H_6, H_2, CO, CO_2 and N_2 . It is used as a fuel for heating the iron retorts in wood distillation.

(ii) Pyroligneous acid : The aqueous distillate which is collected over wood tar (as shown in figure 21.1) is called pyroligneous acid. In addition to water, it contains, Methyl alcohol = 2.0 to 4.0 %

Acetone = 0.5 %

Acetic acid = 10.0 %

(iii) Wood Tar : It is the thick black liquid, settled at the bottom of the settling tank.

(iv) Wood charcoal : It is the solid residue left in the iron retort after the distillation is over. It consists mainly of carbon and is used as a very good domestic fuel.

Recovery of methyl alcohol from Pyroligneous acid :

Pyroligneous acid is a homogeneous mixture of methyl alcohol, acetone and acetic acid. Hence, methyl alcohol can be recovered from the pyroligneous acid by removing acetone and acetic acid. The process of removal involves the following steps.

(i) **Removal of acetic acid :** First pyroligneous acid is treated with milk of lime [$Ca(OH)_2$]. Acetic acid when reacts with milk of lime produces calcium salt of acetic acid.

$$2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2\,Ca + H_2O$$

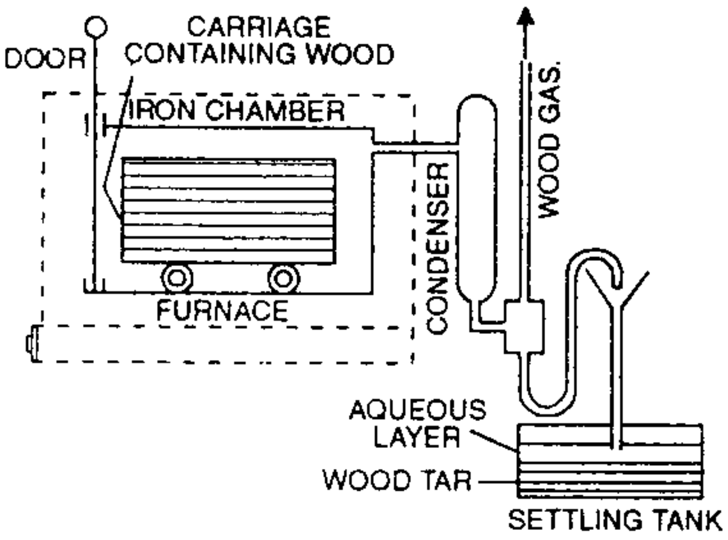


Fig. 21.1 Destructive distillation of wood.

Now the mixture contain, CH_3OH, CH_3COCH_3 and $(CH_3COO)_2\,Ca$. When the mixture is subjected to distillation, methyl alcohol and acetone distil over, leaving calcium acetate in the retort.

When calcium acetate is treated with conc. H_2SO_4, again acetic acid is obtained.

$$(CH_3COO)_2\,Ca + H_2SO_4 \longrightarrow 2CH_3COOH + CaSO_4\,.$$

(ii) **Removal of acetone :** The mixture of methyl alcohol and acetone, obtained is then subjected to fractional distillation. At 329K acetone is collected and at 338 K methyl alcohol is collected.

(ii) Purification of methyl alcohol :

The fraction collected at 338K contains mostly methyl alcohol along with small amount of acetone and water. First, it is treated with anhydrous $CaCl_2$. Methyl alcohol forms a crystalline compound, $CaCl_2\ 4CH_3OH$. Then it is filtered. The crystalline compound is then decomposed by boiling with water to give free alcohol. Finally, it is dried over quick lime and redistilled to obtain pure methyl alcohol.

15.10.1 Uses :

Methyl alcohol is used :

1. As a solvent for fats, oils, paints and varnishes.
2. To denature (to make it unfit for drinking) rectified spirit.
3. As antifreeze for automobile radiators.
4. In the manufacture of formaldehyde, methyl chloride, dimethyl sulphate etc.
5. In the preparation of artificial perfumes like methyl salicylate and methyl anthranilate.
6. In the preparation of dyes, perspex, plastics etc.

15.10.2 Tests :

1. When heated with salicylic acid and concentrated sulphuric acid, methyl alcohol forms methyl salicylate, which has characteristic smell of oil of winter-green or Amritanjan like smell (distinction from ethyl alcohol.)
2. Does not form iodoform when warmed with iodine and alkali (distinction from ethyl alcohol).

15.11 MANUFACTURE OF ETHYL ALCOHOL FROM STARCHY MATERIALS :

Ethyl alcohol is commercially prepared from starchy grains, such as potatoes, barley, rice, wheat etc. by **fermentation** process. The process of fermentation is defined as the slow decomposition of complex organic compounds into simpler compounds by the catalytic action of enzyme.

The different steps involved in this process are,

1. Saccharification

2. Alcoholic fermentation

and 3. Distillation

1. **Saccharification :** Starch can not be directly fermented by yeast. First starch is converted to maltose, which on fermentation produces alcohol. The process of conversion of starch into maltose is called saccharification and it involves the following steps.

(i) **Preparation of malt extract :** First the moist barley seeds are allowed to germinate in dark at the 15^{0}C for a few days. After germination is complete, the temperature is raised to 60^{0}C in order to check the growth. After that, the seeds are crushed and extracted with water. This extract is called **malt extract,** which contain the enzyme **diastase**.

(ii) **Mashing :** The starchy materials like potato, rice etc. are heated in steam under pressure. Then a paste like starchy material is obtained, which is called **mash**.

(iii) **Hydrolysis :** When malt extract is added to mash at 50^{0}C, hydrolysis takes place and maltose results.

$$2\,(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{diastase}} n\,C_{12}H_{22}O_{11}$$

Starch (mash) (Maltose)

2. **Alcoholic Fermentation :** The solution of maltose obtained after saccharification is cooled to 30^{0}C. Then to it yeast is added. Yeast contains enzymes like, **maltase** and **zymase**. Here, the maltase, converts maltose into glucose and zymase converts glucose into ethyl alcohol.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{present in yeast}]{\text{Maltase}} 2\,C_6H_{12}O_6$$

(Maltose) (glucose)

$$C_6H_{12}O_6 + H_2O \xrightarrow[\text{present in yeast}]{\text{zymase}} 2\,C_2H_5OH + 2\,CO_2\uparrow$$

(Glucose) (ethyl alcohol)

3. **Distillation :** The fermented liquor obtained above contains 4.8% of ethyl alcohol along with water and impurities. Then pure ethyl alcohol can be prepared by fractional distillation.

15.11.1 Uses of Ethyl alcohol :

1. Ethyl alcohol is used in the preparation of various alcoholic beverages for drinking purpose.
2. In the manufacture of pharmaceutical preparation and medicines.
3. In the manufacture of varnishes, polishes, dyes, perfumes, transparent soaps, fruit essences etc.
4. In the manufacture of chloroform, ether, chloral, iodoform etc.
5. As a solvent in the laboratory.
6. As a fuel in the form of alcohol.
7. For preservation of dead animals in biological laboratories.

15.11.2 Tests :

(i) **Iodoform test :** When a few drops of alcohol are warmed with iodine and potassium hydroxide, yellow precipitate of iodoform with characteristic smell is obtained.

(ii) **Fruity odour test :** When alcohol is heated gently with sodium acetate and sulphuric acid, a characteristic fruity odour of ethyl acetate is obtained.

(iii) Heat the alcohol with potassium dichromate and dilute sulphuric acid in test tube, a characteristic smell of acetaldehyde is obtained.

15.11.3 Distinction of Ethanol form Methanol :

Ethanol can be distinguished from methanol by the following:

(i) Ethanol give iodoform test, whereas methanol does not.

(ii) Ethanol give acetic acid on oxidation while methanol gives formic acid. Formic acid being a powerful reducing agent is readily distinguished from acetic acid.

[Formic acid reduces ammoniacal $AgNO_3$ solution to metallic silver.]

15.11.4 Iodoform reaction :

Principle : A compund containing CH_3CO group or a compound which on oxidation produces another compound containing CH_3CO group responds to iodoform reaction.

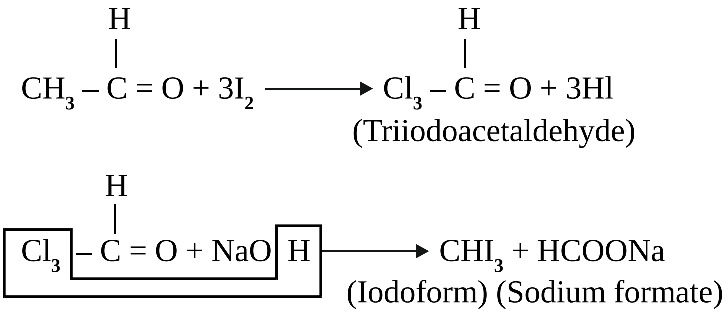
Example : CH_3CHO, CH_3COCH_3 etc., respond to iodoform reaction. C_2H_5OH on oxidation produces CH_3CHO and therefore responds to iodoform reaction. But CH_3OH on oxidation produces HCHO which does not contain CH_3CO group. Hence CH_3OH does not respond to iodoform reaction.

Statement : When warmed with iodine and alkali C_2H_5OH produces yellow solid iodoform with a characteristic odour.

Reaction :

$$CH_3CH_2OH + I_2 \longrightarrow CH_3CHO + 2HI$$

Ethyl alcohol Acetaldehyde



$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O+3I_2 \longrightarrow Cl_3-\overset{\overset{\displaystyle H}{|}}{C}=O+3Hl$$

(Triiodoacetaldehyde)

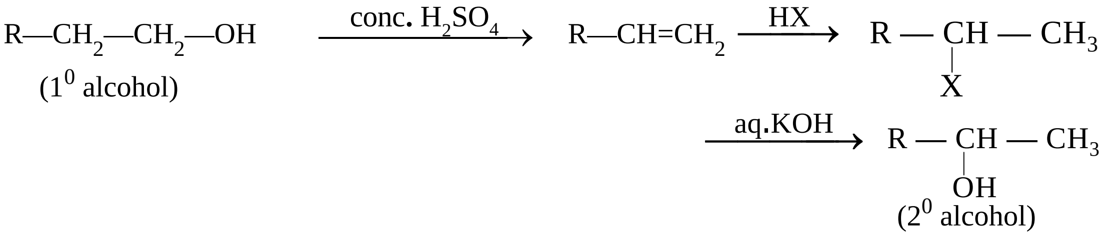
$$\boxed{Cl_3}-\overset{\overset{\displaystyle H}{|}}{C}=O+NaO\boxed{H} \longrightarrow CHI_3+HCOONa$$

(Iodoform) (Sodium formate)

(b) Ethyl alcohol similarly reacts with Cl_2 and alkali or with bleaching powder to give chloroform.

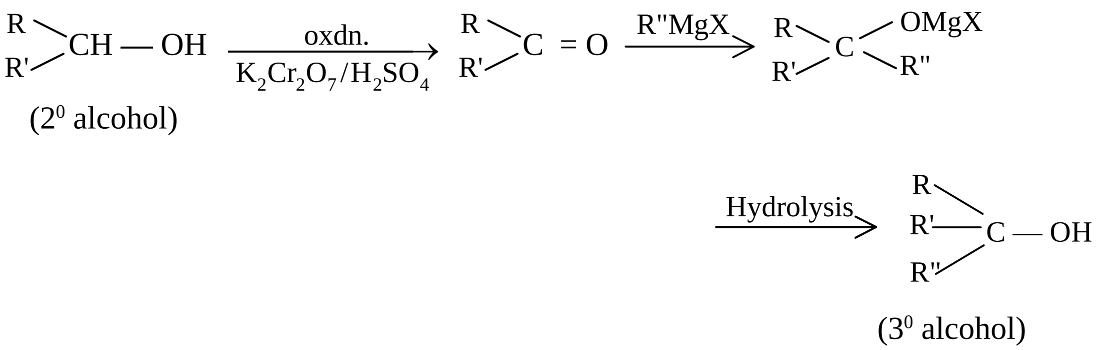
15.12 SOME IMPORTANT CONVERSIONS :

1. Primary to secondary alcohol :

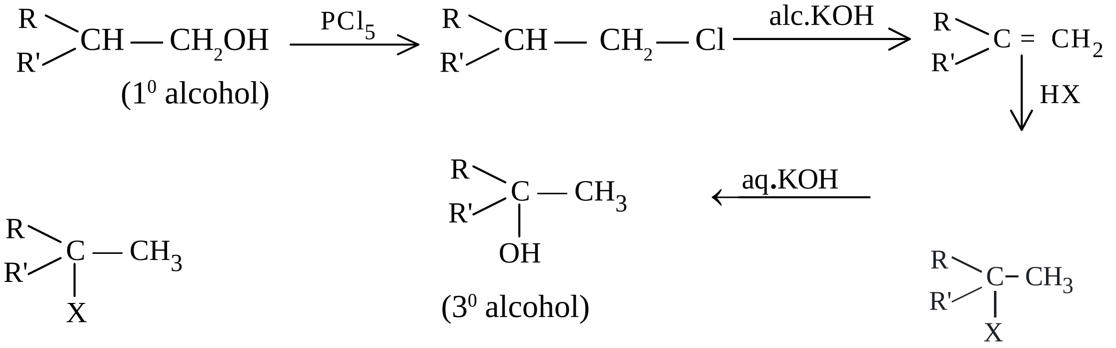


$$\underset{(1^0\text{ alcohol})}{R\text{—}CH_2\text{—}CH_2\text{—}OH} \xrightarrow{\text{conc. }H_2SO_4} R\text{—}CH{=}CH_2 \xrightarrow{HX} R-\underset{X}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{aq.KOH}} \underset{(2^0\text{ alcohol})}{R-\underset{OH}{\underset{|}{CH}}-CH_3}$$

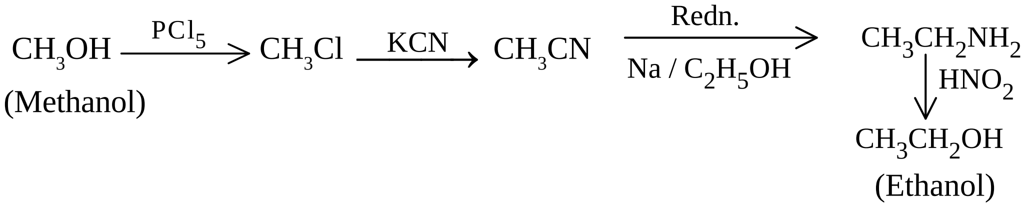
2. Secondary to tertiary alcohol :



3. Primary to tertiary alcohol :

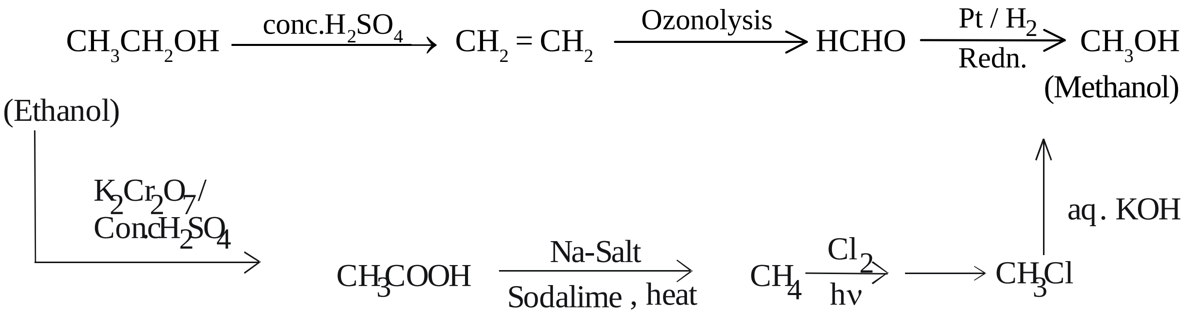


4. Methyl alcohol to ethyl alcohol :



$$\begin{tikzcd}
\underset{(\text{Methanol})}{CH_3OH} \arrow[r, "PCl_5"] & CH_3Cl \arrow[r, "KCN"] & CH_3CN \arrow[r, "\text{Redn.}", "Na / C_2H_5OH"'] & CH_3CH_2NH_2 \arrow[d, "HNO_2"] \\
 & & & \underset{(\text{Ethanol})}{CH_3CH_2OH}
\end{tikzcd}$$

5. Ethyl alcohol to methyl alcohol :



$$\begin{tikzcd}
\underset{(\text{Ethanol})}{CH_3CH_2OH} \arrow[r, "\text{conc.}H_2SO_4"] \arrow[dr, "K_2Cr_2O_7/\text{ Conc}H_2SO_4"'] & CH_2 = CH_2 \arrow[r, "\text{Ozonolysis}"] & HCHO \arrow[r, "Pt / H_2", "\text{Redn.}"'] & \underset{(\text{Methanol})}{CH_3OH} \\
 & CH_3COOH \arrow[r, "\text{Na-Salt}", "\text{Sodalime , heat}"'] & CH_4 \arrow[r, "Cl_2", "h\nu"'] & CH_3Cl \arrow[u, "\text{aq. KOH}"']
\end{tikzcd}$$

CHAPTER (15) AT A GLANCE

Monohydric alcohols

General Formula : R — OH, $C_nH_{2n+2}O$

Methods of Preparation :

1. *From alkyl halides*

$R-X + KOH_{aq} \longrightarrow R-OH + KX$

$R-X + AgOH \longrightarrow R-OH + AgX$

2. *From esters : Hydrolysis*

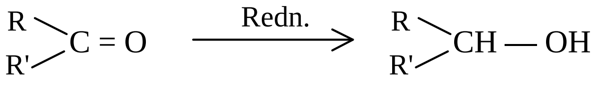
$RCOOR' + KOH_{aq} \longrightarrow RCOOK + R'OH$

3. *From aldehydes and Ketones :*

Reduction by Na/C_2H_5OH or $H_2/Pt,Pd$ or Ni, or

$NaBH_4$ or $LiAlH_4$

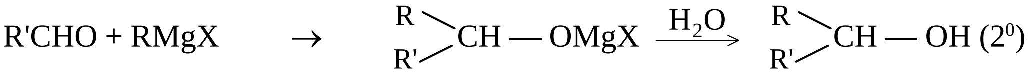
$R-CHO \xrightarrow{\text{Redn.}} R\,CH_2OH$



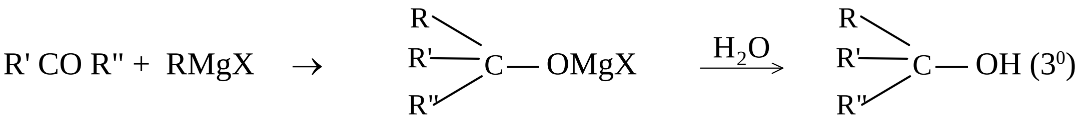
$$\begin{matrix}R\\R'\end{matrix}\!\!>C=O \xrightarrow{\text{Redn.}} \begin{matrix}R\\R'\end{matrix}\!\!>CH-OH$$

4. *From Grignard reagent :*

$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH\ (1^0)$



$$R'CHO + RMgX \rightarrow \begin{matrix}R\\R'\end{matrix}\!\!>CH-OMgX \xrightarrow{H_2O} \begin{matrix}R\\R'\end{matrix}\!\!>CH-OH\ (2^0)$$



$$R'COR'' + RMgX \rightarrow \begin{matrix}R\\R'\\R''\end{matrix}\!\!>C-OMgX \xrightarrow{H_2O} \begin{matrix}R\\R'\\R''\end{matrix}\!\!>C-OH\ (3^0)$$

5. *From aliphatic primary amines :*

$R-NH_2 + HNO_2 \rightarrow R-OH + N_2 + H_2O$ (except CH_3NH_2)

Reactions :

(a) Reactions involving H— atom of — OH group

Reactivity : $1^0 > 2^0 > 3^0$

(i) With alkali metals like Na or K or Li

$2R-OH + 2Na \rightarrow R-ONa + H_2$ (Exothermic)

(ii) With carboxylic acids, acid chlorides

$$R — OH + HOOCR' \xrightarrow{conc.H_2SO_4} R'COOR + H_2O$$

$$R — OH + ClOCR' \rightarrow R'COOR + HCl$$

(b) Reactions involving —OH group

Reactivity : $3^0 > 2^0 > 1^0$

(i) *With mineral acids :* HI > HBr > HCl in reactivity

$$R — OH + HCl\ (dry) \xrightarrow{anh.\ ZnCl_2} R — Cl + H_2O$$

$$R — OH + HBr \xrightarrow{heat} R — Br + H_2O$$

$$R — OH + HI \xrightarrow{heat} R — I + H_2O$$

(ii) *With PCl_5, PCl_3, PBr_3, PI_3, or $SOCl_2$*

$$R — OH + PCl_5 \rightarrow R — Cl + POCl_3 + HCl$$

$$3R — OH + PBr_3(P_4+Br_2) \rightarrow 3R — Br + H_3PO_3$$

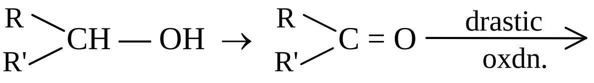
$$3R — OH + PI_3(P_4+ I_2) \rightarrow 3R — I + H_3PO_3$$

$$R — OH + SOCI_2 \rightarrow R — Cl + SO_2 +HCl$$

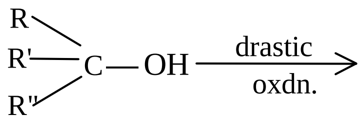
(c) Reactions involving the entire molecule

(i) *Oxidation :* Acidified $K_2Cr_2O_7$, or alkaline $KMnO_4$ or acidified $KMnO_4$

$$R — CH_2 — OH \rightarrow RCHO \rightarrow RCOOH$$



Mixture of acids with less no. of C — atoms.

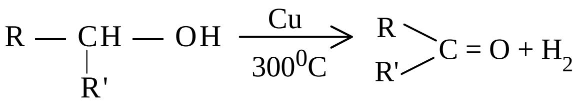


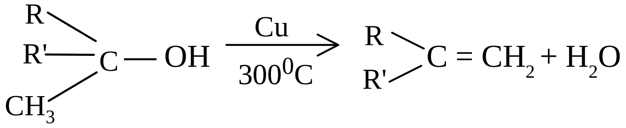
Mixture of ketone and acid with less no.of C– atoms.

(ii) *Catalytic dehydrogenation.*

Alcohol vapour passed over reduced Cu at 300^0C

$$RCH_2OH \xrightarrow[300^0C]{Cu} RCHO + H_2$$





Distinction between 1^0, 2^0 and 3^0 alcohols

1. *Oxidation :* 1^0 alcohol $\xrightarrow[H_2SO_4]{K_2Cr_2O_7}$ Aldehyde and acid (with same no. of C - atoms)

   2^0 alcohol → ketones $\xrightarrow{\text{oxdn}}$ Acids (with less no. of C - atoms)
   3^0 alcohol → ketones and acids (with less no. of C - atoms)

2. *Catalytic dehydrogenation :* Reduced Cu at 300^0C

1^0 alcohol	→	Aldehyde
2^0 alcohol	→	Ketone
3^0 alcohol	→	Olefin

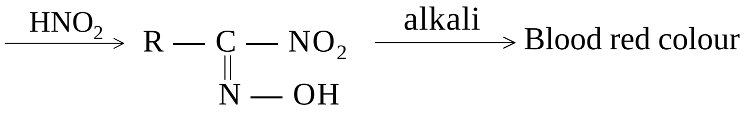
3. *Lucas Test : Conc. HCl in presence of anhydrous $ZnCl_2$*

3^0 alcohol	→	Immediate turbidity
2^0 alcohol	→	Turbidity after 5 minutes
1^0 alcohol	→	Turbidity on heating only. (No turbidity in cold)

4. *Victor Meyer's Test :*

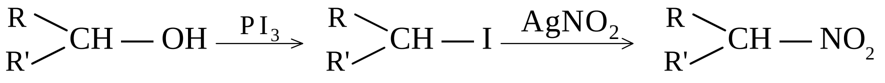
$$R - CH_2 - OH \xrightarrow{PI_3} R - CH_2 - I \xrightarrow{AgNO_2} R - CH_2 - NO_2$$

(1^0 alcohol)

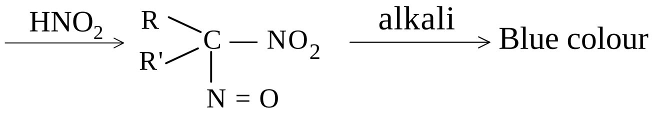


$$\xrightarrow{HNO_2} R - \underset{\underset{N - OH}{\|}}{C} - NO_2 \xrightarrow{\text{alkali}} \text{Blood red colour}$$

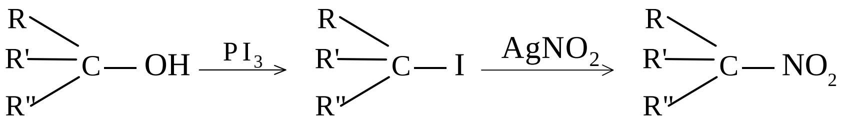
(Nitrolic acid)



(2^0 alcohol)



(Pseudonitrol)

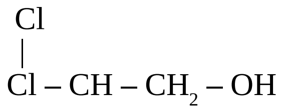


$$\xrightarrow{HNO_2} \text{No reaction} \xrightarrow{\text{alkali}} \text{No colour}$$

QUESTIONS

Very short Anser Questions (1 mark each)

1. What class of compounds have a molecular formula $C_nH_{2n+2}O$
2. How does metallic sodium react with methyl alcohol ?
3. Methyl alcohol does not give iodoform test, why ?
4. Complete the following equation.
   $CH_3CH_2OH + SOCl_2 \rightarrow$ —— + —— + HCl $\uparrow$
5. What is the name of the functional group in CH_3CH_2OH
6. Give the IUPAC name of a compound which is isomeric with diethyl ether.
7. How ethyl alcohol can be converted to acetic acid ?
8. Ethanol is obtained by —— reaction of acetaldehyde. (oxidation, reduction, polymerisation)
9. What is the IUPAC name of the following compound ?



$$Cl-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_2-OH$$

10. What alcohol is present in pyroligneous acid ?
11. Write the structural formula of Butan - 2 - ol.
12. What organic compound is obtained when ethyl bromide reacts with aqueous NaOH solution.
13. What happens when ethanol is treated with conc. H_2SO_4 at 443 K ?
14. Complet the following equation- $C_2H_5OH + CH_3COCl \rightarrow$ —— + ——

Short answer Questions (2 marks each) :

1. Give equation for the reaction of ethyl bromide with aqueous and alcoholic KOH. Name the products giving equation for the reaction.
2. A primary alcohol is treated with PCl_5. Name the products giving equation for the reaction.
3. Isopropyl alcohol is oxidised with $K_2Cr_2O_7$ and H_2SO_4. Write the products giving equation.
4. Give one chemical test to distinguish between CH_3CH_2OH and CH_3OH.
5. Write with equation, what happens when ethyl alocohol vapour is passed over reduced copper at 300^0C.
6. In the preparation of aldehydes from primary alcohol on oxidation, aldehyde is distilled out. Why is it so ?
7. Complete the following reactions assigning structures of A, B, and C

$$CH_3CH_2OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow[H_2O]{H^+} C.$$

8. (a) How do you distinguish between a primary and secondary alcohol ?

   (b) How different classes of alcohols can be tested by Lucas test ?

9. What happens when acetic acid reacts with ethyl alcohol in presence of conc.H_2SO_4 ?

10. How do you distinguish between primary and secondary alcohol by catalytic dehydrogenation ?

11. How is maltose converted to ethyl alcohol by fermentation process.

12. Write the equations for the oxidation of aliphatic primary, secondary and tertiary alcohols.

13. How many structural isomers of alcohol with molecular formula C_4H_9OH are possible ? Give their IUPAC name. Which one of the isomers is optically active ?

14. Alcohols are freely soluble in water but alkyl halides are not, explain why ?

15. Boiling points of alcohols are higher than the corresponding alkane. Give reasons.

16. Arrange the following in order of their increasing reactivity towards Lucas reagent. Butan-2-ol, 2-methylpropan - 2-ol, Butan-1-ol.

17. (a) Write a method of conversion of methyl alcohol to ethyl alcohol. Give equation.

    (b) How will you convert ethyl alcohol to methyl alcohol?

18. How can you get ethyl chloride from ethyl alcohol ? Give equation.

19. What happens when acetyl chloride is treated with ethyl alcohol ? Give equation.

20. How will you convert ethanol to 2-hydroxy -3-butenoic acid.

21. Molecular mass of ethanol and dimethyl ether is the same. Explain why ethanol is a liquid at room temperature and dimethyl ether is a gas.

22. Explain why sodium can not be preserved in alcohol.

23. A neutral liquid A on treatment with Lucas reagent produces a compound B, which upon treatment with alc.KOH yields a compound C. The compound C decolourises bromine water and upon ozonolysis forms only methanal. Deduce the structures of A,B and C and explain the reactions.

24. (a) Identify A, B, C and D in the following sequence of reactions :

$$\begin{tikzcd}
C_2H_5OH \arrow[r, "K_2Cr_2O_7", "H_2SO_4"'] & A \arrow[r, "{[O]}"] & B \arrow[r, "NH_3"] & C \arrow[d, "heat"] \\
 & & & D
\end{tikzcd}$$

    (b) Identify A & B in the following reaction :

$$A \xrightarrow[573\ K]{Cu} B \xrightarrow[H_2O/Zn]{O_3} CH_2O + CH_3COCH_3$$

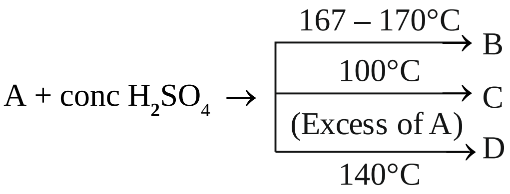
25. An organic compound A ($C_4H_{10}O$) reacts with HI giving a compound B (C_4H_9I), which on reduction gives n-butane. On oxidation 'A' gives a compound C (C_4H_8O) and then an acid D ($C_4H_8O_2$).

    Deduce the structures of A, B, C and D and mention their IUPAC names.

26. Describe a method to distinguish a primary alcohol from a secondary alcohol.

Short Answer type Question (3 marks each) :

1. How are the alkanols classified ? Give an example of each class with their IUPAC names.
2. These are three unlabelled bottles containing methyl alcohol, ethyl alcohol and diethyl ether. How will you identify each of them?
3. How will you convert methanol to ethanol and vice versa?
4. How many different isomeric alcohols having molecular formula $C_4H_{10}O$ are possible? Name them. How will you diffentiate them?
5. Ethyl alcohol (A) reacts with conc. H_2SO_4 at differnt temperatures to give different products B, C and D.



    Name the compounds B, C and D.

6. An organic compound gives hydrogen on reacting with sodium metal. It also gives iodoform test and forms an aldehyde of molecular formula C_2H_4O on oxidation with acidified dichromate. Name the compound and give the equation of these reactions.
7. How will you convert ethanol to iodoform and chloroform?
8. Exaplain why :
    (i) Ethanol is less acidic than phenol.
    (ii) Though dimethyl ether and ethanol are isomers, still the dimethyl ether is a gas and ethonol is a liquid at room temperature.

Long Answer type Question (7 marks each) :

1. Describe two methods of preparation of alcohol. Write its reaction with (a) PCl_5 (b) CH_3COOH. How would you prepare methyl alcohol from it.
2. How ethyl alcohol can be converted to methyl alcohol and vice-versa ? Write any two reactions by which ethyl alcohol is distinguished from methyl alcohol.

3. Write notes on any two of the following :

   (a) Victor Meyer's method for distinction of different classes of alcohols ?

   (b) How methyl alcohol can be converted into ethyl alcohol and vice versa ?

4. What are primary, secondary and tertiary alcohol ? How can you obtain each one of these by using a Grignard reagent ? What happens when these classes of alcohols are (i) oxidised with $K_2Cr_2O_7$ and H_2SO_4 (ii) passed over heated copper.

5. What is fermentation ? How is ethanol obtained commercially by fermentation of starch ? What happens when ethanol reacts with (i) sodium metal (ii) copper at 300^0C (iii) ethanoic acid and (iv) Red phosphorus and I_2.

6. How can you distinglish between primary, secondary and tertiary alcohols by oxidation method ?

   Write the principle of manufacture of ethyl alcohol from starchy materials.

   How can you prepare (a) ethyl alcohol from methyl alcohol (b) methyl alcohol from ethyl alcohol.

7. Describe the principle of manufacture of methyl alcohol from wood. Give the conversion of methyl alcohol to ethyl alcohol and vice versa.

8. How would you distinguish between 1^0, 2^0 & 3^0 alcohols by

   (a) Oxidation method (b) Catalytic dehydrogenation method ?

9. How do you classify different types of monohydric alcohols? Distinguish the different classes of alcohols by Victor Meyer's method. How can methyl alcohol be converted to ethyl alcohol.

MULTIPLE CHOICE QUESTIONS WITH ANSWERS

1. Which of the following compound is optically active ?

   (a) CH_3CH_2OH (b) $CH_2OH . CHOH . CH_2OH$

   (c) $CH_3CHOH\ C_2H_5$ (d) CCl_2F_2

2. An isomer of ethanol is

   (a) methanol (b) dimethyl ether

   (c) acetone (d) diethyl ether

3. How many optically active stereoisomers are possible for Butane - 2, 3-diol ?

   (a) 1 (b) 3

   (c) 4 (d) 2

4. Butan - 1 - ol and Butan - 2 - ol are

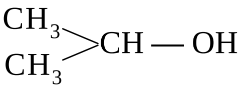
(a) Chain isomers (b) Functional isomers

(c) Position isomers (d) Optical isomers

5. Which of the following compound is called carbinol ?

(a) CH_3OH (b) C_2H_5OH

(c) C_3H_7OH (d)



$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH — OH$

6. How many structural isomers of alcohol with molecular formula C_4H_9OH are possible ?

(a) 5 (b) 7

(c) 3 (d) 6

7. Which one is primary alcohol ?

(a) Butan – 2 – ol (b) Propan – 2 – ol

(c) Butan – 1 – ol (d) 2,3 dimethylhexan – 4 – ol

8. Action of nitrous acid on ethyl amine gives

(a) C_2H_6 (b) C_2H_5OH

(c) C_2H_5OH and C_2H_4 (d) C_2H_5OH and NH_3

9. Ethyl alcohol is heated with conc. H_2SO_4 . The product formed is,

(a) $CH_3CO\,.\,OC_2H_5$ (b) C_2H_6

(c) C_2H_4 (d) C_2H_2

10. The compound 'B' formed in the following sequence of reaction .

$CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{alc.KOH} B$, is

(a) Propyne (b) Propanal

(c) Propane (d) Propene

11. The compound which reacts fastest with Lucas reagent at room temperature is,

(a) Butan – 1 – ol (b) Butan – 2 – ol

(c) 2–methylpropan –2–ol (d) 2 – methylpropan – 1 – ol

12. Primary and Secondary alcohols on action of reduced copper gives

(a) aldehydes and ketones respectively (b) ketones and aldehydes respectively

(c) only ketones (d) only aldehydes.

13. When vapours of an alcohol are passed over hot reduced copper, alcohol is converted into alkene, the alcohol is

(a) Primary (b) Secondary

(c) Tertiary (d) None of these

14. Dehydrogenation of 2 – butanol gives

(a) 2 – butene (b) butanone

(c) Butanal (d) None of these

15. Which of the following compounds is oxidised to prepare methyl ethyl ketone ?

(a) Propan – 2 – ol (b) Butan – 1 – ol

(c) Butan – 2 – ol (d) t – butyl alcohol

16. Which of the following gives secondary alcohol

(a) $CH_3CO\,CH_3$ (b) CH_3CHO

(c) CH_3COOH (d) $CH_3—O—CH_3$

17. Fermentation of starch solution to ethyl alcohol does not require

(a) diastase (b) invertase

(c) maltase (d) zymase

18. The boiling point of ethyl alcohol should be less than

(a) Propane (b) dimethyl ether

(c) Formic acid (d) None of the above

19. A low boiling alcohol failed to give the Lucas test, but gives a positive iodoform test. The alcohol is :

(a) Methanol (b) Propan – 1 – ol

(c) Butan – 1 – ol (d) Ethanol

20. A compound 'X' having molecular formula $C_4H_{10}O$ when oxidised produces an acid having formula $C_4H_8O_2$. The compound 'X' is

(a) secondary alcohol (b) primary alcohol

(c) tertiary alcohol (d) an ether

21. The enzyme which can catalyse the conversion of glucose to ethanol is

(a) Zymase (b) Invertase

(c) Maltase (d) Diastase

22. An organic compound 'X' on treatment with acidified $K_2Cr_2O_7$ gives a compound 'Y' which reacts with I_2 and sodium carbonate to form tri-iodomethane. The compound 'X' is,

(a) CH_3OH (b) CH_3COCH_3

(c) CH_3CHO (d) $CH_3CH(OH)\,CH_3$

23. The compound which does not respond to iodoform test is,

(a) CH_3OH (b) CH_3CHO

(c) CH_3COCH_3 (d) C_2H_5OH

24. The reaction between alcohol and carboxylic acid is called.

(a) Hydrolysis (b) Saponification

(c) Esterification (d) Hydrogenation

25. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is,

(a) C – C (b) C – O

(c) C – H (d) O – H

26. Which one of the following is an isomer of diethyl ether ?

(a) $(CH_3)_3$ C – OH (b) $(CH_3)_2$ CH OH

(c) C_3H_7 OH (d) $(C_2H_5)_2$ CH OH

27. 1 – Chlorobutane on reaction with alcoholic potash gives,

(a) But – 1 – ene (b) Bnt – 2 – ene

(c) Butan – 1 – ol (d) Butan – 2 – ol

28. Ethyl alcohol is miscible with water in all proportions. It is because,

(a) It is acidic in nature (b) It dissociates in water

(c) It is basic in nature (d) It forms hydrogen bonding with water

29. Which of the following compounds has the highest boiling point ?

(a) $CH_3CH_2CH_3$ (b) CH_3CH_2OH

(c) CH_3Cl (d) CH_3—O — CH_3

30. Which of the following compounds has the lowest boiling point ?

(a) n – butyl alcohol (b) sec – butyl alcohol

(c) tert – butyl alcohol (d) 2 – methyl propan – 1 – ol

31. Hydrogen bonding is maximum in,

(a) Ethyl chloride (b) Ethanol

(c) Diethyl ether (d) Triethylamine

32. Which one of the following is soluble in water ?

(a) CCl_4 (b) C_6H_6

(c) CH_3OH (d) CH_4

33. Hydrochloric acid reacts fastest with,

(a) Propan – 1 – ol (b) Propan – 2 – ol

(c) 2 – methyl propan – 1 – ol (d) 2 – methylpropan – 2 – ol

34. A mixture of water and alcohol can be separated by

(a) evaporation (b) decantation

(c) distillation (d) filtration

35. Secondary alcohol on oxidation gives,

(a) Ketone (b) Aldehyde

(c) Ether (d) Hydrocarbon

ANSWERS

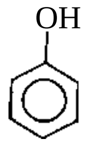
1. c 2. b 3. d 4. c 5. a 6. b 7. c
8. b 9. c 10. d 11. c 12. a 13. c 14. b
15. c 16. a 17. b 18. c 19. d 20. b 21. a
22. d 23. a 24. c 25. d 26. a 27. a 28. d
29. b 30. c 31. b 32. c 33. d 34. c 35. a

* * *

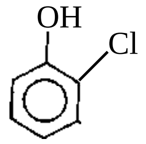
CHAPTER - 16

PHENOLS

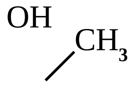
Phenols are compounds with the general formula Ar – OH, where Ar is phenyl, substituted phenyl or other aryl groups. Phenols differ from alcohol in having –OH group directly attached to an aromatic ring. Phenols are often considered as derivatives of benzene, the simplest member of the family being **phenol**. Methyl phenols are called **cresols**. Phenols are classified as mono–, di – or trihydric phenols according as they contain one, two or three –OH groups attached directly to aromatic nucleus. Monohydroxy benzene is called phenol.



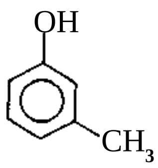
Phenol



o-Chlorophenol



o- cresol



m-cresol

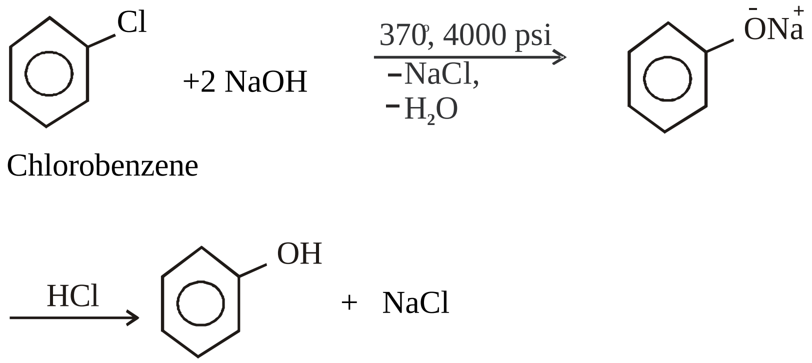
p-cresol

The functional group in phenol is phenolic –OH group. Phenol is also known as **carbolic acid**.

16.1 METHODS OF PREPARATION :

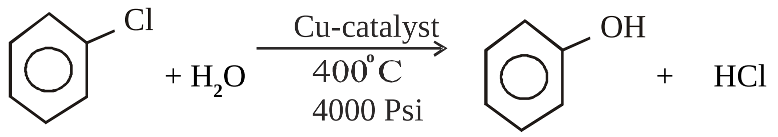
The following general methods of synthesis of phenols are used for their preparation.

(i) Hydrolysis of Aryl halides : Aryl halides yield phenol when hydrolysed with aqueous sodium hydroxide. For example chlorobenzene is hydrolysed to phenol at high temperture and pressure by NaOH. The is known as **Dow's Process**.



Chlorobenzene

The above hydrolysis can also be effected by water in presence of copper as catalyst at 400^0C temperature and 4000 psi pressure.



(ii) Alkali fusion of sodium arenesulphonates

Simple phenols are prepared conveniently by fusing sodium arenesulphonates with sodium hydroxide at about 300°C. A mixture of sodium phenoxide and sodium sulphite is produced from which phenol is liberated by acidification.

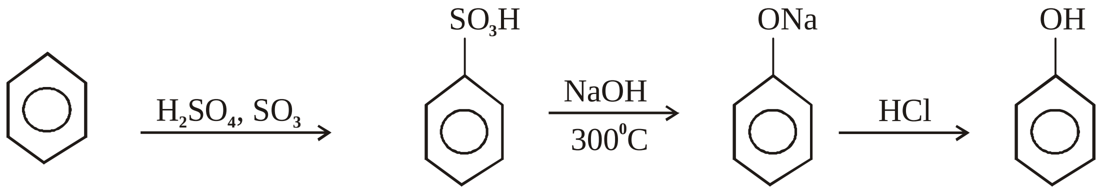
$Ar-SO_3^-Na^+ \quad + \quad 2\,NaOH \longrightarrow ArO^-Na^+ \quad + \quad Na_2SO_3 + H_2O$

Sodium arenesulphonate Sodium phenoxide

$Ar\,O^-Na^+ + HCl \longrightarrow ArOH + NaCl$

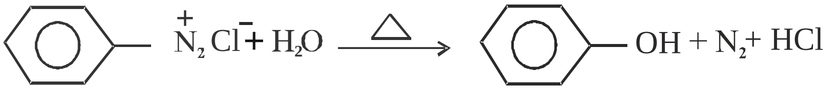
For example, phenol is synthesised from benzene as follows.

Benzene sulphonic acid can be obtained from benzene upon sulphonation with fuming sulphuric acid. Benzene sulphonic acid is fused with NaOH at 300° C. A mixture of sodium phenoxide and sodium sulphite is produced which upon acidification yields phenol.



Benzene sulphonic acid Sod. phenoxide Phenol

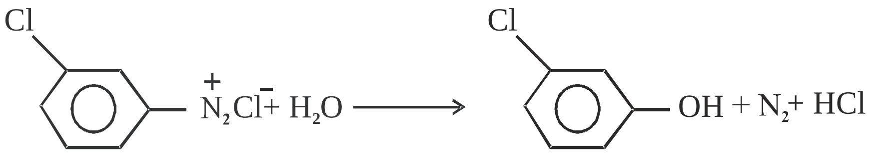
(iii) **From diazonium salts :** When an aqueous solution of aryldiazonium chloride is heated, the diazonium group is replaced by –OH group and phenol is formed.



benzene diazonium chloride Phenol

This reaction is usually conducted in an acid medium to prevent the coupling of phenol with unreacted diazonium salt.

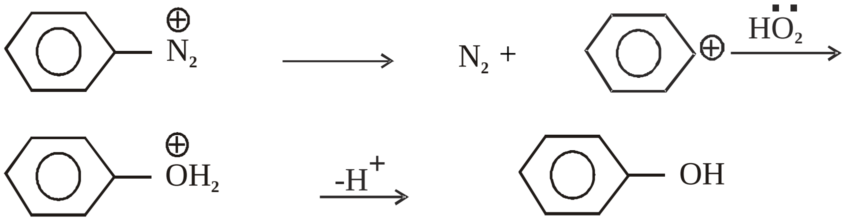
Application : The method is useful for the preparation of *m*-chlorophenol which cannot be prepared by electrophilic chlorination of phenol.



m-chlorophenol

Mechanism :

In this process, water H_2O is the nucleophile.

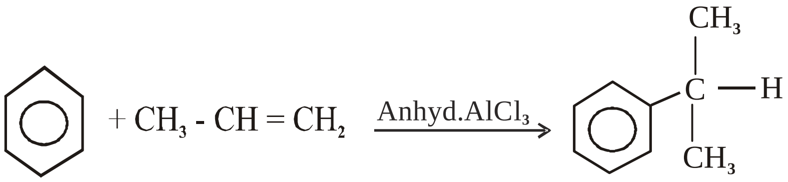


Phenol

(iv) **From Cumene :** The most recent commercial synthesis of phenol is from cumene, isopropyl benzene. The process involves two steps.

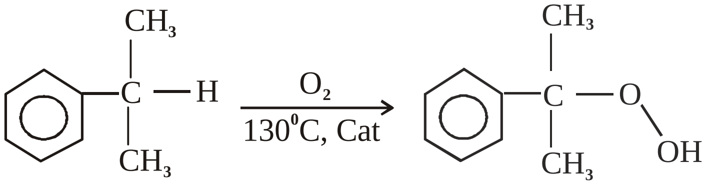
(a) Preparation of cumene (isopropylbenzne)

Cumene is synthsised from benzene and propylene, both derived from petroleum by Friedel-Crafts Reaction.

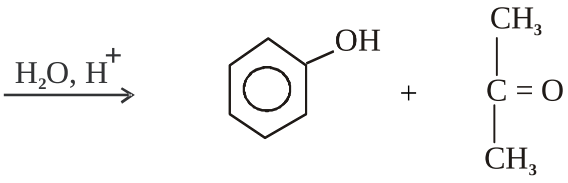


Cumene

(b) Cumene is then oxidised by aerial oxygen at 130^{0}C in the presence of metal catalyst (or initiator) to cumene hydroperoxide, which is converted by aqueous acid (dilute sulphuric acid) into phenol and acetone. This process is of great importance as it provides the principal source for the commercial preparation of phenol and acetone.



Cumene hydroperoxide



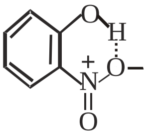
Acetone

16.2 PROPERTIES :

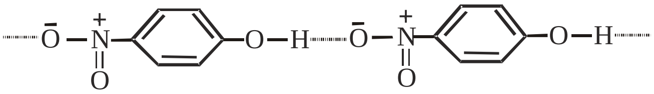
(A) Physical properties :

The simplest phenols are either liquids or low melting solids having quite high boiling points. Phenol is a colourless crystalline solid with low melting point (43^0C), fairly soluble in water ($9g/100gH_2O$). The solubility is due to the hydrogen bonding with water molecules. Most of the other phenols are insoluble in water, but soluble in organic solvents. Phenol has a characteristic odour and is very poisonous.

While comparing the physical properties of nitrophenols, it has been observed that *o*-nitrophenol has low m.p. and is volatile. It has low solubility ($0.2g/100g\ H_2O$ at 25^0C). This is because of the proximity of –OH and – NO_2 group in the benzene ring for which they form *intramolecular hydrogen bonding*.



Intramolecular hydrogen bonding in *o*-nitrophenol



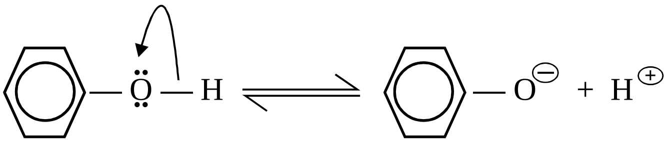
Intermolecular hydrogenbonding in *p*-nitrophenol.

This gives rise to a stable six membered ring (chelation) and can not form associated molecules. Therefore, it exists as a single unit and it has low m.p, low b,p, low solubility and high volatility compared to its other isomers. On the other hand, due to the greater distance between –OH and –NO_2 group in *m*-nitrophenol and *p*-nitrophenol, such intramolecular hydrogen bonding is not possible. They form associated molecules by intermolecular hydrogen bonding and have higher m.p., b.p than *o*-isomer. They are much less volatile than *o*-isomer. Their solubility is more in water because they form hydrogen bonding with water. This is the reason why *o*-nitrophenol is steamvolatile and it can be separated from *m*-and *p*-isomers by steam distillation.

(B) Chemical properties

ACIDITY OF PHENOLS

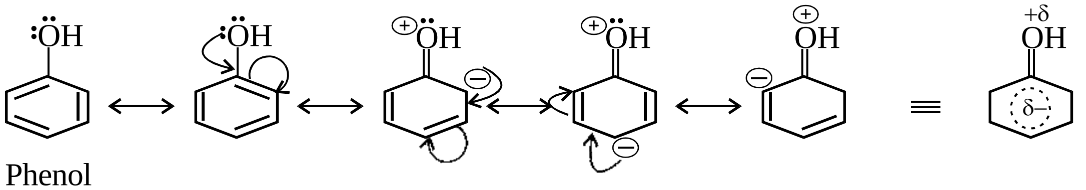
The acidity of a compound is defined as its ability to release a proton in presence of water. Phenols when dissolves in water form phenoxide ions, hence acidic in nature.



Phenol Phenoxide ion

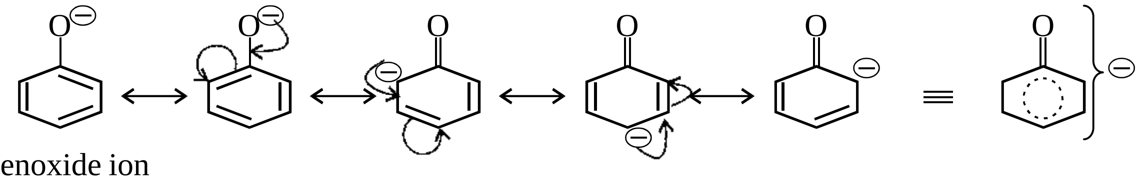
Phenols are weaker acids than carboxylic acid. This is evident from their K values. (K for phenol is 10^{-10} and that of CH_3COOH is 10^{-5})

Both phenol and phenoxide ion exhibit resonance. A number of resonating structures can be written for both phenol and phenoxide ion.



Phenol

I II III IV V Resonance hybrid



Phenoxide ion

I II III IV V Resonance hybrid

In case of phenol forms I and II are the two Kekule resonating structures. In forms III, IV and V, there is charge separation. Since separation of charge costs energy, these forms are known as high energy forms and they do not contribute to the resonance hybrid.

One the otherhand, in case of phenoxide ion structures I to V contribute to the resonance hybrid. In this case there is no charge separation, rather there is charge delocalisation. Thus resonance hybrid of phenoxide ion is more stable than that of phenol. The equilibrium between the two is represented as

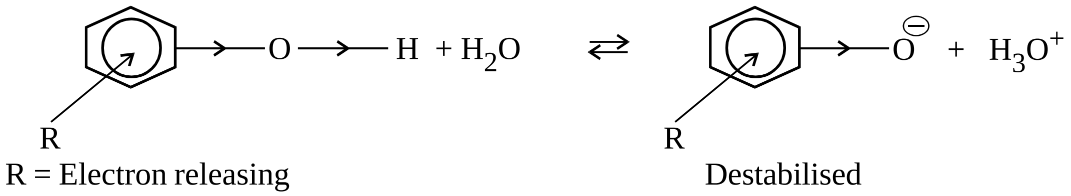
Phenol
(resonance hybrid structure)

Phenoxide ion
(resonance hybrid structure)

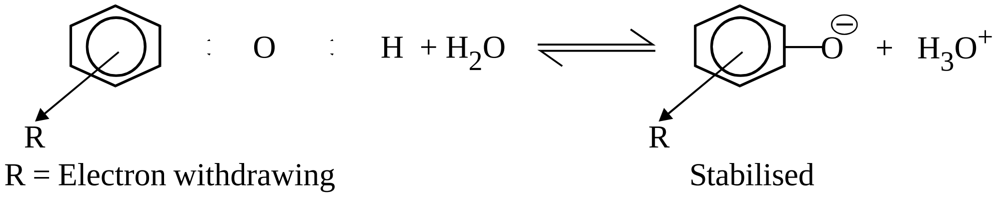
Since the phenoxide ion is more resonance stablised thean phenol itself, the equilibrium is shifted towards right releasing H^+ ions. This explains why phenol behaves as a weak acid.

Effect of substituents on acidity of phenol

Presence of electron releasing group decreases the acidity of phenol whereas presence of electron withdrawing group enhances the acidity. When an electron releasing group (say CH_3 – , C_2H_5 – etc) present the –ve charge on the phenoxide ion gets intensified. As a result the anion becomes less sable and acidity of phenol decreases.



On the other hand, when an electron withdrawing group (-X, -CHO, - NO_2, - COOH etc.) is present, electrons from the ring system are withdrawn and that results in greater dispersal of the –ve charge of the phenoxide anion. The phenoxide ion thus gets stabilised and acidity of phenol is enhanced.

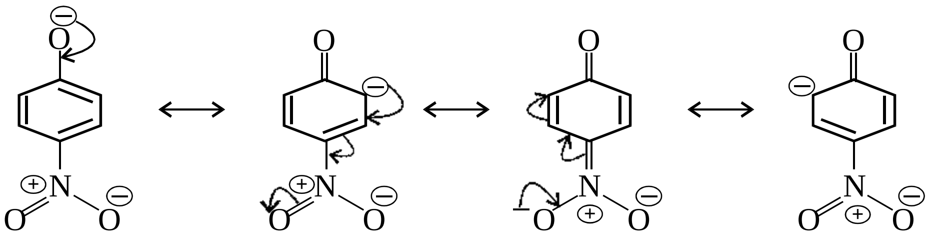


Thus, methyl phenols are less acidic than phenol whereas chlorophenols are more acidic than phenol.

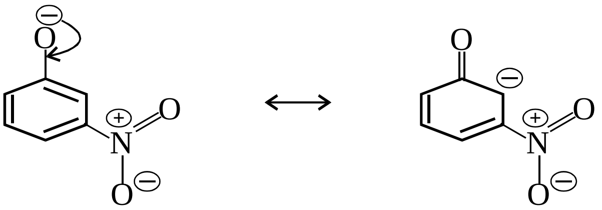
Again, since inductive effect of a substituent operates only through the covalent bonds, its intensity gets reduced with increase in distance from the reaction centre.

In case of isomeric chlorophenols, the K_a *ortho* > K_a *meta* >K_a *para.*

However in all the cases the acidity of phenol can not be explained by taking only inductive effect into account. For example, among nitrophenols meta isomer is the weakest acid whereas among alky1 phenols, meta isomer is the strongest. This can be explained by taking resonance effect into account along wit inductive effect. The phenoxide anion gets stabilized by the dispersal of –ve charge.

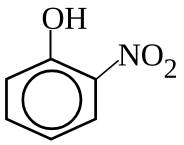


The lower acidity of metanitro isomer is due to the fact that m-nitro phenoxide anion is stabilised by inductive effect only and no resonance effect is operating due to absence of conjugate system.



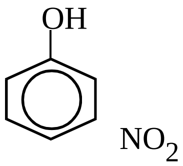
(no further resonance with NO_2 group)

The values of K_a for three nitrophenols are metioned below.



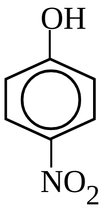
o-nitrophenol

$K_a = 600 \times 10^{-10}$



m-nitrophenol

$K_a = 50 \times 10^{-10}$

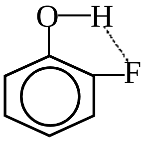


p-nitrophenol

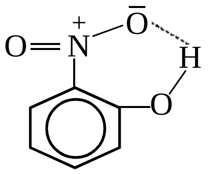
$K_a = 690 \times 10^{-10}$

It is important to mention here that presence of electron withdrawing group at the ortho position in some cases makes the phenol weaker than the para isomer. For example, *o* –fluorophenol and *o*-nitrophenol are weaker than their corresponding *p*-isomers.

The reason behind this is that the acidic hydrogen is involved in intramolecular hydrogen bonding with fluorine and oxygen.



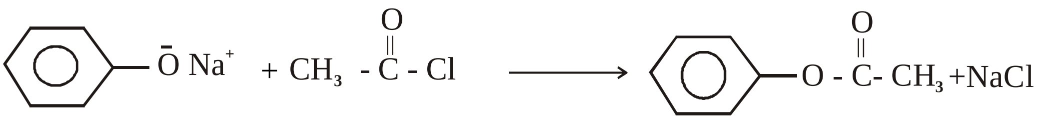
o - Fluorophenol



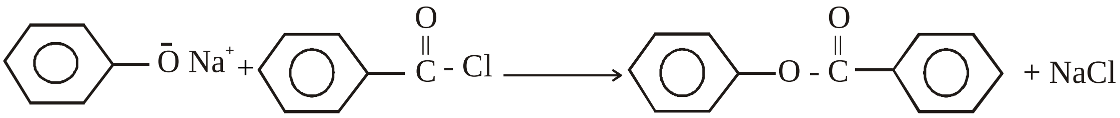
o - Nitrophenol

(a) Esterification Reaction : Phenol reacts with acid chlorides or acid anhydrides in presence of aqueous alkali solution to give phenyl esters. The alkali first forms the phenoxide ion which then reacts with the acid chloride to form the ester.

(Phenol) (Sodium phenoxide)



(Sodium phenoxide) (Phenyl acetate)



(Sodium phenoxide) (Phenyl benzoate)

Introduction of acetyl group ($CH_3CO–$) in phenol forming an ester is called **acetylation**. Acetylation of salicylic acid gives acetyl salicylic acid (**aspirin**).

COOH COOH

OH + $(CH_3CO)_2O \xrightarrow{H^+}$ $OCOCH_3$ + CH_3COOH

Salicylic acid Acetylsalicylic acid (aspirin)

When a mixture of phenol and benzoylchloride is shaken with excess of aqueous NaOH, the ester phenyl benzoate is formed and this is called **benzoylation** and the reaction is known as **Schotten Baumann reaction**.

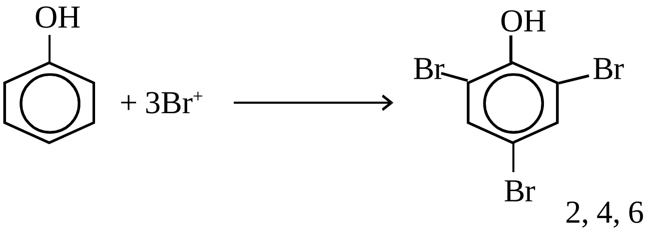
(b) Electrophilic Substitution reactions

As already discussed the –OH group activates the benzene ring to electrophlic attack and is ortho paradirecting.

(i) HALOGENATION :

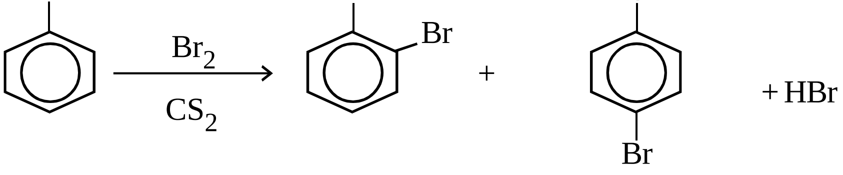
When treated with excess of aqueous bromine solution phenol produces 2, 4, 6–tribromophenol. Br^+ is the electrophile.

$$Br_2 + Br_2 \rightleftharpoons Br^+ + Br_3^-$$



2, 4, 6 tribromophenol

But when phenol is treated with limited amount (1 mole) of Br_2 dissolved in less polar solvents like $CHCl_3$, CS_2 etc monobromophenols are produced

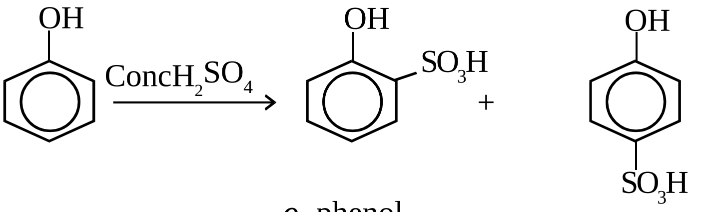


o-bromo phenol *p*- bromophenol

(ii) SULPHONATION

When treated with conc H_2SO_4 phenol is readily sulphonated to produce o-phenol sulphonic acid and *p*–phenol sulphonic acid. $\overset{(+)}{SO_3}H$ is the electrophile.

$$2H_2SO_4 \rightleftharpoons \overset{+}{S}O_3H + HSO_4^{-} + H_2O$$



o- phenol sulphonicacid

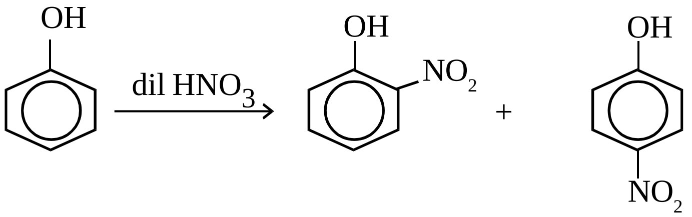
p- phenol sulphonicacid

At room temperature, ortho isomer is the main product while at 100^{0}c, para isomer is the main product.

(iii) NITRATION

Phenols undergo nitration when treated with dilute HNO_3. The products are o-nitro phenol and p-nitro phenol. NO_2^+ is the electrophile.

$$2HNO_3 \rightleftharpoons NO_2^{+} + NO_3^{-} + H_2O$$



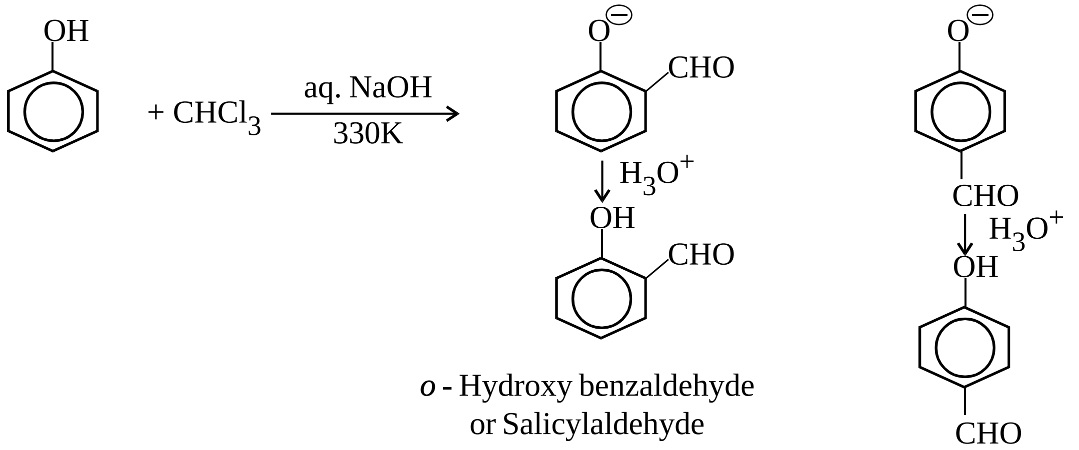
o-nitro phenol

p- nitrophenol

(iv) Reimer – Tiemann Reaction

When phenol is treated with chloroform ($CHCl_3$) is presence of aq. NaOH at 330 K, to –CHO group is introduced mainly in the ortho position to –OH group. The process is known *formylation.* Though ortho isomer is the major product, yet para isomer is obtained to a smaller extent. Bot the isomers can be separated by steam distillation after acidification. This reaction is known as **Reimer - Tiemann Reaction**.

Reimer Tiemann reaction :



o - Hydroxy benzaldehyde
or Salicylaldehyde
(Major product)

p - Hydroxy benzaldehyde
(Minor product)

Mechanism:

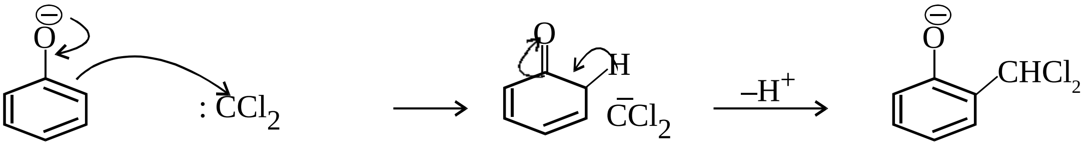
Formation of very reactive intermediate dichlorocarbene by the action of base on chloroform.

$$\overset{\ominus}{OH} + H-CCl_3 \xrightarrow{-H_2O} :\overset{-}{C}Cl_3 \xrightarrow{-Cl^-} :CCl_2$$

Dichlorocarbene.
(electrophile)

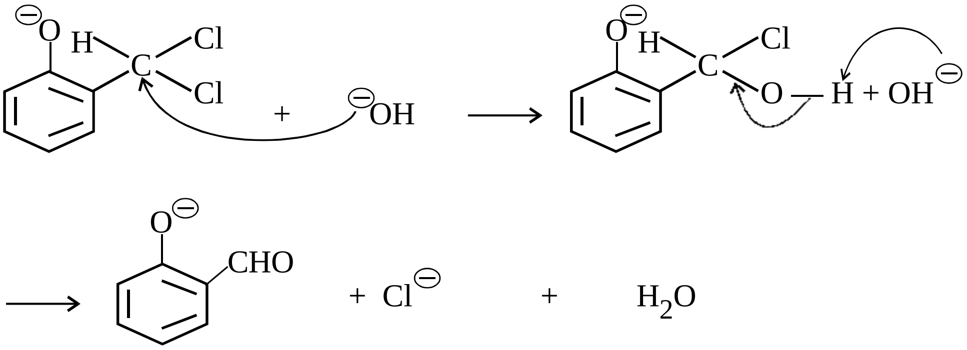
The carbon atom in $:CCl_2$ contains only six valence electrons, thus acts as an electrophile in aromatic substitution.

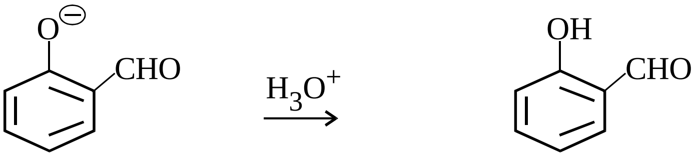
Electrophilic substitution in benzene ring



o - (dichloromethyl)
phenoxide ion.

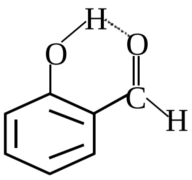
Hydrolysis and acidification :





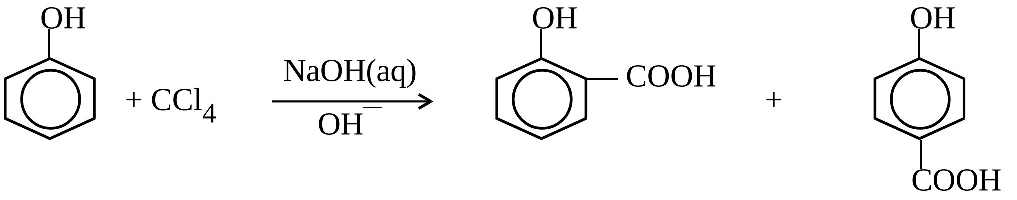
Salicylaldehyde
(Major product)

Ortho-isomer predominates due to its greater stability resulting from intramolecular hydrogen bonding which is shown below.



Intramolecular hydrogen bonding in salicylaldehyde

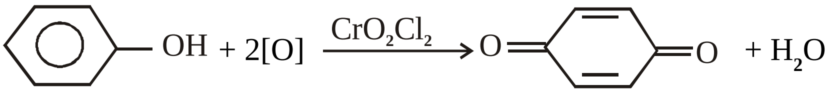
If CCl_4 is taken in place of $CHCl_3$, salicylic acid is obtained instead of salicylaldehyde



o - Hydroxy benzoic acid
or Salicylic acid
(Major product)

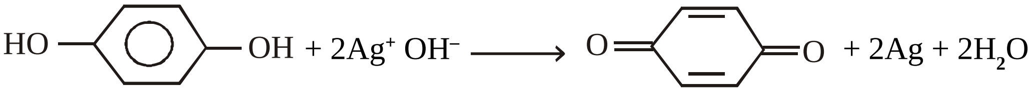
p - Hydroxy benzoic acid
(Minor product)

(c) Oxidation : Phenol is easily oxidised without disruption of its carbon skeleton to form *p*-benzoquinone.



Phenol *p*-Benzoquinone

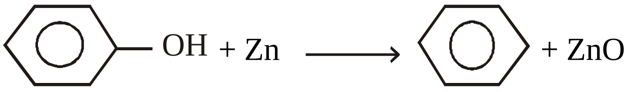
Similarly, hydroquinone on oxidation with silver salts yield *p*-benzoquinone



Hydroquinone *p*- benzoquinone

The oxidation of phenols is explained by the fact that the presence of – OH group in the ring furnishes electrons to the ring which thus renders susceptible to oxidation especially in alkaline medium.

(d) Reaction with zinc dust : When a phenol is distilled with zinc dust, the –OH group is replaced by a hydrogen atom. Zinc removes the oxygen of the phenolic group as zinc oxide, to yield the parent hydrocarbon.



Phenol Benzene

CHAPTER (16) AT A GLANCE

1. **Dow's Process :** Chlorobenzene reacts with aqueous sodium hydroxide under high temperature and pressure to form phenol.
2. Acidity of phenol is due to resonance stabilisation of phenoxide ion.
3. Presence of electron releasing group decreases the acidity of phenol whereas presence of electron withdrawing group increases its acidity.
4. **Reimer-Tiemann reaction :** Phenol is treated with chloroform in presence of aq.NaOH at 330 K forming salicylaldehyde upon acidification.
5. Phenolic –OH group can be acetylated or benzoylated forming esters. **Benzoylation process** is known as **Schotten Baumann** reaction.

QUESTIONS

A. Very Short Answer Type (1 Mark)

(i) Phenol is acidic because ________ is more stable than ________.

(ii) Formylation of phenol is ________ reaction

(iii) Benzene can be obtained by heating phenol with ________

(iv) Phenol reacts with ________ to give *o*-and *p*- Nitrophenols.

(v) Phenol gives ________ with CrO_2Cl_2

B. Short Answer Type (2 Marks)

1. Complete the following reaction giving the names of the products :

   (i) $C_6H_5OH + \text{Zn dust} \longrightarrow$

   (ii) $C_6H_5OH + Br_2 \text{ water} \longrightarrow$

   (iii) $C_6H_5OH + HNO_3 \xrightarrow{\text{conc } H_2SO_4}$

   (iv) $C_6H_5OH + HNO_2 \longrightarrow$

   (v) $C_6H_5OH + CHCl_3 + KOH \longrightarrow$

   (vi) $C_6H_5OH + CCl_4 + KOH \longrightarrow$

   (vii) $C_6H_5OH + CO_2 \longrightarrow$

2. Give the resonating structures for phenol and phenolate ion.

3. How will you distinguish between ethyl alcohol and phenol.

4. Give the reaction of phenol with benzene diazonium chloride.

5. How will you obtain the following form phenol.

   (i) Salicyladehyde (ii) Benzene

   (iii) Picric acid (iv) Nitrophenol

   (v) Salicylic acid (vi) p-cresol

C. Short answer type (3 Marks)

(i) What is Dow's process ?

(ii) What is Reimer-Tiemann reaction ?

(iii) Why phenol is acidic, but alcohol is neutral. Explain.

(iv) How can you carry nitration is phenol ? Explain.

(v) What is the directive influence of phenolic group ? Explain with reasons.

D. Long answer type (7 marks each)

(i) How is phenol prepared from benzene ? How can phenol be converted to (i) benzene (ii) salicylaldehyde.

(ii) How can phenol be prepared from cumene ? Convert phenol to aspirin and *p*-benzoquinone.

(iii) Starting from benzene diazonium chloride, how can phenol be prepared ? How can phenol be sulphonated ? What is the electrophile for this reaction ?

E. Multiple choice type questions

(i) When phenol is distilled with zinc dust, the product is

(a) toluene (b) benzene (c) xylene (d) none of these

(ii) Phenol is less acidic than

(a) acetic acid (b) *p*-methoxy phenol (c) *o*-nitrophenol (d) ethanol

(iii) Electrophilic substitution in phenol takes place at

(a) *o*-position only (b) *p*-position only (c) *o*- and *p*-position (d) *m*-position only.

(iv) Sodium salt of benzene sulphonic acid on fusion with caustic soda gives

(a) C_6H_5OH (b) C_6H_6 (c) C_6H_5COOH (d) none of these

(v) Phenol gives salicylaldehyde on heating with $CHCl_3$ & NaOH. The reaction is called

(a) Cannizzaro's reaction (b) Claisen condensation

(c) Reimer-Tiemann reaction (d) Perkin reaction

(vi) Chlorobenzene on heating with NaOH at high temperature and pressure gives

(a) Phenol (b) Benzaldehyde (c) Benzene (d) Chlorophenol

(vii) Phenol reacts with Br_2 in CCl_4 at low temperature to give

(a) *m*-bromophenol (b) *o*- and *p*-bromophenol (c) *p*-bromophenol (d) 2,4,6-tribromophenol

(viii) Intramolecular hydrogen bonding is found in

(a) phenol (b) *o*-nitrophenol (c) *p*-nitrophenol (d) *m*-nitrophenol

(ix) *p*-nitrophenol is stronger acid than phenol because nitrogroup is

(a) Electron donating (b) Electron withdrawing (c) Acidic (d) Basic

(x) The most convenient method of removing a phenolic group from a compound is by

(a) reduction with Sn + HCl

(b) heating strongly

(c) heating strongly with copper

(d) distilling with zinc dust.

ANSWER

A. (i) phenoxide, phenol (ii) Riemer-Tiemann (iii) Zinc (iv) dil HNO_3 (v) *p*-benzoquinone

D. (i) b (ii) a (iii) c (iv) a (v) c (vi) a (vii) b (viii) b (ix) b (x) d.

❑❑❑

CHAPTER - 17

ETHERS

The general formula of ethers is R–O–R'. Both the alkyl or aryl groups (R/Ar or R'/Ar') may be same or different. The functional group of ether is 'OR / OAr' (alkoxy/aryloxy).

17.1 CLASSIFICATION OF ETHERS :

Ethers are classified as simple or **symmetrical ethers** if the two alkyl or aryl groups attached to the oxygen atom are the same, and mixed or **unsymmetrical ethers** if the two groups are different.

(a) **Simple or Symmetrical ethers :**

$CH_3—O—CH_3$	$CH_3CH_2—O—CH_2CH_3$	$C_6H_5—O—C_6H_5$
Dimethyl ether	Diethyl ether	Diphenyl ether

(b) **Mixed or Unsymmetrical ethers :**

$CH_3—O—CH_2CH_3$	$C_6H_5—O—CH_3$	$C_6H_5—O—CH_2C_6H_5$
Ethyl methyl ether	Methyl phenyl ether	Benzyl phenyl ether

1. **Aliphatic ethers** in which R and R' are both alkyl groups. For example,

$CH_3—O—CH_3$	$CH_3—O—CH_2CH_3$	$CH_3CH_2—O—CH_2CH_3$
Demethyl ether	Ethyl methyl ether	Diethyl ether

2. **Aromatic ethers** in which either one or both R and R' are aryl groups.

Aromatic ethers are further subdivided into phenolic ethers and diaryl ethers.

Ethers in which one of the groups is aryl while the other is alkyl are called **phenolic ethers or alky aryl ethers**. On the other hand, ethers in which both the groups are aryl are called **diaryl ethers**. For example,

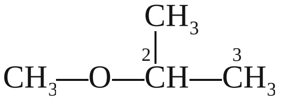
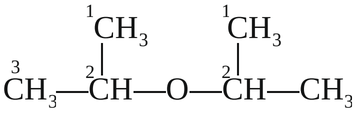
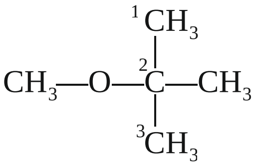
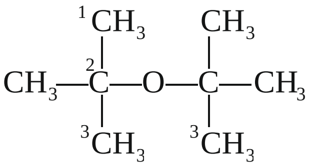
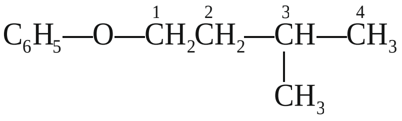
$C_6H_5—O—CH_3$	$C_6H_5—O—C_6H_5$
Methyl phenyl ether	Diphenyl ether
(Phenolic ether)	*(Diaryl ether)*

17.2 NOMENCLATURE OF ETHERS :

1. Common system : The common names of ethers are derived by naming the two akyl or aryl groups linked to the oxygen atom as separate words in alphabetical orders and adding the word ether. In case of symmentrical ethers, the prefix *di* is used before the name of the alkyl or aryl group.

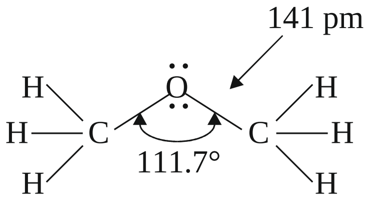
2. IUPAC system : The IUPAC system, ethers are named as **alkoxyalkanes**. The ethereal oxygen is taken with the smaller group and forms a part of the alkoxy group while the larger group is considered to be a part of the alkane or arene.

The common and IUPAC names of some ithers are given below:

Structural formula	**Common name**	**IUPAC name**
$CH_3—O—CH_3$	Dimethyl ether	Methoxymethane
$CH_3—O—CH_2CH_3$	Ethyl methyl ether	Methoxyethane
$CH_3CH_2—O—CH_2CH_3$	Diethyl ether	Ethoxyethane
$CH_3—O—CH_2CH_3CH$	Methl *n*-proply ether	1-Methoxypropane
 $CH_3—O—\overset{CH_3}{\overset{\vert}{\overset{2}{C}H}}—\overset{3}{C}H_3$	Isopropyl methyl ether	2-Methoxypropane
 $\overset{3}{C}H_3—\overset{^1CH_3}{\overset{\vert}{\overset{2}{C}H}}—O—\overset{^1CH_3}{\overset{\vert}{\overset{2}{C}H}}—CH_3$	Di-isopropyl ether	2-(2-Propoxy) propane
 $CH_3—O—\underset{^3CH_3}{\underset{\vert}{\overset{^1CH_3}{\overset{\vert}{\overset{2}{C}}}}}—CH_3$	*tert*-Butyl methyl ether	2-Methoxy-2-methylpropane
 $CH_3—\underset{^3CH_3}{\underset{\vert}{\overset{^1CH_3}{\overset{\vert}{\overset{2}{C}}}}}—O—\underset{^3CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}—CH_3$	Di-*tert*-Butyl ether	2-(2-Methyl-2 propoxy) methylphropane
$C_6H_5—O—CH_3$	Methyl phenyl ether (Anisole)	Methoxy benzene
$C_6H_5—O—CH_2CH_3$	Ethyl phenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5—O—C_6H_5$	Diphenyl ether or phenyl ether	Phenoxy benzene
$C_6H_5—O—(CH_2)_6CH_3$	n-Heptyl phenyl ether	1-Phenoxyheptane
 $C_6H_5—O—\overset{1}{C}H_2\overset{2}{C}H_2—\underset{CH_3}{\underset{\vert}{\overset{3}{C}H}}—\overset{4}{C}H_3$	Isopentyl phenyl ether	(3-Methyl-1-butoxy) benzene
$CH_3O—CH_2—CH_2—OCH_3$		1, 2 Dimethoxyethane

17.3 STRUCTURE OF ETHERS :

Since ether is regarded as dialkyl or diaryl dervatives of water, its structure is similar to that of water. The structure is V-shaped with bond angle ≈110°. Bond angle in ether is greater than water (105°) due to the repulsion between two bulky alkyl groups. As size of R increases, bond angle also increases.



Methoxymethane

17.4 PREPARATION OF ETHERS :

Ethers are prepared by the following general methods.

1. From alcohols : (a) Simple or symmetrical ethers are prepared by heating a primary alcohol with concentrated sulphuric acid at lower temperature (413K). Two molecules of the alcohol eliminate a molecule of water (dehydration) to form ether.

$$R—\boxed{O—H + H}—O—R \xrightarrow[413k]{H_2SO_4} R—O—R + H_2O$$

$$2CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} CH_3CH_2—O—CH_2CH_3$$

Ethyl alcohol Diethyl ether

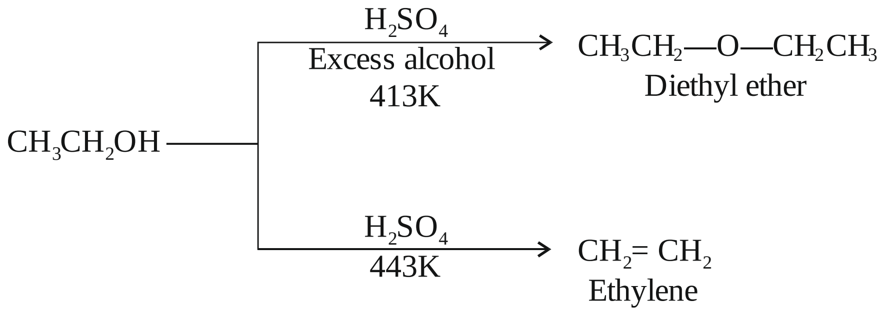
Diethyle ether boils at 35°C (308K) and is removed from the reaction mixture as it is produced.

Note : (a) The success of this method depends upon the careful control of experimental conditions. The **temperature is kept at 413K** and **alcohol is used in excess**. If the temperature is increased to 443K, the product from ethyl alcohol is mainly **ethylene** which is produced by intramolecular dehydration of alcohol.

$$CH_3CH_2OH \xrightarrow[413K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethyl alcohol Ethylene

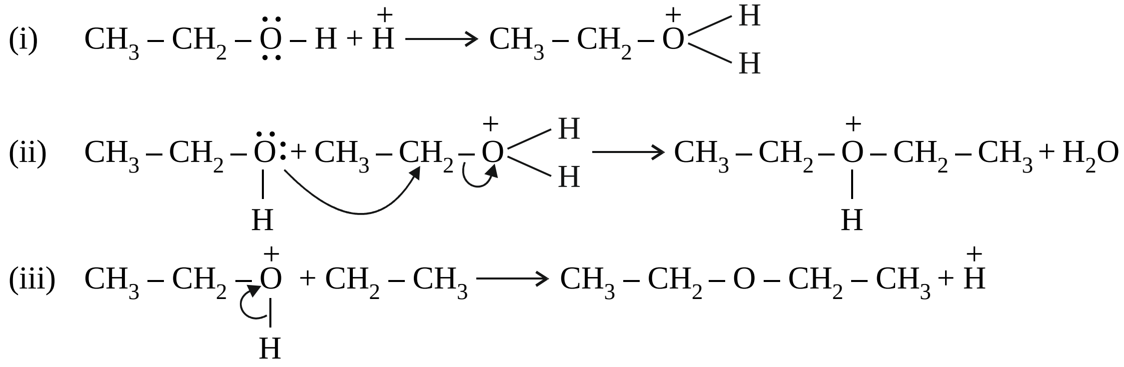
Remember, lower temperature favours the formation of ether whereas higher temperature favours the formation of alkene.



$$CH_3CH_2OH \xrightarrow[\text{413K}]{H_2SO_4,\ \text{Excess alcohol}} \underset{\text{Diethyl ether}}{CH_3CH_2—O—CH_2CH_3}$$

$$CH_3CH_2OH \xrightarrow[\text{443K}]{H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}\,CH_2}$$

Mechanism : The formation of ether is a bimolecular reaction (S_N2) involving the attack of the alcohol on a protonated alcohol molecule. It consists of the following three steps:

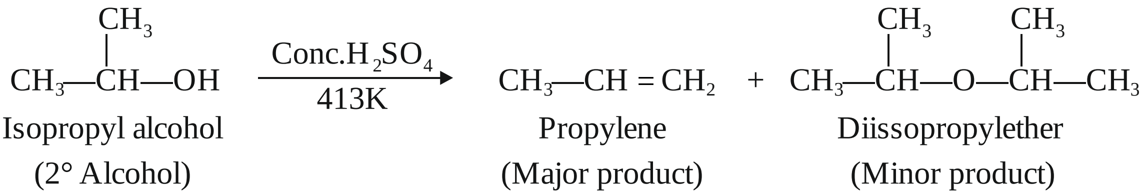


(i) $CH_3 - CH_2 - \ddot{\underset{\cdot\cdot}{O}} - H + \overset{+}{H} \longrightarrow CH_3 - CH_2 - \overset{+}{O}\!\begin{smallmatrix} H \\ H \end{smallmatrix}$

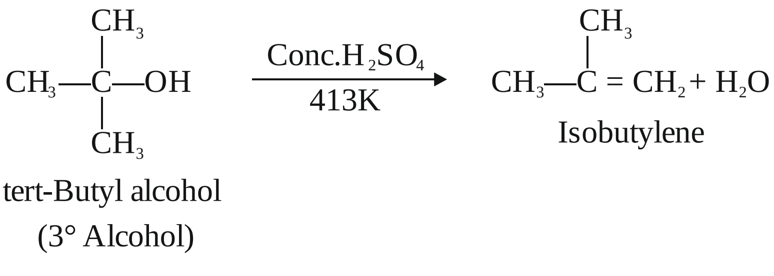
(ii) $CH_3 - CH_2 - \underset{\displaystyle H}{\underset{|}{\ddot{O}}}\!: + CH_3 - CH_2 - \overset{+}{O}\!\begin{smallmatrix} H \\ H \end{smallmatrix} \longrightarrow CH_3 - CH_2 - \underset{\displaystyle H}{\underset{|}{\overset{+}{O}}} - CH_2 - CH_3 + H_2O$

(iii) $CH_3 - CH_2 - \underset{\displaystyle H}{\underset{|}{\overset{+}{O}}} + CH_2 - CH_3 \longrightarrow CH_3 - CH_2 - O - CH_2 - CH_3 + \overset{+}{H}$

(b) Mostly primary alcohols and to some extent secondary alcohols, react with sulphuric acid at 413K to form ethers, tertiary alcohols almost exclusively yield alkenes.



$$\underset{\substack{\text{Isopropyl alcohol} \\ (2^\circ\ \text{Alcohol})}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}H—OH} \xrightarrow[\text{413K}]{\text{Conc.}H_2SO_4} \underset{\substack{\text{Propylene} \\ \text{(Major product)}}}{CH_3—CH = CH_2} + \underset{\substack{\text{Diissopropylether} \\ \text{(Minor product)}}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}H—O—\overset{\overset{\displaystyle CH_3}{|}}{C}H—CH_3}$$



$$\underset{\substack{\text{tert-Butyl alcohol} \\ (3^\circ\ \text{Alcohol})}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—OH} \xrightarrow[\text{413K}]{\text{Conc.}H_2SO_4} \underset{\text{Isobutylene}}{CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} + H_2O$$

The order of dehydration of alcohols leading to the formation of ethers follows the sequence: primary > secondary > tertiary.

Limitations : (i)This methods is generally not suitable for the preparation of unsymmetrical ethers since complex mixtures are obtained. For example.

$$ROH + R'OH \xrightarrow{\text{Conc.}H_2SO_4} ROR + ROR' + R'OR'$$

(ii) This method of preparation of ethers is suitable only for industries since reaction conditions must be carefully controlled.

In place of H_2SO_4 other protonic acid like H_3PO_4 can also be used for preparation of ethers.

(c) **Catalytic dehydration** of alcohols to ether can also be achieved by passing the vapours of an alcohol over heated alumina at 513–523K. For example,

$$\underset{\text{Ethyl alcohol (two molecules)}}{CH_3CH_2\text{—}\boxed{OH + H}\text{—}OCH_2CH_3} \xrightarrow[513\text{–}523K]{Al_2O_3} \underset{\text{Diethyl ether}}{CH_3CH_2\text{—}O\text{—}CH_2CH_3} + H_2O$$

(d) **By the action of diazomethane on alcohols**. Methyl ethers can also be prepared by the action of diazomethane (CH_2N_2) on alcohols in presence of tetrafluoroboric acid (HBF_4) as catalyst.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow{HBF_4} \underset{\text{Ethyl methyl ether}}{CH_3CH_2\text{—}O\text{—}CH_3} + N_2$$

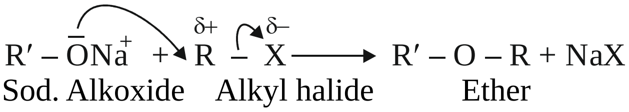
2. From Sodium Alkoxide, Williamson Synthesis : It is an important laboratory method for the preparation symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide. The sodium alkoxide is prepared by the action of sodium on a suitable alcohol.

$$\underset{\text{Alcohol}}{2R'-OH} + 2Na \longrightarrow \underset{\text{Sod. alkoxide}}{2R'-\overset{-}{O}\overset{+}{Na}} + H_2O$$

$$\underset{\text{Alkyl halide}}{R-X} + R'-ONa \longrightarrow \underset{\text{Ether}}{R-O-R'} + NaX$$

Ethers containing substituted alkyl group (secondary or tertiary) may also be prepared by this method.

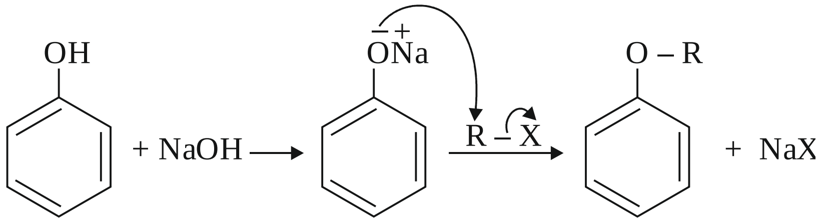
Mechanism : The reaction involves S_N2 attack of an alkoxide ion on **primary** alkyl halide.



$$\underset{\text{Sod. Alkoxide}}{R'-\overset{-}{O}\overset{+}{Na}} + \underset{\text{Alkyl halide}}{\overset{\delta+}{R}-\overset{\delta-}{X}} \longrightarrow \underset{\text{Ether}}{R'-O-R} + NaX$$

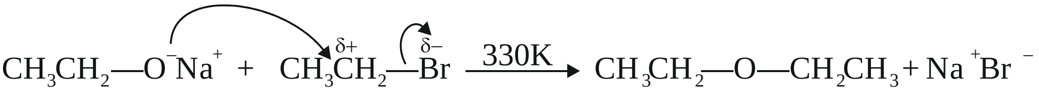
Limitations : Williamson synthesis is very sucessful with primary alkyl halides. The alkoxide ions are both powerful nucleophiles and bases and bring about dehydrohalogenation of the tertiary and secondary halides to form alkenes preferentially.

Phenols are also converted to ethers by this method. In this, phenol is used as the phenoxide moiety.



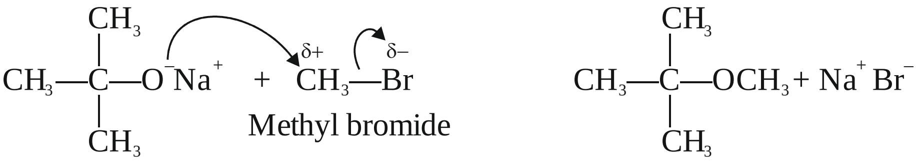
Phenol Sod. Phenoxide Ether

This method can also be used for the preparation of both symmetrical and unsymmentrical ethers. For example,



$$CH_3CH_2—\overset{-}{O}\overset{+}{Na} + \overset{\delta+}{CH_3}CH_2—\overset{\delta-}{Br} \xrightarrow{330K} CH_3CH_2—O—CH_2CH_3 + \overset{+}{Na}\overset{-}{Br}$$

Sod. ethoxide Ethyl bromide Diethyl ether

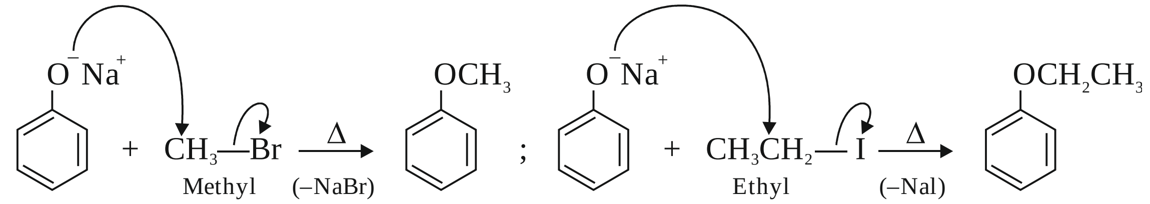


$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\overset{-}{O}\overset{+}{Na} + \overset{\delta+}{CH_3}—\overset{\delta-}{Br} \longrightarrow CH_3—\underset{CH_3}{\overset{CH_3}{C}}—OCH_3 + \overset{+}{Na}\overset{-}{Br}$$

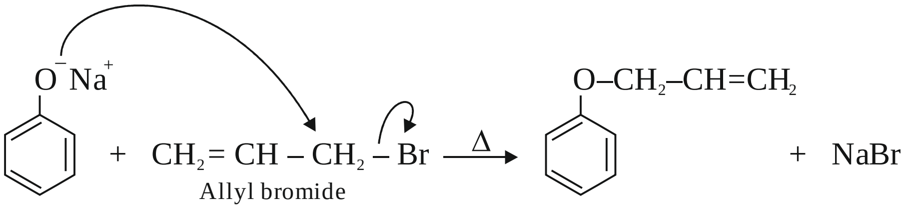
Methyl bromide

Sod. tert-butoxide tert-Butyl methyl ether

Similarly, alkyl aryl ethers (phenolic ethers) can be easily prepared by treating sodium phenoxide with suitable alkyl halides. For example,

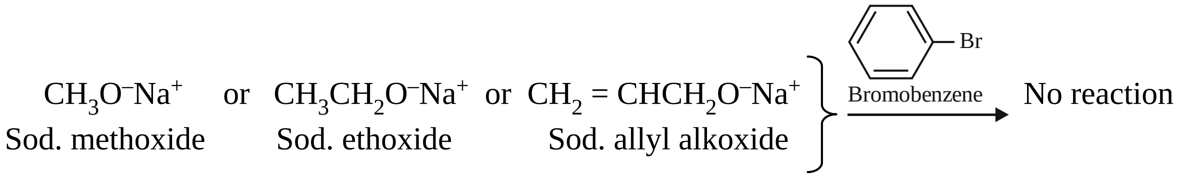


Sod. phenoxide Methyl bromide (–NaBr) Anisole ; Sod. phenoxide Ethyl iodide (–NaI) Phenetole



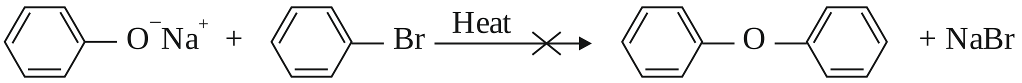
Sod. phenoxide Allyl bromide o-Allyphenol or o-Allyl phenyl ether

However, these ethers cannot be prepared by treating bromobenzene or iodobenzene with sodium salts of the corresponding alcohols, i.e. sodium methoxide, sodium ethoxide or sodium allyl alkoxide



This is due to the reason that the halogen is attached to the sp^2 carbon atom of the aromatic ring and the halides are much less reactive than alkyl halides towards nucleophilic substitution reaction.

Further, this method **cannot be used for preparing diaryl ethers** since aryl halides do not undergo nucleophilic substitutions easily.

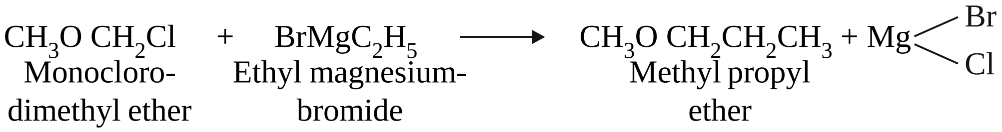


Sod. phenoxide Bromobenzene Diphenyl ether

3. From alkyl halides : Simple ethers can be prepared by boiling alkyl halides with dry silver oxide.

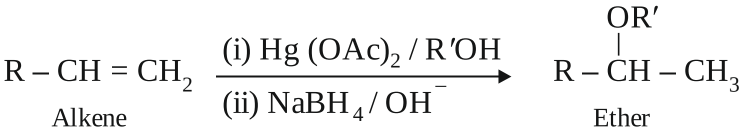
$$\begin{matrix} R-I \\ R-I \end{matrix} + Ag_2O \longrightarrow \underset{\text{Ether}}{R-O-R} + 2AgI$$

4. From Grigrand reagent : This is a good method for preparing higher ethers from lower members. Thus, the action of a lower halogenated ether react with Grignard reagent to give a higher member. Thus,



$$\underset{\substack{\text{Monocloro-}\\\text{dimethyl ether}}}{CH_3O\,CH_2Cl} + \underset{\substack{\text{Ethyl magnesium-}\\\text{bromide}}}{BrMgC_2H_5} \longrightarrow \underset{\substack{\text{Methyl propyl}\\\text{ether}}}{CH_3O\,CH_2CH_2CH_3} + Mg\begin{matrix} Br \\ Cl \end{matrix}$$

5. From alkenes : Alkenes can be converted into ethers by the following reaction.



$$\underset{\text{Alkene}}{R-CH=CH_2} \xrightarrow[\text{(ii) } NaBH_4 / OH^-]{\text{(i) } Hg(OAc)_2 / R'OH} \underset{\text{Ether}}{R-\overset{\overset{\displaystyle OR'}{|}}{C}H-CH_3}$$

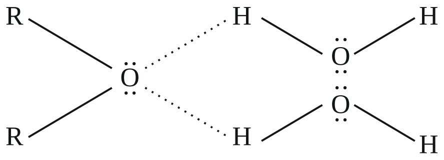
17.5 PHYSICAL PROPERTIES OF ETHERS :

1. Colour, state and odour : Lower members like dimethyl ether and ethylmethyl ether are gases at ordinary temperature while the other lower homologues are colourless liquids with characteristic pleasant odour 'ether smell'.

2. Dipolar nature : Ether molecules are slightly polar and thus have dipole moment. The dipole moment of ethers is due to the polar character of the C–O bonds. The dipole moment of dimethyl ether is 1.3D and that of diethyl ether is 1.18D.

3. Boiling point : The weak polarity of ethers do not appreciably affect their boiling points which are comparable to those of the alkanes of comparable molecular masses but are much lower than the boiling points of isomeric alcohols. The large difference in boiling points of alcohols and ethers of same molecular masses (isomeric) is due to the presence of hydrogen bonding in alcohols.

4. Solubility : The solubility of lower ethers in water is due to the formation of hydrogen bonds between water and ether molecules.



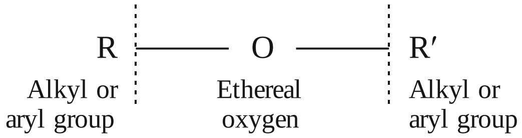
Diethyl ether is 7.5 percent soluble in water. As the molecular mass increases, the solubility of ethers in water decreases due to the corresponding increase in hydrocarbon portion of the molecule. Ethers are, however, fairly soluble in common organic solvents such as alcohol, benzene, chloroform, acetone etc.

Diethyl ether is itself a good solvent for organic solutes. Apart from the polar character of C–O bond in ether, ether has the ability to solvate cations (electrophile) by donating an electron pair from their oxygen atom. These properties make diethyl ether a good solvent.

5. Density : All ethers are lighter than water. Their density and boiling points show a gradual increase with increase in molecular masses.

17.6 CHEMICAL PROPERTIES :

In ethers two alkyl (or aryl) groups are linked to an oxygen atom.

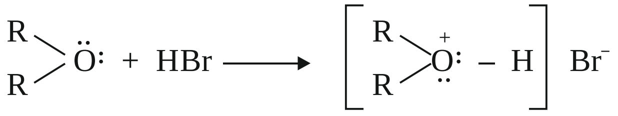


The aryl – oxygen bond is more stable than the alkyl–oxygen bond. Owing to the absence of active groups and multiple bonds, ethers are comparatively inert substances. The reagents like ammonia, alkalies, dilute acids and metallic sodium have no action upon them in cold. They are not readily oxidised or reduced. However, under specific conditions, ethers undergo the following reactions in accordance with their structural features.

I. Reactions of ethereal oxygen :

Ethers behave as Lewis bases on account of the presence of two lone pairs on the oxygen atom.

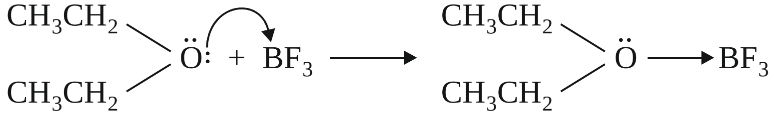
1. Formation of oxonium salts : Ethers like alcohols are weakly basic and thus dissolve in strong inorganic acids (e.g. H_2SO_4, $HClO_4$, HBr etc.) to form stable oxonium salts. thus,



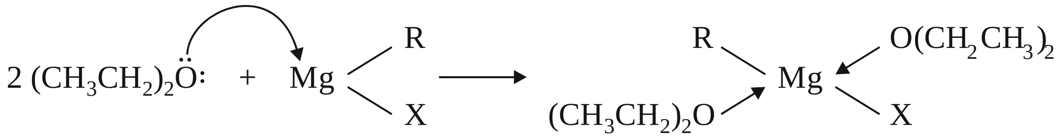
Ether Dialkyloxonium bromide

Oxonium salts are stable in high concentration of acids. When their acid solutions are diluted with water, the oxonium salts are dissociated into original ether and acid because water is a stronger base than ether.

2. Formation of coordination complexes : Ethers form relatively stable coordinate complexes with Lewis acids (e.g. BF_3, $AlCl_3$ and RMgX etc.) The complexes are known as **etherates**.



Diethyl Ether Boron trifuoride etherate



Diethyl ether Grignard reagent Grignard reagent etherate

Due to the formation of these complexes, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers.

II. Reactions involving the cleavage of C–O bonds in ethers :

1. Action of Halogen acids : The cleavage of C–O bond in ethers takes place under drastic conditions with excess of hydrogen halides. First, the ethers are cleaved to form alkyl halide and alcohol. The alcohol thus formed reacts with excess of the halogen acid to form the corresponding halide.

$$R-O-R + HX \longrightarrow R\text{–}X + R-OH$$

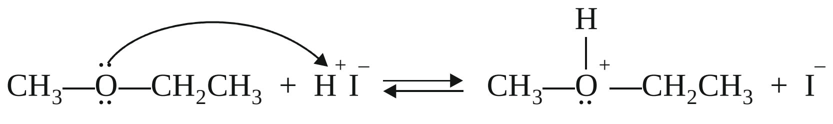
Ether Alkyl halide Alcohol

$$R-O-H + HX \longrightarrow R-X + H_2O$$

Thus, dialkyl ether gives two alkyl halide molecules.

Mechanism : The cleavage of ethers by halogen acids occurs by the following mechanism:

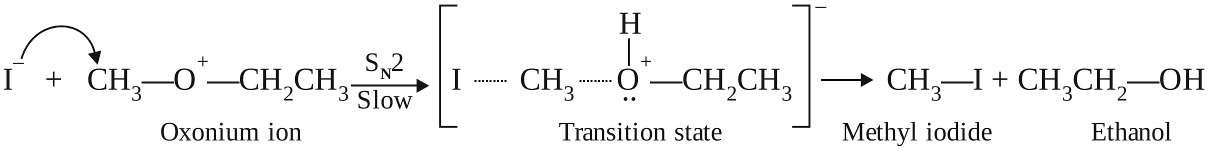
Step 1 : Ethers being Lewis bases, undergo protonation to form oxonium ion.



$$CH_3\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}CH_2CH_3 + \overset{+}{H}\overset{-}{I} \rightleftharpoons CH_3\text{—}\overset{\overset{H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}\text{—}CH_2CH_3 + \overset{-}{I}$$

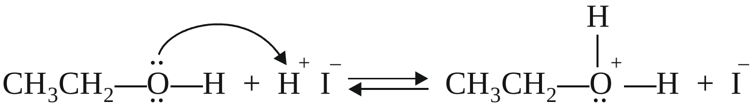
Ethyl methyl ether Oxonium ether

Step 2 : Iodide ion is a good nucleophile. Due to **steric hindrance**, it attacks the smaller alkyl group of the oxonium ion formed in **step 1** and displaces the alcohol molecule by S_N2 mechanism as shown below :

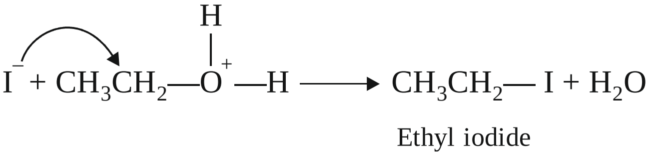


$$\overset{-}{I} + \underset{\text{Oxonium ion}}{CH_3-\overset{+}{O}-CH_2CH_3} \xrightarrow[\text{Slow}]{S_N2} \underset{\text{Transition state}}{\left[I \cdots CH_3 \cdots \overset{\overset{H}{|}}{\underset{..}{\overset{+}{O}}}-CH_2CH_3 \right]^-} \longrightarrow \underset{\text{Methyl iodide}}{CH_3-I} + \underset{\text{Ethanol}}{CH_3CH_2-OH}$$

Step 3 : When axcess of HI is used, ethanol thus formed reacts with another molecule of HI of form ethyl iodide.



$$CH_3CH_2-\ddot{\underset{..}{O}}-H + \overset{+}{H}\ \overset{-}{I} \rightleftharpoons CH_3CH_2-\overset{\overset{H}{|}}{\underset{..}{\overset{+}{O}}}-H + \overset{-}{I}$$



$$\overset{-}{I} + CH_3CH_2-\overset{\overset{H}{|}}{\overset{+}{O}}-H \longrightarrow \underset{\text{Ethyl iodide}}{CH_3CH_2-I} + H_2O$$

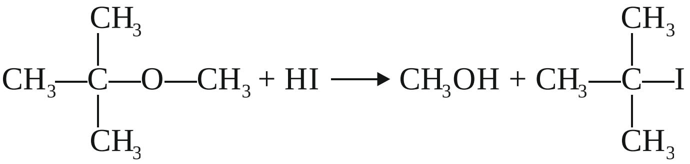
Reactivity of halogen acids : The order of reactivity of halogen acids follows the sequence:

HI > HBr > HCI.

Greater the nucleophilicity of the halide ion, more reactive is the halogen acid. Since the nucleophilicity of the halide ions follows the sequence $I^- > Br^- > Cl^-$, the reactivity of of halogen acids follows the same sequence i.e. HI > HBr > HCl.

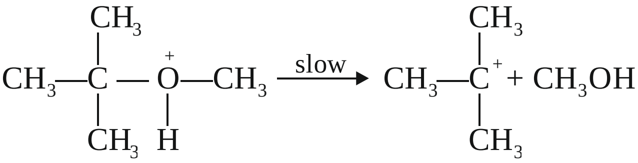
Site of cleavage :

(a) However, when one of the alkyl groups is a tertiary group the halide first formed is a teritiary halide.

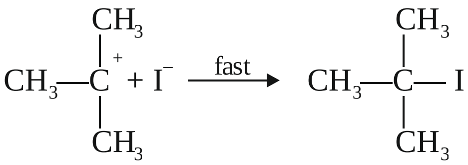


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I$$

It is because in step 2 of the reaction, the departure of leaving group ($HO-CH_3$) creates a more stable carbocation $[(CH_3)_3C^+]$ and the reaction follows S_N1 meachanism.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3 \xrightarrow{\text{slow}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{C}}} + CH_3OH$$



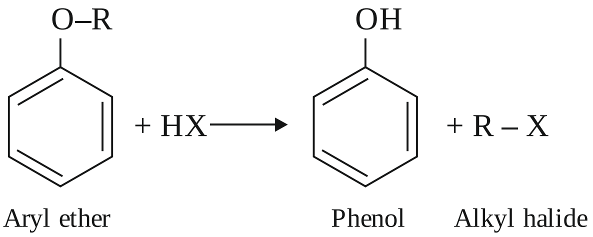
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + I^- \xrightarrow{\text{fast}} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I$$

Ethers with two different alkyl groups are also cleaved in same manner and the mechanism of the cleavage is ascertained by the nature of the leaving group and the stability of intermediate carbocation ion.

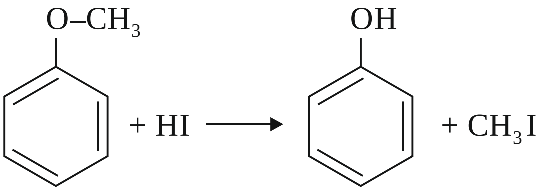
$$R-O-R' + HX \longrightarrow R-X + R'-OH$$

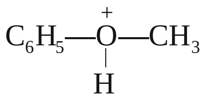
(b) Cleavage of alkyl aryl ethers : Alkyl aryl ethers (or phenyl) ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond.

In case of phenolic ethers, the products are always phenol and an alkyl halide.

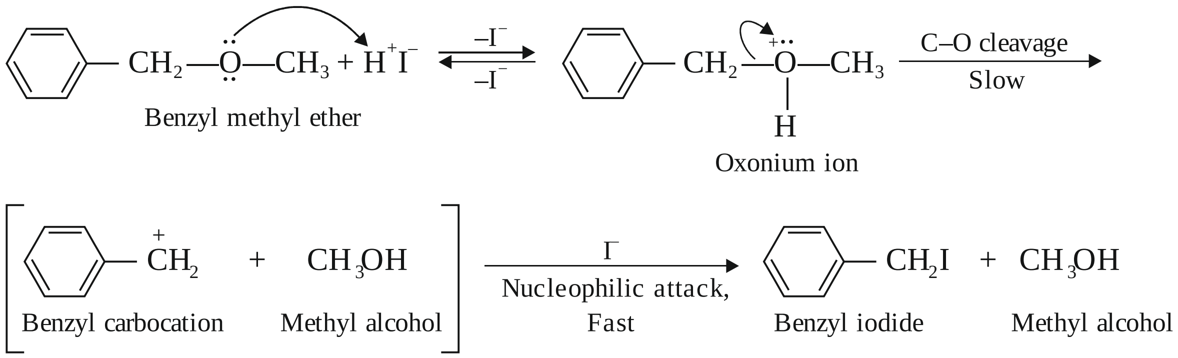


Thus, in case of anisole, when it reacts with HI, the products are phenol and methyl iodide.



In the first step, as per the mechanism, the methylphenyl oxonium ion,  $C_6H_5-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3$ is formed by protonation of anisole. The bond between O–CH_3 is weaker than the bond between O–C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore attack by I^- ion exclusively breaks the weaker O–CH_3 bond forming methyl iodide and phenol. Phenols thus formed, do not react further to give aryl halides because sp^2 hybridised carbon of phenol does not undergo nucleophilic substitution reaction by the halide ion to form the corresponding aryl halides.

Cleavage of benzyl alkyl ethers : In case of benzyl alkyl ethers containing a primary alkyl group such as benzyl ether, the reaction proceeds by S_NI mechanism. Since the benzyl carbocation is more stable than the methyl carbocation, therefore, cleavage of C–O bond gives methyl alcohol and benzyl carbocation. This carbocation then reacts with I^- ion to form benzyl iodide as shown below :



Cleavage of diaryl ethers : Diaryl ethers such as diphenyl ether are, however, not cleaved by HI. The reason being that the C–O bond has some double bond character due to resonance between the lone pairs of electrons on the O atom and the C atoms of the aryl groups directly linked to the O atom.

2. Hydrolysis : On heating with dilute sulphuric acid under presence, ethers are hydrolysed to alcohols.

$$R\text{–}O\text{–}R + H_2O \xrightarrow[\text{under pressue}]{\text{Dil } H_2SO_4,\ \Delta} \underset{\text{Alcohol}}{2R - OH}$$

3. Action of Sulphuric Acid : Cold concentrated sulphuric acid has no action on ethers except that it dissolves them forming oxonium salts. However, if the solution is heated, cleavage of carbon-oxygen bond takes place leading to the formation of alcohol and alkyl hydrogen sulphate.

$$\underset{\text{Diethyl ether}}{C_2H_5\text{–}O\text{–}C_2H_5} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\text{ethyl alcohol}}{C_2H_5\text{–}OH} + \underset{\text{ethyl hydrogen sulphate}}{C_2H_5HSO_4}$$

4. Action of Phosphorus Pentachloride : Phosphorus pentachloride brings about the cleavage of both the carbon oxygen bonds of ethers forming alkyl chlorides.

$$\underset{\text{Diethyl ether}}{CH_3CH_2 - O - CH_2CH_3} + PCl_5 \xrightarrow{\Delta} \underset{\text{Ethyl Chloride}}{2CH_3CH_2Cl} + POCl_3$$

5. Reaction with acid chlorides and anhydrides : Acid chlorides react with ethers when heated in the presence of anhyd. $ZnCl_2$ or $AlCl_3$ to form alkyl halides and esters.

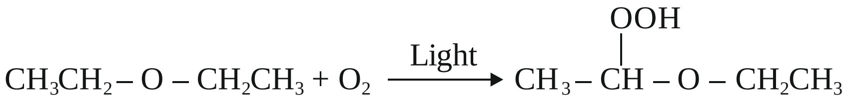
$$\underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\Delta]{\text{Anhyd.}ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

However, with anhydrides only esters are formed

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} \quad + \quad \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \quad \xrightarrow[\Delta]{\text{Anhyd.ZnCl}_2} \quad \underset{\text{Ethyl acetate}}{2\ CH_3COOC_2H_5}$$

III. Reactions involving the alkyl group :

1. Action of air and light : *Formation of peroxides.* When exposed to air and light for a long time ethers are oxidised to form hydroperoxides or simple peroxides.

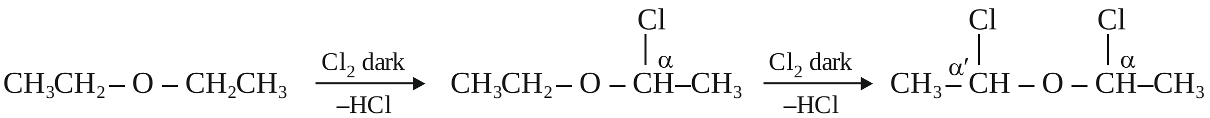


$$\underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3} + O_2 \xrightarrow{\text{Light}} \underset{\text{1-Ethoxyethyl hydroperoxide}}{CH_3-\overset{\overset{\displaystyle OOH}{|}}{CH}-O-CH_2CH_3}$$

It is a free radical reaction and oxidation occurs at the carbon atom next to the ethereal oxygen to form hydroperoxides. These peroxides are very dangerous compunds since they decompose violenly at high temperatures. ***Therefore, serious explosions may occur during distillation of old samples of ethers if peroxides are not removed.***

A simple method to remove peroxide is to shake the old sample with ferrous salt solution when the ether peroxides are reduced to ethers and Fe^{2+} salts are oxidised to Fe^{3+} salts. The Fe^{3+} ions thus formed are removed by washing with water.

2. Halogenation : Ethers react with Cl_2 or Br_2 to give substitution products. The extent of halogenation, however, depends upon the reaction conditions. For example, diethyl ether reacts with chloride in the dark to give α, α′ -dichlorodiethyl ether.

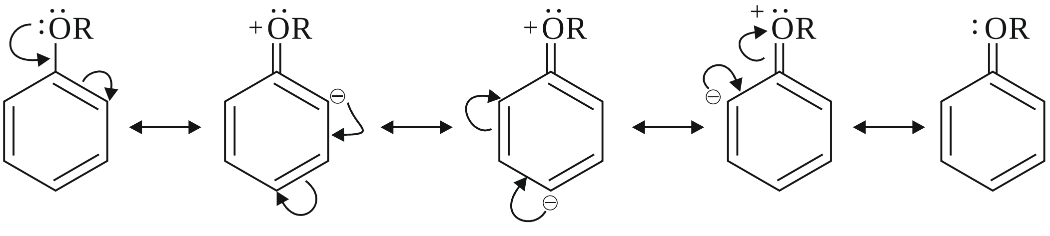


$$\underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3} \xrightarrow[-HCl]{Cl_2\ \text{dark}} \underset{\alpha\ \text{Chlorodiethyl ether}}{CH_3CH_2-O-\overset{\overset{\displaystyle Cl}{|\,\alpha}}{CH}-CH_3} \xrightarrow[-HCl]{Cl_2\ \text{dark}} \underset{\alpha,\ \alpha'\ \text{-Dichlorodiethyl ether}}{CH_3-\overset{\overset{\displaystyle Cl}{\alpha'\,|}}{CH}-O-\overset{\overset{\displaystyle Cl}{|\,\alpha}}{CH}-CH_3}$$

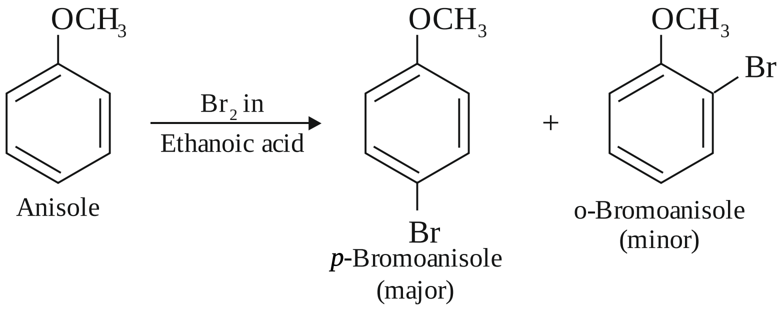
However, in the presence of light and excess of chlorine, all the hydrogen atoms are substituted to give perchlorodiethyl ether.

$$\underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3} \quad + \quad \underset{\text{(excess)}}{10\ Cl_2} \xrightarrow{hv} \underset{\text{Perchlorodiethyl ether}}{CCl_3CCl_2-O-CCl_2CCl_3} + 10\ HCl$$

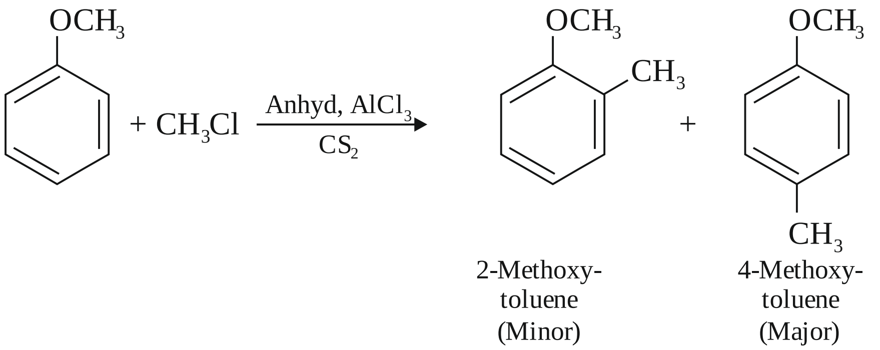
3. Electrophilic substitution : In aryl alkyl ethers the alkoxy group (–OR) is ortho, para directing and activates the aromatic ring towards electrophilic substitution in the same way as in phenol. However, aromatic ethers are less reactive than phenols.

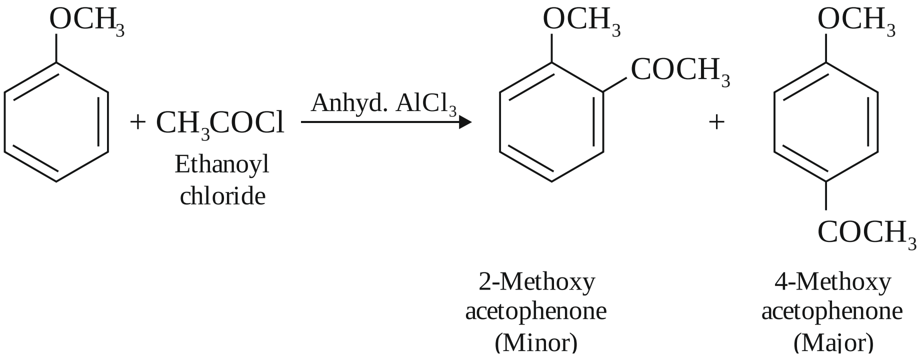


(i) *Halogenation* : Phenylalkyl ethers undergo usual halogenation in the benzene ring, *e.g.*, anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. *Para* isomer is obtained in 90% yield.

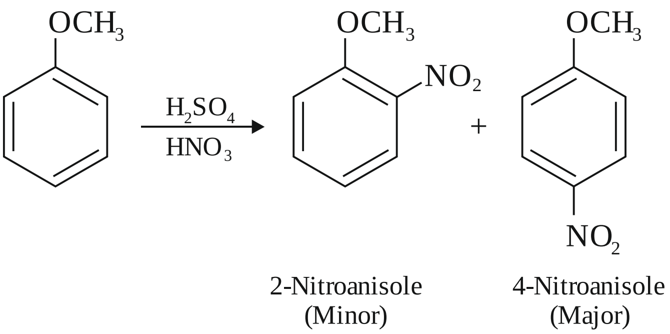


(ii) *Friedel-Crafts reaction* : Anisole undergoes Friedel-Crafts reaction, i.e. the alkyl and acyl groups are introduced at *ortho* and *para* positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.





(iii) *Nitration* : Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and para nitroanisole.



17.7 USES OF ETHERS :

Important uses of diethyl ethers :

1. As a solvent both in laboratory and industry. Ethers are almost inert in nature and have good dissolving power. In industry it is used as solvent for oils, resins, gums etc.
2. As an extracting solvent in laboratory and industry.
3. As a reaction medium for the preparation of Grignard and organometallic reagents, also for carrying out $LiAlH_4$ reductions.
4. Diethyl ether finds its use as an anaesthetic agent in surgery.
5. A number of naturally occurring ethers are used as perfumes and flavouring agents because of their pleasant odour.
6. Diphenyl ether is used as a heat transfer medium because of its high boiling point, 531K.
7. Lower ethers are volatile liquids which on evaporation produce low temperatures. They are therefore, used as refrigerants.

Diethyl Ether, Ether, $C_2H_5OC_2H_5$:

This is the most important representative of this class and often referred to as simply ether. It can be prepared in the laboratory by:

(i) Williamsons synthesis

(ii) On a large scale by dehydration reaction of ethyl alcohol by Conc. H_2SO_4

Equal volumes of alcohol and conc. H_2SO_4 are heated in a flask fitted with a dropping funnel and cold water running condenser. When the temperature of the content in the flask reaches 413K, ether begins to distil over. Alcohol is now run in from the dropping funnel at the same rate at which ether distills over. The process is continuous and hence the name Continous Etherfication Process.

Estimation of Methoxy (or Ethoxy) Groups :

The methoxy (or ethoxy) groups are estimated by **Zeisel's method**. A known mass of the sample is heated with conc. HI to form methyl iodide (or ethyl iodide). The iodide is then treated with alcoholic silver nitrate to give a precipitate of AgI

$$ROCH_3 + HI \rightarrow ROH + CH_3I$$

$$CH_3I + AgNO_3 \rightarrow AgI + CH_3NO_3$$

In this reaction : $-OCH_3$ is equivalent to AgI, mass of methoxy group is 31 and that of AgI 234.88. Thus, % of methoxy group = $\dfrac{31 \times \text{mass of AgI} \times 100}{234.88 \times \text{mass of ether}}$

CHAPTER (17) AT A GLANCE

1. Two important methods of preparation of ethers are :
   (i) Dehydration of alcohol and
   (ii) Williamson synthesis
2. Weakly polar ethers have much lower boiling points compared to their isomeric alcohols.
3. The lower members are fairly soluble in water due to the formation of hydrogen bonding.
4. Diethyl ether is a good solvent and all the ethers are lighter than water.
5. Owing to the absence of of active groups and multiple bonds, ethers are comparatively inert. However, under specific conditions ethers undergo the following reactions in accordance with their structural features.
   (i) Reaction at ethereal oxygen
   (ii) Reactions involving cleavage of C–O bonds particularly with HI, HBr and PCl_5
   (iii) Reactions involving the alkyl group.

   Ethers undergo halogenation at the alkyl groups. In aryl alkyl ethers the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions in electrophilic substitution reactions.

QUESTIONS

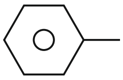
I. Multi choice type questions. (one mark) :

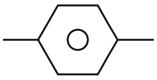
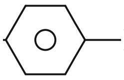
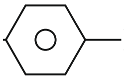
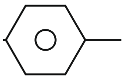
1. Which of the following will exhibit highest boiling point ?

(a) $CH_3CH_2O\ CH_2CH_3$
(b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3O\ CH_2CH_2CH_3$
(d) $CH_3CH_2CH_2CH_2CH_2OH$

2. Which of the following cannot be prepared by Williamson synthesis ?

(a) Methoxybenzene
(b) Methoxy ethane
(c) Di-*tert*-butyl ether
(d) *tert*-butyl methyl ether

3. In the reaction,  — $OCH_3 \xrightarrow[\text{Acetic acid}]{Br_2}$ the products are

(a) Br —  — $OCH_3 + H_2$
(b)  —Br + CH_3Br
(c)  —Br + CH_3OH
(d)  —OH + CH_3Br

4. The ether $C_6H_5 - O - CH_2C_6H_5$ when treated with HI produces

(a) $C_6H_5CH_2I$ (c) $C_6H_5CH_2OH$

(b) C_6H_5I (d) $C_6H_5 - O - C_6H_5$

5. Which of the following ethers is not cleaved by HI ?

(a) Methyl phenyl ether (c) Ethyl methyl ether

(b) Diphenyl ether (d) Ethyl phenyl ether

6. The molecular formula of alkyl ethers is

(a) $C_nH_{2n}O$ (c) $C_nH_{2n+2}O$

(b) C_nH_{2n+I} (d) $C_nH_{2n}O\ C_nH_{2n}$

7. Ethers react with Conc. H_2SO_4 to form

(a) Alkyl free radicals (c) Oxyanion

(b) Zwitter ion (d) Oxonium ion

8. Ether gives chemical reactions due to

(a) C – O bond cleavage (c) Lone pair present on oxygen

(b) C – H bond cleavage (d) All of the above

9. Which of the following pairs will give ether ?

(a) C_2H_5ONa and C_2H_5I (c) $C_2H_5I \xrightarrow{\text{Dry } Ag_2O}$

(b) $C_2H_5OH \xrightarrow[373K]{H^+}$ (d) All of the above

10. Which of the following solvents is used for the preparation of Grignard reagent.

(a) Ethyl alcohol (c) Cyclohexonol

(d) Diethyl ether (d) Benzene

11. When $(CH_3)_3\ COCH_3$ is treated with hydriodic acid, the fragments after the reaction obtained are :

(a) $(CH_3)_3C - I + HOCH_3$ (c) $(CH_3)_3\ CH + CH_3OCH_3 + I_2$

(b) $(CH_3)_3C - OH + I - CH_3$ (c) $(CH_3)_3\ C - OH + CH_4 + I_2$

12. $C_6H_5COCH_3$, when treated with HI at 373K the following are the products.

(a) CH_3OH and C_6H_5I (c) C_6H_5I and CH_3I

(b) CH_3I and C_6H_5OH (d) C_6H_5OH and CH_3OH

ANSWERS

1. (d), 2. (c), 3. (a), 4. (a), 5. (b), 6. (c), 7. (d), 8. (d), 9. (d), 10. (b), 11. (a), 12. (b)

II. Fill in the blanks

1. Ethers exhibit functional isomerism with ______ .
2. $C_4H_{10}O$ has ______ metamers, one of them is diethyl ether while the others are ______ and ______.
3. Williamson's synthesis involves the reaction of an ______ with an ______.
4. Ethers behave as weakly ______ substances due to the presence of two lone pairs of electrons on the oxygen atom.
5. ______ is widely used as a solvent for the preparation of Grignard reagent.
6. Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove ______ which are formed on prolonged standing in contact with air.
7. Cleavage of phenolic ether, anisole, by HI, gives ______ and ______.
8. Alkyl aryl ethers are best prepared by treating sodium salt of ______ with ______ halide.

ANSWERS

1. alcohols, 2. three, methyl n-propyl ether, isopropyl methyl ether, 3. alkoxide, alkyl halide, 4. basic, 5. Diethyl ether, 6. peroxides, 7. Phenol, methyl iodide, 8. phenol, alkyl.

III. Choose the True (T) and Flase (F) statement : (one mark)

1. Cleavage of ethyl methyl ether with HI at 373K gives methyl iodide and ethanol.
2. Phenetole reacts with HI at 373K to give iodobenzene and ethanol.
3. Dimethyl ether and ethyl alcohol have the some boiling point as both have same molecular masses.
4. *tert*-Butyl ether can be prepared by heating sodium ethoxide with *tert*-butyl bromide.
5. Alkyl aryl ethers are less reactive than phenols towards electrophilic substitution reactions.
6. Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.

ANSWERS

1. (T), 2. (F), 3. (F), 4. (F), 5. (T), 6. (T).

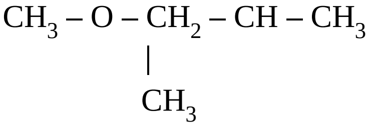
IV. Very short answer type questions (one mark) :

1. Give the IUPAC names the following :

   (i) $CH_3CH_2CH_2OCH_3$

   (ii) $CH_3COCH_2CH_2Cl$

   (iii) $C_6H_5OC_2H_5$

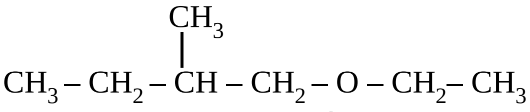
   (iv) 

   $CH_3 - O - CH_2 - \underset{\substack{|\\ CH_3}}{CH} - CH_3$

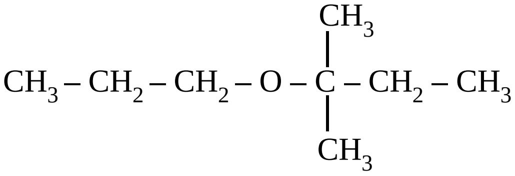
2. Write the structure of the compounds whose names as follows :
   - (i) 2-Ethoxy-3-methyl pentane
   - (ii) 1-Ethoxypropane
   - (iii) 1-Phenoxyheptane
   - (iv) Anisole and phenetole
3. Name one metamer of diethyl ether.
4. Which method is used for the estimation of a methoxy group in organic compounds.
5. Which class of ethers are not cleaved by HI.
6. Which product is formed by the Friedel crafts reaction of anisole with CH_3Cl.
7. Between anisole and phenol, which is more reactive towards electrophilic substitution reaction.
8. Give the order of reactivity of halogen acids towards the cleavage of carbon-oxygen bond of ethers.
9. Which reagent brings about the cleavage of carbon-oxygen bond of ethers leading to the formation of only alkyl halides.
10. Give the order of polarity of alcohol, phenol and ether.

V. Short answer type questions (two marks) :

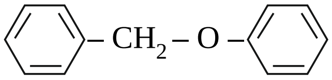
1. Give the reason of the higher boiling point of ethanol in comparision to methoxy methane.
2. Write the names of reagents and equation for the preparation of the following ethers by Williamson's synthesis:
   - (i) Ethoxy ethane
   - (ii) Ethoxy benzene
   - (iii) 1-Methoxyethane
   - (iv) 1-Propoxypropane
3. Write the equations for the following reaction
   - (i) Nitration of anisole
   - (ii) Bromination of anisole in ethanoic acid medium.
4. Give tthe major products that are formed by heating each of the following with HI

(i) 

$$CH_3 - CH_2 - \overset{\overset{CH_3}{|}}{CH} - CH_2 - O - CH_2 - CH_3$$

(ii) 

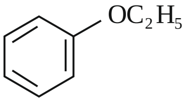
$$CH_3 - CH_2 - CH_2 - O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - CH_3$$

(iii) 

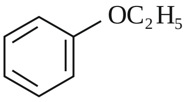
5. Predict the product of the following reactions :

   (i) $CH_3 - CH_2 - CH_2 - O - CH_3 + HI \longrightarrow$

   (ii) $(CH_3)_3\,C - O - C_2H_5 + HI \longrightarrow$

   (iii) 

$+ HBr \longrightarrow$

   (iv) 

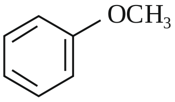
$\xrightarrow[\text{Conc.}HNO_3]{\text{Conc.}H_2SO_4}$

6. Explain why diphenyl ether is not cleaved by HI.

7. $(CH_3)_3\,C - O - CH_3 + HI \longrightarrow (CH_3)_3\,CI + CH_3OH$

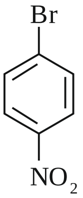
   Justify the preferential formation of the products.

8. Predict the products A and B

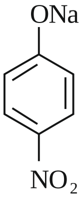


$\xrightarrow[373K]{HI} A + B$

9. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?

   (i) 

$+ CH_3ONa$

   (ii) 

$+ CH_3Br$

10. How you will distinguish $C_2H_5 - O - C_2H_5$ and $C_6H_5 - O - C_6H_5$ by treating with HI ?

11. Why can ethers be cleaved preferentially by hot conc.HI and HBr but not by conc.HCl.

VI. Short answer type questions (3 marks) :

1. Illustrate with examples the limitations of Williamson sysnthesis for the preparation of certain type of ethers.

2. How is 1-propoxypropane synthesised from propan-1-ol ? Write the mechanism of this reaction.

3. Preparation of ethers by acid dehydration of secondary and tertiary alcohol is not suitable method. Give reason.

4. Write the mechanism of the reactions of HI with methoxymethane.

5. Write the equations of the the reactions of hydrogen iodide with :

   (i) methoxybenzene

   (ii) benzyl ethyl ether

   (iii) 1-propoxypropane

6. Explain how the alkoxy group (–OR) is *ortho* and *para* directing and activates the aromatic ring towards electrophilic substitution reactions.
7. Give an example for the synthesis of unsymmetrical ether by Williamson synthesis.
8. Write the reaction of Williamson synthesis of 2-ethoxy-3-methyl-pentane starting from ethanol and 3-methylpetan-2-ol.
9. Explain why is bimolecular dehydration not appropriate for the preparation of ethyl methyl ether.
10. Compound (A), $C_4H_{10}O$, is found to be soluble in sulphuric acid. (A) does not react with metallic sodium or potassium permanganate solution. When (A) is heated with excess of HI, it is converted to a single alkyl halide. What is the structural formula of (A).
11. Write the equation of the reaction of hydrogen iodide with
    (i) 1-propoxypropane
    (ii) methoxy benzene
    (iii) benzyl ethyl ether
12. Write a suitable reaction for the preparation of t-butyl ethyl ether.
13. Give the majo products that are formed by reacting each of the following ether with HI.
    (i) methyl propyl ether
    (ii) phenyl methyl ether
    (iii) benzyl phenyl ether
14. Preparation of ethers by acid dehydration of secondary and tertiary alcohol is not suitable method. Give reason.

VII. Long answer type question (7 marks) :

1. Outline two important methods of prepration and three properties of dialkyl ethers.
2. How does diethyl ether react with
   (i) PCl_5, (ii) Conc.H_2SO_4 (iii) Conc.HI (iv) O_2
3. Describe Williamson synthesis of ethers. What are its limitations? Discuss the mechanism.
4. How is diethyl ether prepared in the laboratory? How will you distinguish it from ethanol and diphenyl ehter. What happens when it is treated with hot HI?
5. Explain the following with an example.
   (i) Unsymmetrical ether
   (ii) Cleavage of benzyl alkyl ethers by HI
   (iii) Williamson ether synthesis
6. Discuss the electrophilic substitution reaction like halogenation, nitration and Friedel-Crafts reactions of aryl alkyl ethers.
7. Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming group to *ortho*-and *para*-positions in the benzene ring.

❑❑❑

UNIT - XII

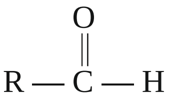
CHAPTER - 18

ALDEHYDES AND KETONES

18.1 INTRODUCTION :

The aldehydes and ketones belong to the class of oxygen containing organic compounds that have a $>C=O$ group, for which they are termed as **carbonyl compounds**.

(i) In aldehydes, the carbonyl group is attached to one hydrogen atom and one alkyl or aryl group or another hydrogen atom, whereas in ketones, the carbonyl group is attached to either one alkyl and one aryl group or to two alkyl (or aryl) groups.

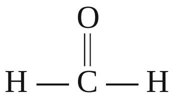
(a) 

$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}$

Aldehyde

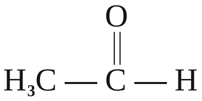
(Where R = H or any

alkyl or aryl group)

Examples : 

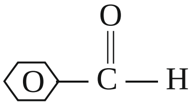
$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-H}$

Formaldehyde

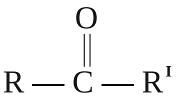


$\mathrm{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H}$

Acetaldehyde



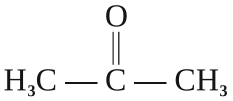
Benzaldehyde

(b) 

$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'}$

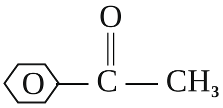
Ketone

(Where R and R′ may be same or different alkyl or aryl groups)

Examples : 

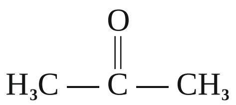
$\mathrm{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$

Acetone



Acetophenone

(ii) When two alkyl (or aryl) groups i.e. R and R′ are same, the ketone is termed as a simple ketone, where as when R and R′ are different, the ketone is named as a mixed ketone.

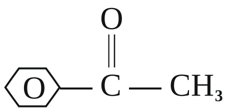


$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

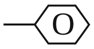
Acetone

$R = R' = -CH_3$

Simple ketone

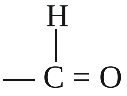


Acetophenone

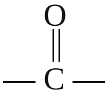
R = 

$R' = -CH_3$

Mixed ketone

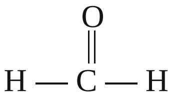
(iii) Aldehydes are characterised by the functional group  $-\overset{\overset{\displaystyle H}{|}}{C}=O$ (aldehydic group) and the functional group of ketones is $>C=O$ (ketonic group).

(iv) Aldehydes and ketones have some similar characteristics because of the presence of same carbonyl group, but differ in some properties due to the presence of a hydrogen atom on the carbonyl group of aldehydes.

(v) In case of aldehydes the —CHO group always occurs at the end of the carbon chain, where as the  $-\overset{\overset{\displaystyle O}{\|}}{C}-$ group in case of keones occurs within the carbon chain.

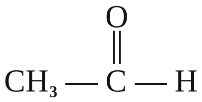
(vi) Carbonyl compounds may be aliphatic or aromatic in nature depending on the presence of only alkyl group or an aryl group (may be in addition to alkyl or aryl group in case of ketones).

(a) Aliphatic aldehydes and ketones



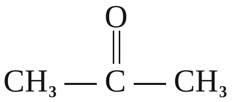
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Formaldehyde



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

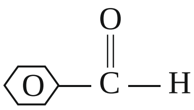
Acetaldehyde



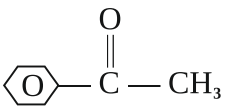
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Acetone

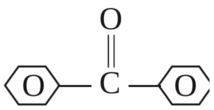
(b) Aromatic aldehydes and ketones



Benzaldehyde



Acetophenone



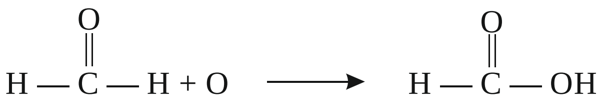
Benzophenone

18.2 NOMENCLATURE OF CARBONYL COMPOUNDS :

A. Nomenclature of Aldehydes :

(i) Common system :

(a) In the common system, the names of aliphatic and aromatic aldehydes are derived from the common names of the acids which they form on oxidation by replacing the terminal ‘ic acid’ by the suffix aldehyde.

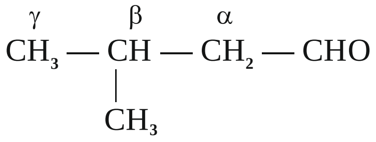


$$H-\overset{\overset{\large O}{\|}}{C}-H + O \longrightarrow H-\overset{\overset{\large O}{\|}}{C}-OH$$

Formaldehyde Formic acid

Formic acid – ic acid + aldehyde = formaldehyde

(b) In case of substituted aldehydes, the positions of the substituents are indicated by Greek letters α, β, γ, δ etc with the carbon atom next to the —CHO group being designated as α.

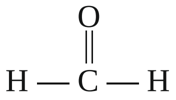


$$\overset{\gamma}{CH_3}-\underset{\underset{\large CH_3}{|}}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-CHO$$

β – Methylbutyraldehyde

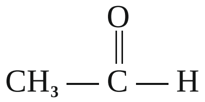
(ii) IUPAC system :

(a) In IUPAC system the aliphatic aldehydes are named as **alkanals** which are derived from the names of the corresponding alkanes by replacing the ending – e with – al.



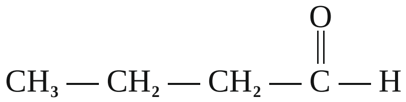
$$H-\overset{\overset{\large O}{\|}}{C}-H$$

Methanal



$$CH_3-\overset{\overset{\large O}{\|}}{C}-H$$

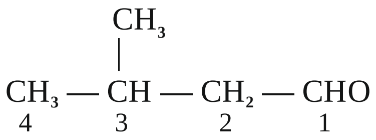
Ethanal



$$CH_3-CH_2-CH_2-\overset{\overset{\large O}{\|}}{C}-H$$

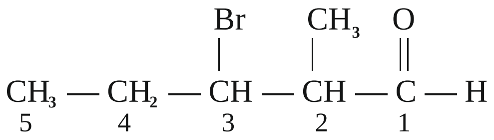
Butanal

(b) In case of substituted aldehydes, the longest carbon chain is choosen having —CHO group and the substituents are prefixed in the alphabetical order along with numerals indicating their positions in the carbon chain with the carbon atom of the —CHO group given number 1.



$$\underset{4}{CH_3}-\underset{3}{\overset{\overset{\large CH_3}{|}}{CH}}-\underset{2}{CH_2}-\underset{1}{CHO}$$

3-Methylbutanal



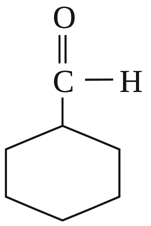
$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{\large Br}{|}}{CH}}-\underset{2}{\overset{\overset{\large CH_3}{|}}{CH}}-\underset{1}{\overset{\overset{\large O}{\|}}{C}}-H$$

3-Bromo-2-methylpentanal

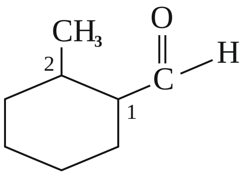
$$\overset{5}{OHC}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CHO}$$

Pentan - 1, 5 - dial

(c) When aldehyde group is attached to an alicyclic ring, the suffix **carbaldehyde** is added after the full name of the cycloalkane, with the numbering starting from the carbon atom containing –CHO group.

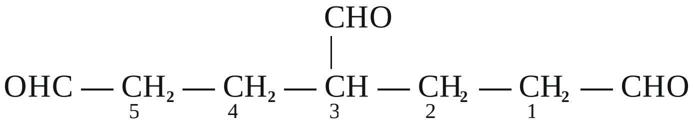


Cyclohexanecarbaldehyde



2-Methylcyclohexanecarbaldehyde

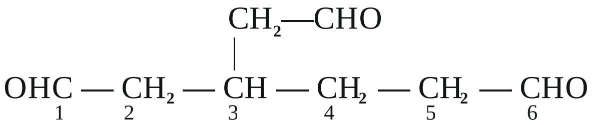
(d) The suffix carbaldehyde is used when an unbranched carbon chain is attached to more than two aldehyde groups, where the compound is considered as a derivative of the parent alkane which does not include the carbon atom of the functional groups.



$$OHC - \underset{5}{CH_2} - \underset{4}{CH_2} - \overset{\overset{CHO}{|}}{\underset{3}{CH}} - \underset{2}{CH_2} - \underset{1}{CH_2} - CHO$$

Pentane - 1, 3, 5 - tricarbaldehyde

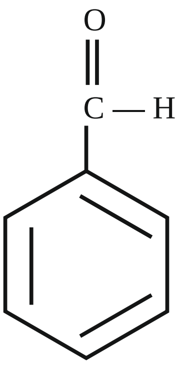
But :



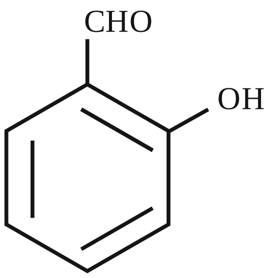
$$\underset{1}{OHC} - \underset{2}{CH_2} - \overset{\overset{CH_2-CHO}{|}}{\underset{3}{CH}} - \underset{4}{CH_2} - \underset{5}{CH_2} - \underset{6}{CHO}$$

3 - (Formylmethyl) hexan - 1, 6- dial

(e) The name **benzenecarbaldehyde** or simply **benzaldehyde** is given to the simple aromatic aldehyde where aldehyde group is attached directly to the benzene ring. In case of substituted benzaldehydes, the positions of substituents in the benzene ring with respect to the –CHO group are indicated by the prefixes *ortho*(o) *meta*(m) and *para*(p) or by the numbers 1, 2, 3 etc. with the carbon having –CHO group being considered as number 1.



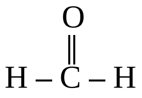
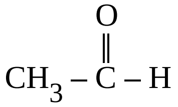
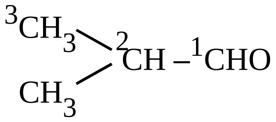
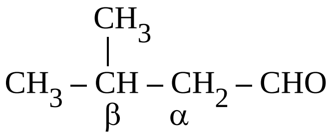
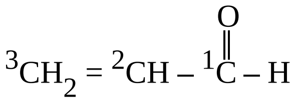
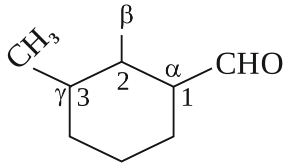
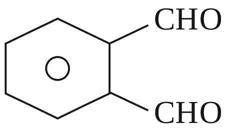
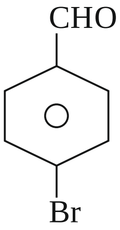
Benzaldehyde



2- Hydroxybenzaldehyde
(o-Hydroxybenzaldehyde
or Salicylaldehyde)

The common and IUPAC names of some aldehydes are given in the Table 18.1

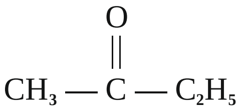
Table 18.1: Common and IUPAC names of some Aldehydes.

Formula	Common Name	IUPAC name
 $H-\overset{\overset{\displaystyle O}{\|}}{C}-H$	Formaldehyde	Methanal
 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	Butyraldehyde	Butanal
	Isobutyraldehyde	2-Methylpropanal
 $CH_3-\underset{\beta}{\overset{\overset{\displaystyle CH_3}{\|}}{CH}}-\underset{\alpha}{CH_2}-CHO$	β-Methyl butyraldehyde	3-Methylbutanal
 ${}^3CH_2={}^2CH-{}^1\overset{\overset{\displaystyle O}{\|}}{C}-H$	Acraldehyde. (Acrolein)	Prop-2 - enal
$CH_3-CH=CH-CHO$	Crotonaldehyde	But-2 - enal
	γ-Methylcyclohexane -carbaldehyde	3-Methylcyclohexanecarbaldehyde
	Phthaldehyde	Benzen-1, 2-dicarbaldehyde
	P-Bromobenzaldehyde	4-Bromobenzaldehyde

A. **Nomenclature of Ketones :**

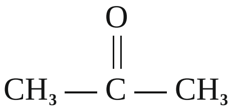
(i) **Common system :**

(a) In the common system, the names of aliphatic and aromatic ketones are derived by naming the two alkyl or aryl groups bonded to the carbonyl group in alphabetical order as two separate words and adding the suffix **ketone**. In case of **symmetrical** ketones the prefix **di** is attached to the name of the alkyl group.



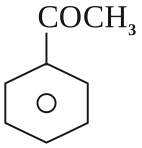
$CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5$

Ethyl methyl ketone



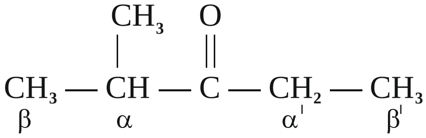
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Dimethyl ketone (Acetone)



Methyl phenyl ketone

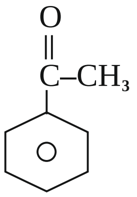
(b) The positions of the substituents are indicated by Greek letters, αα′, ββ′ etc starting from the carbon atoms next to the carbonyl group taken as αα′.



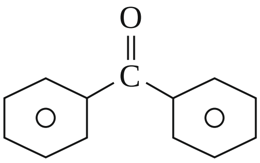
$\underset{\beta}{CH_3}-\underset{\alpha}{\overset{\overset{CH_3}{|}}{CH}}-\overset{\overset{O}{\|}}{C}-\underset{\alpha'}{CH_2}-\underset{\beta'}{CH_3}$

α-Methyl diethyl ketone

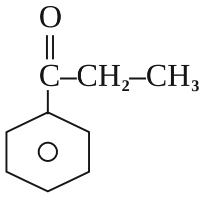
(c) In case of aromatic ketones generally the namings are done by adding the acyl group as prefix to **phenone**.



Acetophenone



Benzophenone

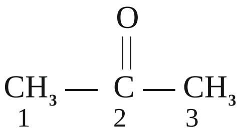


Propiophenone

(ii) IUPAC System :

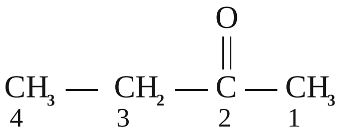
(a) In the IUPAC system, ketones are named as **alkanones**, which are derived by replacing the terminal *-e* of the corresponding alkanes by the suffix - one.

(b) During the naming the longest chain carrying the carbonyl group is choosen and the numbering begins from the end giving lowest number to the carbonyl group. If the chain carries two keto groups, prefix *di* is attached to *-one*.



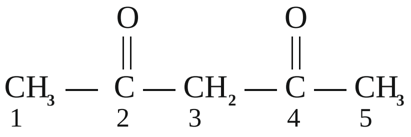
$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_3}$

Propan-2-one



$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$

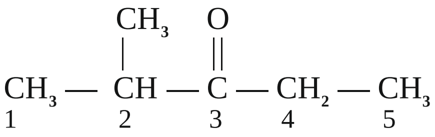
Butan-2-one



$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{O}{\|}}{C}}-\underset{5}{CH_3}$

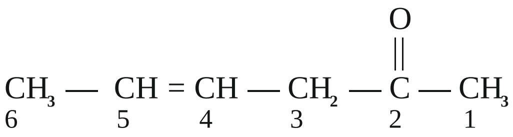
Pentan-2, 4-dione

(c) In case of substitued ketones, the parent chain containing the keto group and the substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain.



$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{\overset{\overset{O}{\|}}{C}}-\underset{4}{CH_2}-\underset{5}{CH_3}$

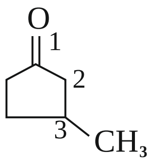
2-Methylpentan-3-one



$\underset{6}{CH_3}-\underset{5}{CH}=\underset{4}{CH}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{1}{CH_3}$

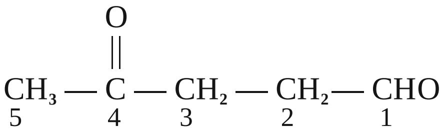
4-Hexen-2-one

The same principle is applied to cyclic ketones, the number 1 being given to the carbonyl group.



3-Methylcyclopentanone

(d) When both aldehyde and keto groups are present in the same compound, aldehyde group is given importance because of its higher reactivity and will be assigned number 1. Keto group will be given the name **oxo** prefixed by its position. For example.

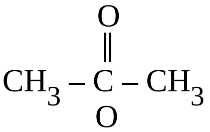
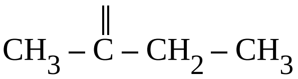
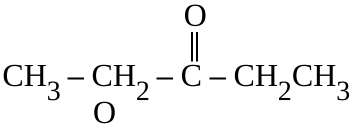
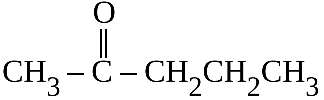
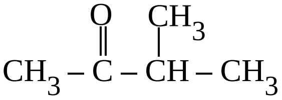
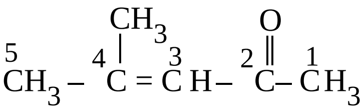
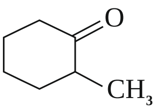
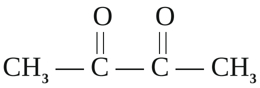
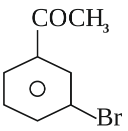
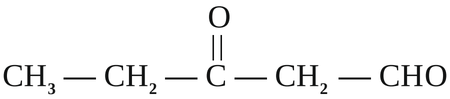


$$\underset{5}{CH_3}-\underset{4}{\overset{O}{\overset{\|}{C}}}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{CHO}$$

4-Oxopentanal

Common and IUPAC names of some ketones are given in Table 18.2.

Table 18.2 : Common and IUPAC names of Ketones

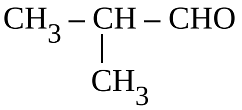
Formula	Common name	IUPAC name
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	Acetone	Propanone
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	Ethyl methyl ketone	Butan - 2 - one.
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$	Diethyl ketone	Pentan - 3 - one.
 $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$	Methyl n-propyl ketone	Pentan-2-one
 $CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}H}-CH_3$	Isopropyl methyl ketone	3-Methylbutan-2-one
 $\overset{5}{CH_3}-\overset{CH_3}{\overset{|}{\overset{4}{C}}}=\overset{3}{C}H-\overset{O}{\overset{\|}{\overset{2}{C}}}-\overset{1}{C}H_3$	Mesityl oxide	4-Methylpent-3-en-2-one.
	α-Methylcyclohexanone	2-Methylcyclohexanone
 $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$	Biacetyl	Butan-2, 4-dione
	m-Bromoacetophenone	3-Bromoacetophenone
 $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CHO$	Propionylacetaldehyde	3-Oxopentanal

18.3 ISOMERISM IN ALDEHYDES AND KETONES :

1. **Aldehydes:** Aldehydes show three types of structural isomerism i.e. chain, functional isomerism and position isomerism.

(a) **Chain isomerism:** The molecular formula C_4H_8O represents compounds like

(i) $CH_3\,CH_2\,CH_2CHO$ Butanal (Straight chain)

(ii) 

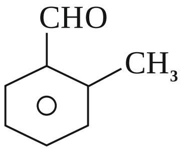
$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CHO$ 2– Methylpropanal. (Branched chain)

(b) **Functional isomerism:** Aldehydes exhibit functional isomerism with ketones. The molecular formula C_3H_6O represents two compounds.

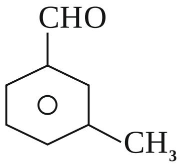
(i) CH_3CH_2CHO
Propanal

(ii) CH_3COCH_3
Propanone.

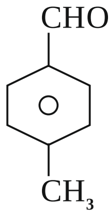
(c) **Position isomerism :** Aromatic aldehydes exhibit position isomerism.



o-Methylbenzaldehyde



m-Methylbenzaldehyde

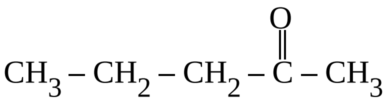


p-Methylbenzaldehyde

2. **Ketones:** Ketones exhibit chain isomerism, functional isomerism and metamerism.

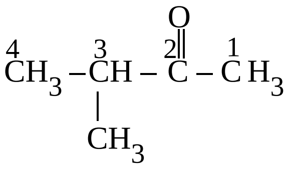
(i) **Chain isomerism:**

Molecular foumula $C_5H_{10}O$ represents the following compounds.



$CH_3 - CH_2 - CH_2 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_3$

Pentan -2-one

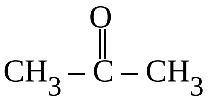


$\overset{4}{C}H_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{3}{C}H}} - \overset{\displaystyle O}{\overset{\|}{\overset{2}{C}}} - \overset{1}{C}H_3$

3 –Methylbutan - 2- one.

(ii) **Functional isomerism:**

Ketones exhibit functional isomerism with aldehydes.



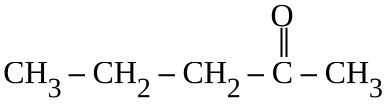
$CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - CH_3$

Propanone

$CH_3 - CH_2 - CHO$

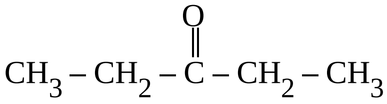
Propanal

(iii) **Metamerism:** The same molecular formula represents two ketones which differ in the nature of alkyl groups linked to the divalent keto group. This is also termed as position isomerism.



$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

Pentan -2-one



$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Pentan-3-one

18.4 STRUCTURE OF CARBONYL GROUP :

Electron diffraction and spectroscopic studies confirm that carbonyl group is planar in nature. The carbon atom of carbonyl group is sp^2 hybridised, thus it has three sp^2 hybrid orbitals. It forms three sigma bonds, one with oxygen and other two with other two atoms or groups. All these sigma bonds lie in one plane at an angle of 120^0 to each other. The unhybridised p–orbital of carbon laterally overlaps with half filled p–orbital of oxygen, thereby forming a π bond. The electron cloud of π bond. lies both above and below the C – O bond. Since oxygen atom is more electronegative the electron cloud is displaced more towards oxygen. This results in polarisation of C – O bond. The carbon end becomes slightly +ve whereas the oxygen end, slightly –ve. Hence the carbonyl carbon is an electrophilic (Lewis acid) and carbonyl oxygen, a nucleophilic (Lewis base) centre.

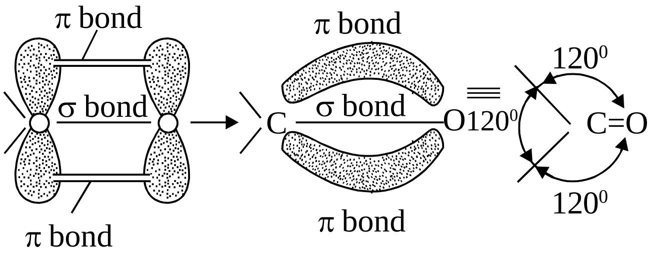
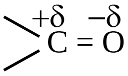
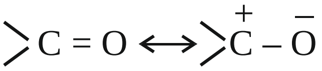


Fig.18.1 Structure of Carbonyl group



$$>\overset{+\delta}{C}=\overset{-\delta}{O}$$

Due to polarity of C – O bond, the aldehydes and ketones are associated with large values of dipole moment (μ =2.3 – 2.8 D) and are more polar than ethers. Due to its polar nature, the carbonyl group can be represented as a resonance hybrid of the following two structures.



$$>C=O \longleftrightarrow >\overset{+}{C}-\overset{-}{O}$$

(I) (II)

COMPARISON BETWEEN $>C=O$ GROUP AND $>C=C<$ BOND

Similarities:

(i) In both the cases ‘C’ atom is sp^2 hybridised.

(ii) Both consist of a σ bond and π bond.

(iii) Both have planar structure.

(iv) Both exhibit addition reactions.

Differences:

(i) $>C=O$ is polar whereas $>C=C<$ is nonpolar.

(ii) $>C=O$ group undergoes nucleophilic addition reactions whereas $>C=C<$ undergoes electrophilic addition reactions.

(iii) Bond length and bond strength are different in both the cases. Due to small size of oxygen C = O length is shorter (1.23A°) than C = C bond length (1.34A°)

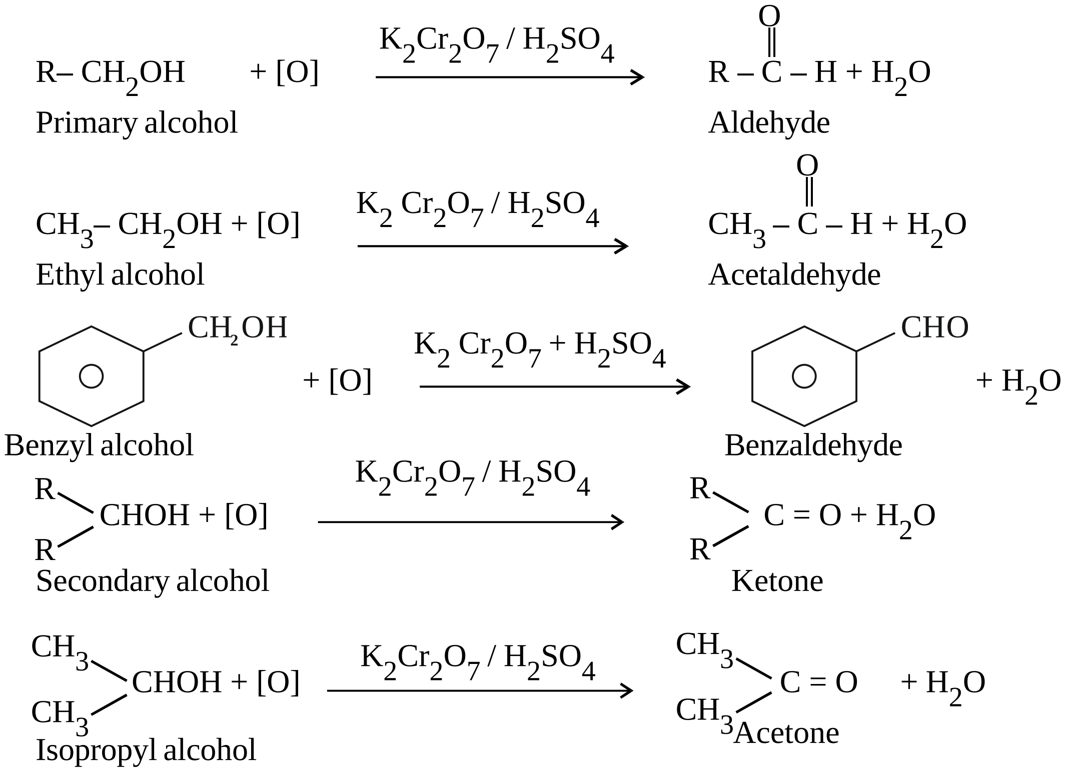
(iv) Geometrical isomerism is possible with C = C whereas no such isomerism in case of $>C=O$ group.

18.5 GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES :

1. From Alcohols

(a) **By oxidation:**

(i) Aldehydes and ketones can be prepared by the oxidation of alcohols. Primary alcohols upon oxidation give aldehydes whereas secondary alcohols give ketones. The most commonly used oxidants are $KMnO_4$ or $K_2Cr_2O_7$ acidified with sulphuric acid.

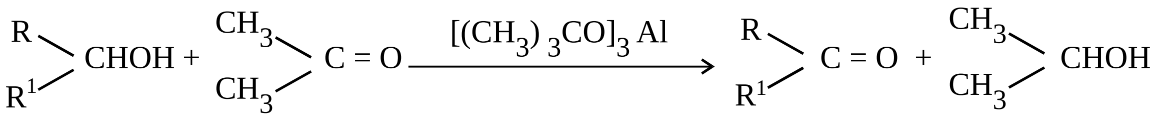


$$\underset{\text{Primary alcohol}}{R-CH_2OH} + [O] \xrightarrow{K_2Cr_2O_7 / H_2SO_4} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3-CH_2OH} + [O] \xrightarrow{K_2Cr_2O_7 / H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

Aldehydes formed by this process are to be removed from the reaction mixture as soon as they are formed. This is because aldehydes are prone to oxidation further to carboxylic acid. The removal of aldehyde from the reaction mixture is usually made by distillation since aldehydes are having lower boiling points than alcohols from which they are formed.

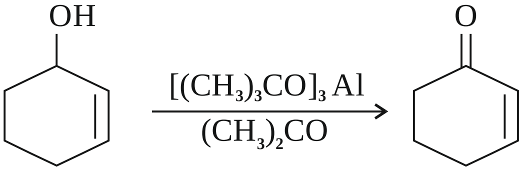
(ii) Ketones can also be prepared from secondary alcohols by an alternate method. The secondary alcohol is refluxed with excess of acetone (solvent) in presence of catalyst aluminium tertiary butoxide [Al(O – tert – Bu)$_3$]producing ketone. This is known as **Oppenauer oxidation.** In this case secondary alcohol is oxidised to ketone whereas acetone is reduced to isopropyl alcohol.



$$\begin{matrix} R \\ R^1 \end{matrix} > CHOH + \begin{matrix} CH_3 \\ CH_3 \end{matrix} > C = O \xrightarrow{[(CH_3)_3CO]_3 Al} \begin{matrix} R \\ R^1 \end{matrix} > C = O + \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CHOH$$

Secondary alcohol Acetone Ketone

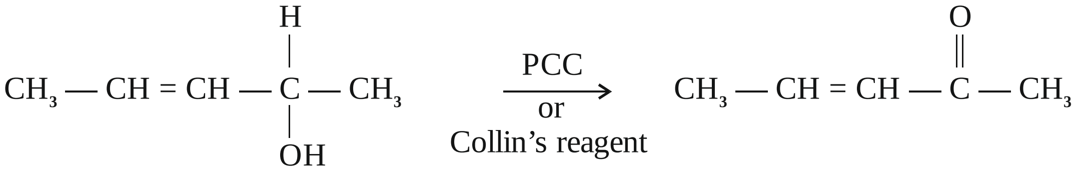
In this case secondary alcohol is oxidised to ketone even in the presence of carbon-carbon double bond whereas acetone is reduced to isopropyl alcohol.



Cyclohex-2-enol Cyclohex-2-enone

(iii) Alcohols can be better oxidised to carbonyl compounds by mild oxidsing agents **Collin's reagent** (chromium trioxide-pyridine complex, ($CrO_3.2C_5H_5N$) and **PCC** i.e.. Pyridinium chlorochromate ($CrO_3.C_5H_5N.HCl$) which are more advantageous than acidified $K_2Cr_2O_7$ as using these reagents oxidation can be stopped at the aldehyde stage preventing further oxidation to carboxylic acids. These reagents do not attack double bonds.

$$CH_3\,CH_2\,CH_2\,OH \xrightarrow[\text{or}\\ \text{PCC}]{\text{Collin's reagent}} CH_3 - CH_2 - CHO$$

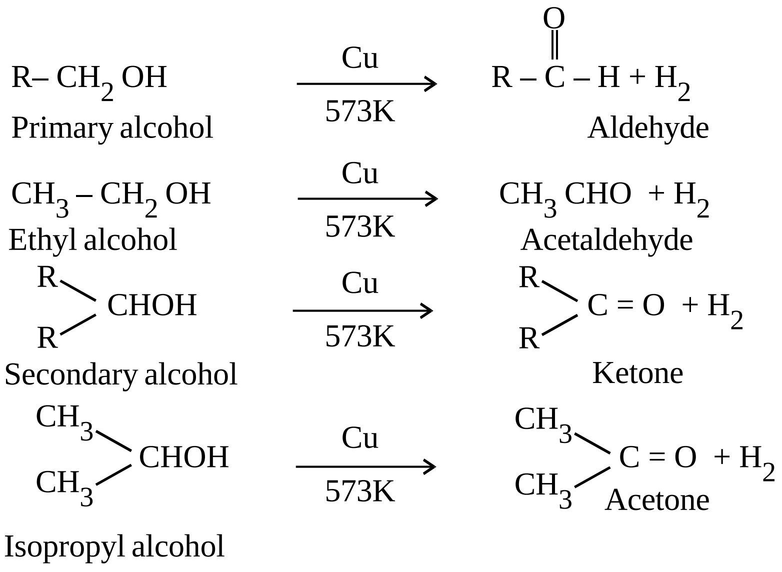


$$CH_3 - CH = CH - \underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}} - CH_3 \xrightarrow[\text{or Collin's reagent}]{\text{PCC}} CH_3 - CH = CH - \overset{O}{\overset{\|}{C}} - CH_3$$

Pent - 3 - en - 2 - ol Pent - 3 - en - 2 - one

(b) By catalytic dehydrogenation of alcohols.

When vapours of alcohols are passed over hot reduced Cu at 573 K, dehydrogenation takes place. Primary alcohols produce aldehydes whereas secondary alcohols produce ketones.



$$R-CH_2OH \xrightarrow[573K]{Cu} R-\overset{\overset{O}{\|}}{C}-H + H_2$$

Primary alcohol → Aldehyde

$$CH_3-CH_2OH \xrightarrow[573K]{Cu} CH_3CHO + H_2$$

Ethyl alcohol → Acetaldehyde

$$R_2CHOH \xrightarrow[573K]{Cu} R_2C=O + H_2$$

Secondary alcohol → Ketone

$$(CH_3)_2CHOH \xrightarrow[573K]{Cu} (CH_3)_2C=O + H_2$$

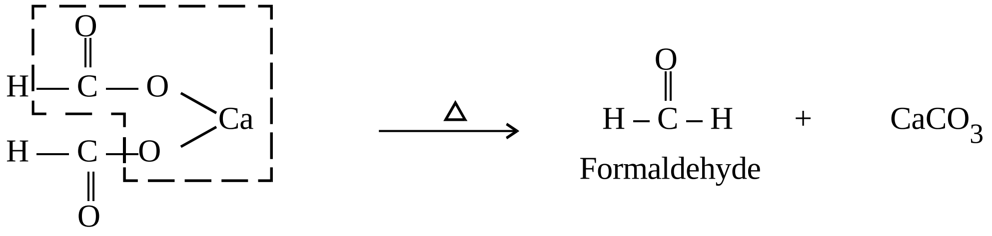
Isopropyl alcohol → Acetone

2. **By dry distillation of Ca-salt of fatty acids.**

Dry distillation of Ca-salts of fatty acids yield aldehydes and ketones.

(a) Aldehydes

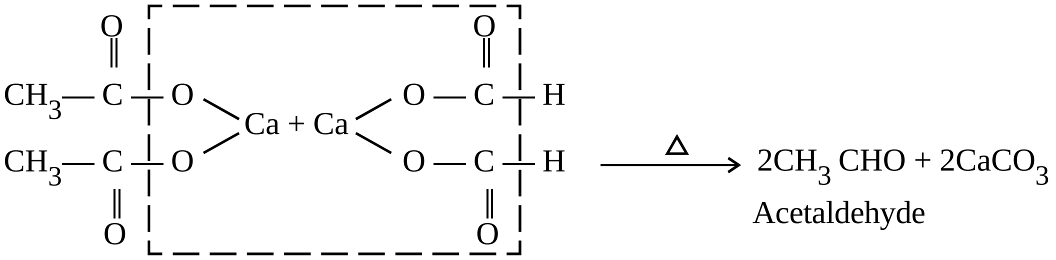
Formaldehyde is obtained by the dry distillation of calcium formate at 670 K.



$$(HCOO)_2Ca \xrightarrow{\Delta} H-\overset{\overset{O}{\|}}{C}-H + CaCO_3$$

Calcium formate → Formaldehyde

A mixture of calcium formate and calcium salt of any other carboxylic acid on dry distillation yields aldehydes.

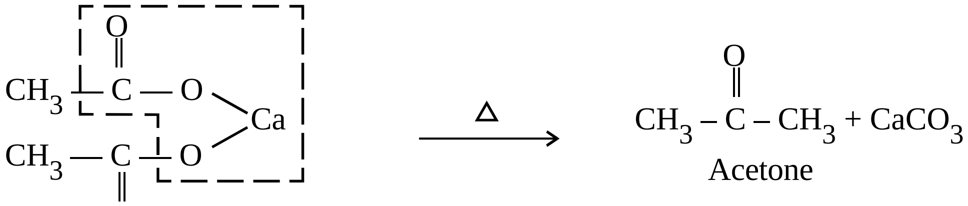


$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{\Delta} 2CH_3CHO + 2CaCO_3$$

Calcium acetate   Calcium formate   Acetaldehyde

(b) Ketones

Calcium salt of any fatty acid other than formic acid on dry distillation yields ketone.



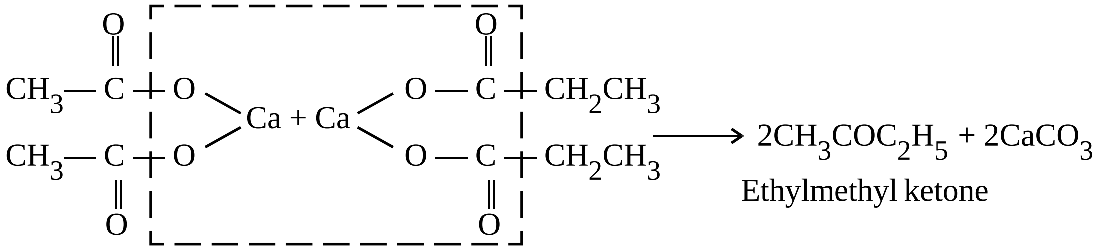
$$(CH_3COO)_2Ca \xrightarrow{\Delta} CH_3-CO-CH_3 + CaCO_3$$

Calcium acetate

Acetone

Mixed ketones can be obtained by dry distillation of a mixture of calcium salt of fatty acids other than HCOOH.

e.g. Ethylmethyl ketone can be obtained by dry distillation of a mixture of calcium acetate and calcium propionate.



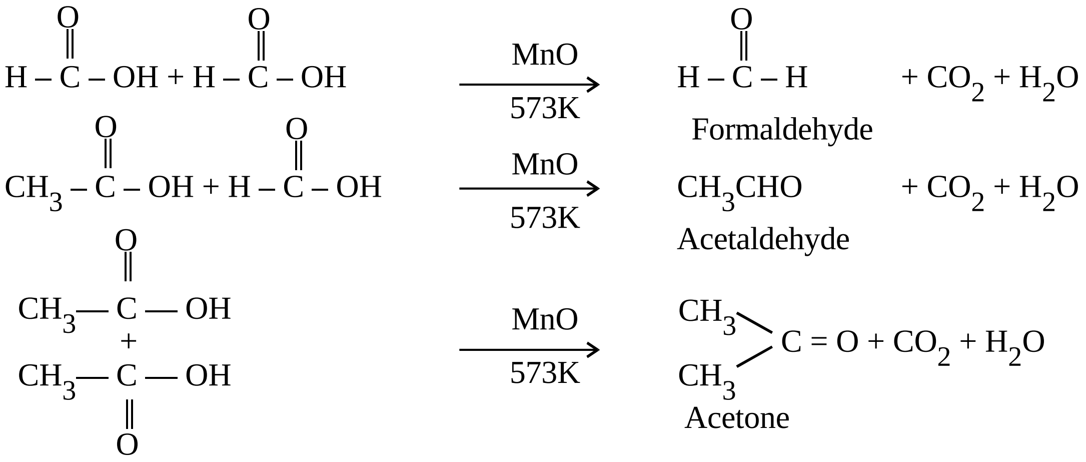
$$(CH_3COO)_2Ca + Ca(OOCCH_2CH_3)_2 \longrightarrow 2CH_3COC_2H_5 + 2CaCO_3$$

Ethylmethyl ketone

However, this method is not suitable for the preparation of mixed ketones. This is because three products are expected when a mixture of two calcium salts are heated. For example, in the above case the dry distillation of a mixture of calcium acetate and calcium propionate yields a mixture of acetone, diethyl ketone and ethylmethyl ketone.

3. From carboxylic acid:

When vapours of fatty acid are passed over heated MnO at 573K, aldehydes or ketones are formed. Formic acid gives formaldyhyde whereas acids other than HCOOH produce ketones. A mixture of formic acid and other fatty acids produces aldehydes.



$$H-CO-OH + H-CO-OH \xrightarrow[573K]{MnO} H-CO-H + CO_2 + H_2O$$

Formaldehyde

$$CH_3-CO-OH + H-CO-OH \xrightarrow[573K]{MnO} CH_3CHO + CO_2 + H_2O$$

Acetaldehyde

$$CH_3-CO-OH + CH_3-CO-OH \xrightarrow[573K]{MnO} (CH_3)_2C=O + CO_2 + H_2O$$

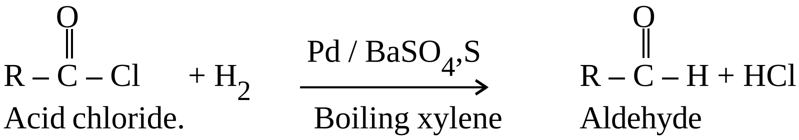
Acetone

4. From acid chlorides.

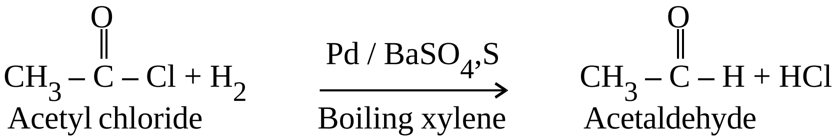
Both aldehydes and ketones can be prepared from acid chlorides.

(a) Aldehydes:

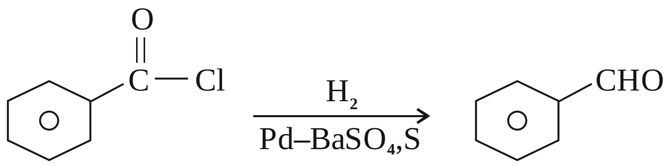
Acid chlorides can be reduced to aldehydes with H_2 in boiling xylene using palladium as catalyst supported by $BaSO_4$ and partially poisoned by addition of sulphur or quinoline.



$$\underset{\text{Acid chloride.}}{R-\overset{\overset{\large O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{Pd / BaSO_4,S} \underset{\text{Aldehyde}}{R-\overset{\overset{\large O}{\|}}{C}-H} + HCl$$



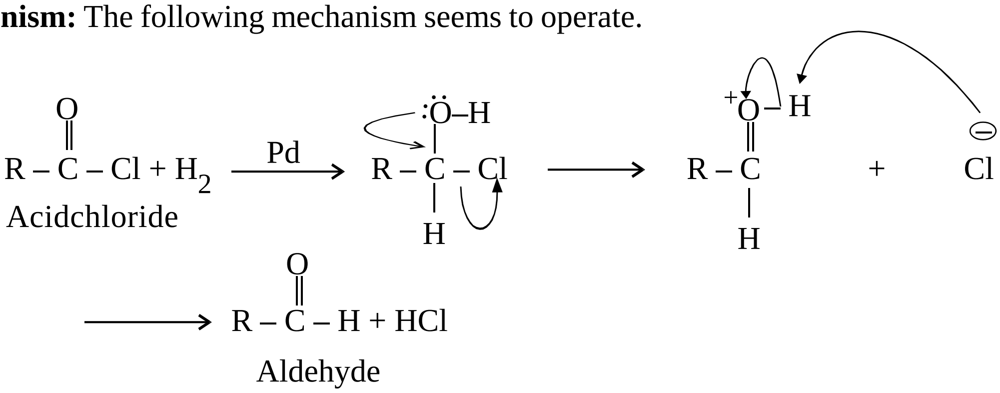
$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{\large O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{Pd / BaSO_4,S} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\large O}{\|}}{C}-H} + HCl$$



Benzoyl chloride Benzaldehyde

The partial poisoning of catalyst is made in order to avoid the further reduction of aldehyde to primary alcohol. This reaction is known as **Rosenmund reduction.**

Mechanism: The following mechanism seems to operate.



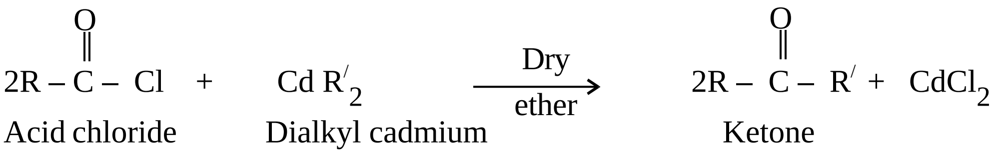
$$\underset{\text{Acidchloride}}{R-\overset{\overset{\large O}{\|}}{C}-Cl} + H_2 \xrightarrow{Pd} R-\overset{\overset{:\ddot{O}-H}{|}}{\underset{\underset{H}{|}}{C}}-Cl \longrightarrow R-\overset{\overset{^{+}O-H}{\|}}{\underset{\underset{H}{|}}{C}} + \overset{\ominus}{Cl}$$

$$\longrightarrow \underset{\text{Aldehyde}}{R-\overset{\overset{\large O}{\|}}{C}-H} + HCl$$

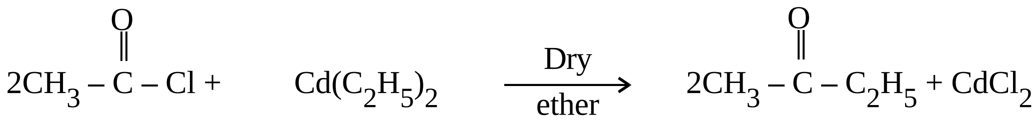
However, formaldehyde can not be prepared by this method since formyl chloride HCOCl is unstable at room temperature.

(b) Ketones:

Ketones can be prepared easily by the action of dialkyl cadmium on acid chlorides.

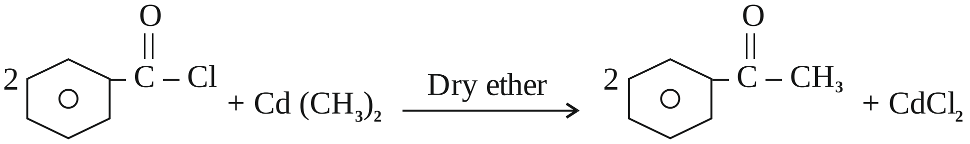


$$\underset{\text{Acid chloride}}{2R-\overset{\overset{\large O}{\|}}{C}-Cl} + \underset{\text{Dialkyl cadmium}}{Cd\,R'_2} \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ketone}}{2R-\overset{\overset{\large O}{\|}}{C}-R'} + CdCl_2$$



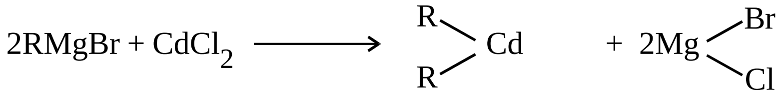
$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + Cd(C_2H_5)_2 \xrightarrow[\text{ether}]{\text{Dry}} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5 + CdCl_2$$

Acetyl chloride Diethyl cadmium Ethylmethyl ketone.



Benzoyl chloride Dimethylcadimium Acetophenone

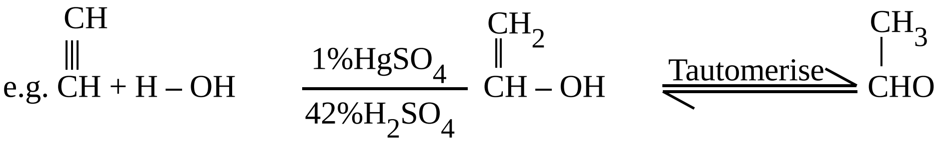
Dialkyl cadmium can be prepared from Grignard's reagent by the action of $CdCl_2$



Dialkyl cadmium

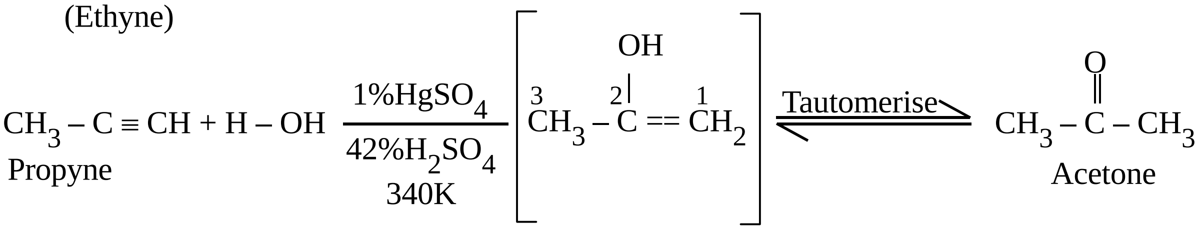
5. **From alkynes:**

Hydration of alkynes in presence of $HgSO_4$ and H_2SO_4 yields enols which readily tautomerise giving aldehydes or ketones. The addition of water to unsymmetrical alkynes is in accordance with Markownikoff's rule.



$$\text{e.g. } \overset{\overset{\displaystyle CH}{|||}}{CH} + H-OH \xrightarrow[\substack{42\%H_2SO_4\\340K}]{1\%HgSO_4} \overset{\overset{\displaystyle CH_2}{\|}}{CH}-OH \xrightleftharpoons{\text{Tautomerise}} \overset{\overset{\displaystyle CH_3}{|}}{CHO}$$

Acetylene (Ethyne) Vinyl alcohol Acetaldehyde



$$CH_3-C\equiv CH + H-OH \xrightarrow[\substack{42\%H_2SO_4\\340K}]{1\%HgSO_4} \left[\overset{3}{C}H_3-\overset{\overset{\displaystyle OH}{|}}{\overset{2}{C}}=\overset{1}{C}H_2\right] \xrightleftharpoons{\text{Tautomerise}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

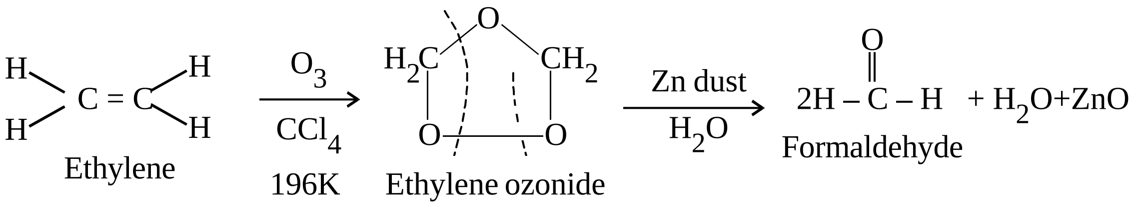
Propyne Acetone

Prop - 1-en-2-ol

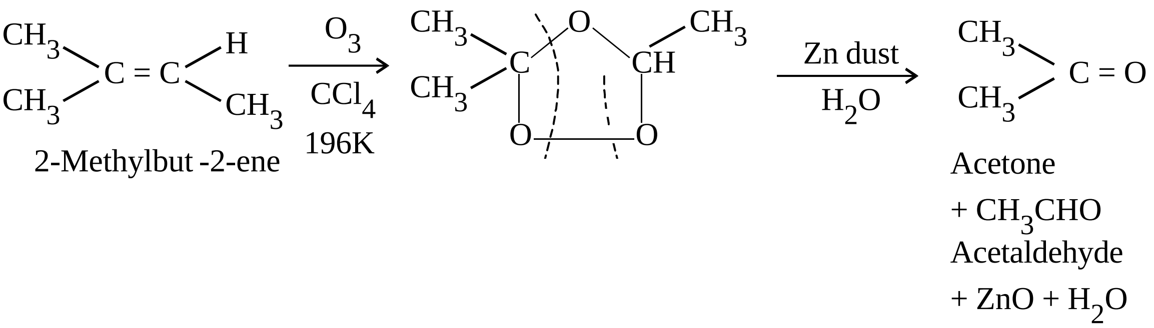
Note: However, aldehydes other than acetaldehyde cannot be prepared by this method.

6. **From alkenes:**

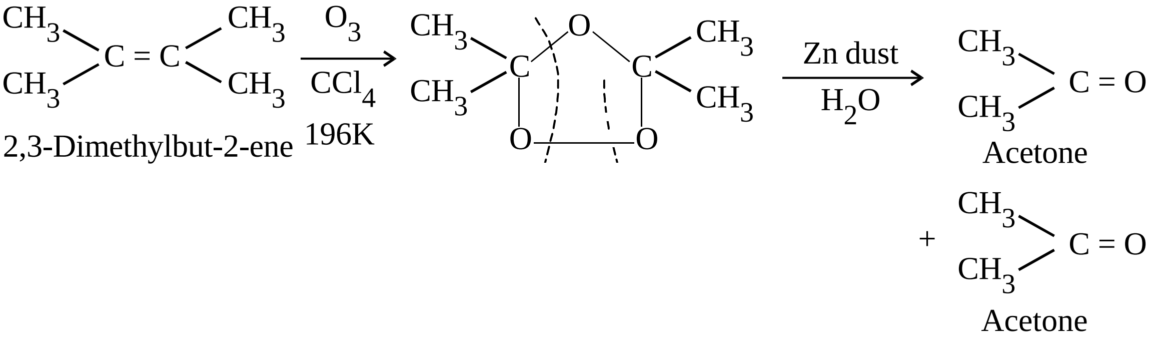
Alkenes add on a molecule of ozone forming the corresponding ozonides. The ozonides are highly unstable due to the peroxide linkage so that these are shortlived, and explosive in nature. On boiling with zinc dust and water ozonides undergo reductive cleavage producing aldehydes or ketones or a mixture of both depending on the substitution pattern of the alkene. Zinc dust helps in removing H_2O_2, else the aldehydes or ketones formed may be oxidised to carboxylic acids.



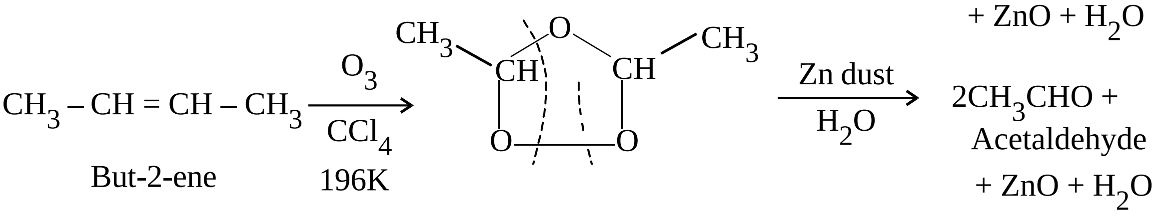
Ethylene 196K Ethylene ozonide Formaldehyde



2-Methylbut -2-ene 196K Acetone + CH_3CHO Acetaldehyde + ZnO + H_2O

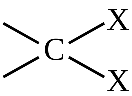


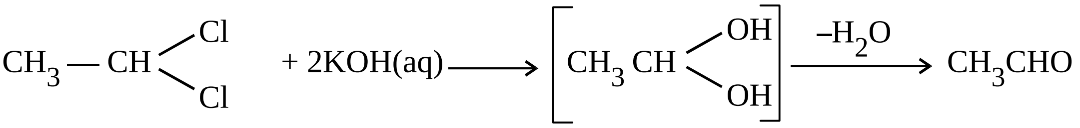
2,3-Dimethylbut-2-ene 196K Acetone + Acetone + ZnO + H_2O



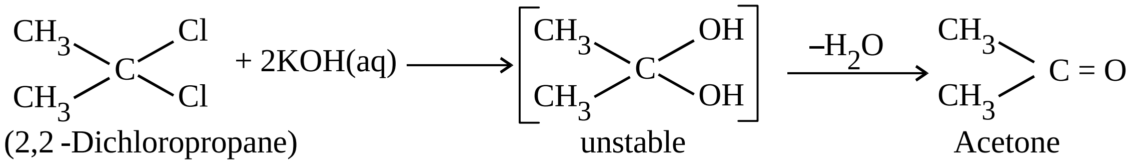
But-2-ene 196K $2CH_3CHO$ + Acetaldehyde + ZnO + H_2O

7. **From gem - Dihalides:**

A gem-dihalide is a compound containing two halogen atoms attached to the same carbon.  (X = Cl, Br). The hydrolysis of a gem-dihalide yields a carbonyl group. Thus, 1.1 dihaloalkanes on hydrolysis with aqueous KOH yield aldehydes whereas 2, 2-dihaloalkanes under similar condition yield ketones.



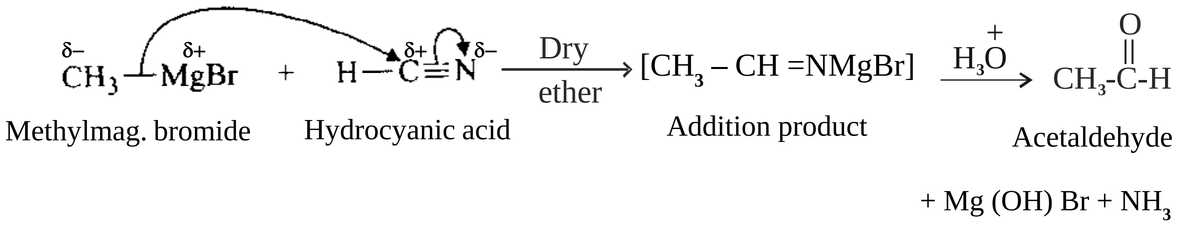
(1, 1 -Dichloroethane) unstable Acetaldehyde



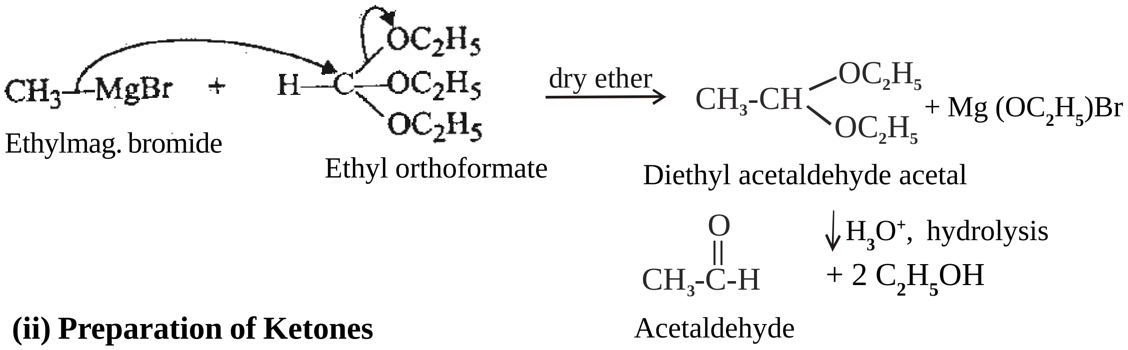
8. From Grignard Reagent

(i) Preparation of Aldehydes

(a) When Grignard reagents react with hydrocyanic acid (HCN) and the products are hydrolysed, aldehydes are formed. For example,



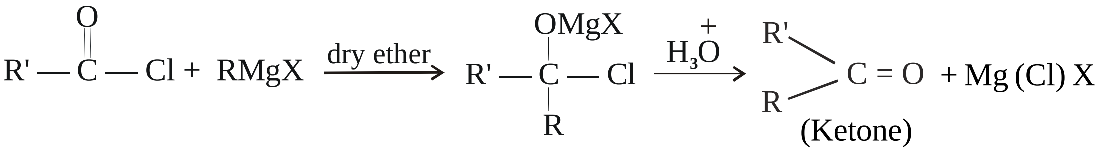
(b) Aldehydes can also be prepared by the action of Grignard reagents on orthoformic esters. For example,



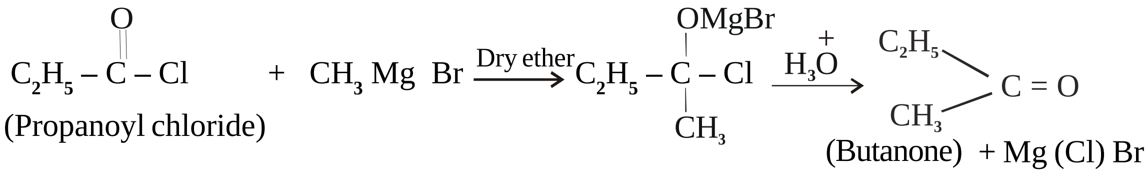
(ii) Preparation of Ketones

(a) From acid chlorides

Acid chlorides react with Grignard reagents in equimolecular proportion (*why* ?) and the products formed on hydrolysis with dilute mineral acid yield ketones. For example,



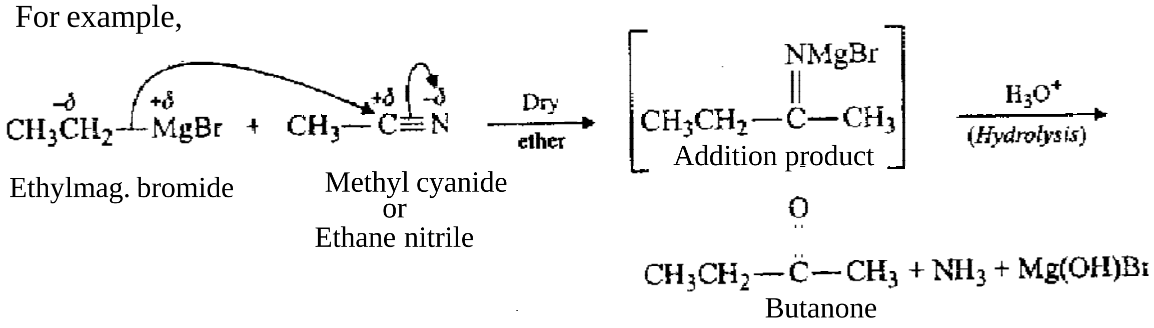
Choosing R, R′ suitable ketones can be prepared using Grignard reagents. For example, methyl magnesium bromide can react with propanoyl chloride (R′ = C_2H_5) to give ethyl methyl ketone (butanone) after hydrolysis of the intermediate addition product with dilute mineral acid.



(b) From nitriles

Ketones can be prepared by the action of a suitable Grignard reagent on an alkane nitrile followed by acid hydrolysis of the intermediate addition product.

For example,



18.6 SPECIAL METHODS OF PREPARATION FOR AROMATIC CARBONYL COMPOUNDS :

A. Preparation of Benzaldehyde

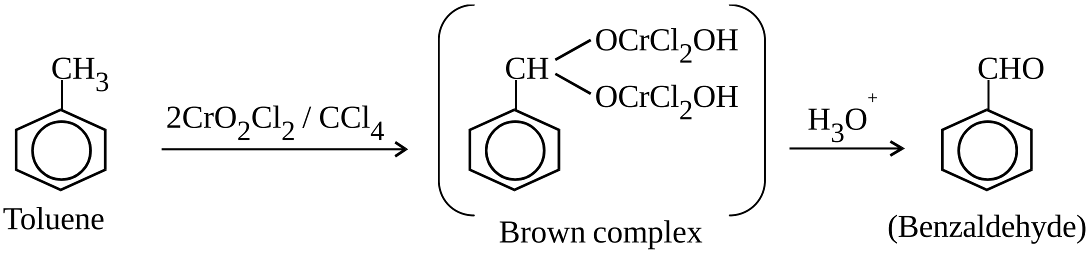
Benzaldehyde may be prepared by the following methods which are applicable to aromatic aldehydes in general

(1) Oxidation of Toluene

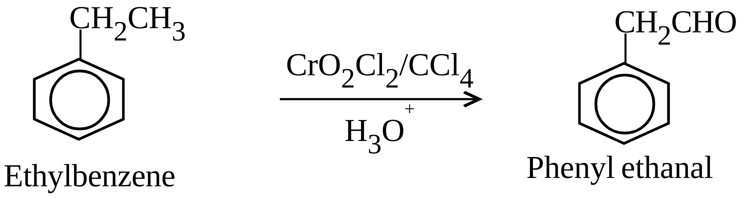
(a) By Etard's reaction :

This reaction involves the preparation of benzaldehyde by the oxidation of toluene.

Toluene, when treated with chromyl chloride (CrO_2Cl_2) in presence of CCl_4 or CS_2, a brown complex is precipitated as intermediate, which on hydrolysis gives benzaldehyde. Here, chromyl chloride is used as oxidising agent. The reaction is called **Etard's reaction.**

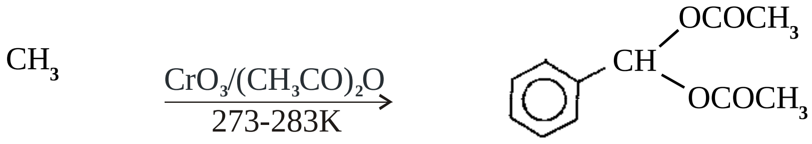


In case of derivatives of benzene having side chain longer than —CH_3, the end carbon is oxidised by chromyl chloride to —CHO group. For example,



(b) Oxidation by Chromium trioxide

Other than Etard's reaction benzaldehyde can also be prepared by the oxidation of toluene with chromium trioxide in acetic anhydride. The gem-diacetate first formed is isolated which upon hydrolysis with dil.alkali or dil. HCl or dil. H_2SO_4 yield benzaldehyde.



toluene gem-diacetate

$$\xrightarrow[\text{(hydrolysis)}]{H_3\overset{+}{O},\ \Delta} CHO + 2\ CH_3COOH$$

benzaldehyde

(2) From Acid Chlorides (Rosenmund Reduction)

Benzaldehyde may be prepared by passing hydrogen gas through boiling xylene solution of benzoyl chloride in the presence of palladium catalyst supported over $BaSO_4$ and partially poisoned by the addition of sulphur or quinoline.

$$\overset{\overset{O}{\|}}{C}-Cl + H_2 \xrightarrow[\text{Boiling xylene}]{Pd\text{-}BaSO_4,\ S} CHO + HCl$$

benzoyl chloride benzaldehyde

(3) From nitriles (Stephen reduction)

When an ethereal solution of benzonitrile is reduced with stannous chloride in presence of hydrogen chloride gas at room temperature, benzaldimine hydrochloride is precipitated. This upon hydrolysis with boiling water gives benzaldehyde.

$$C \equiv N + 2\,[H] + HCl \xrightarrow[\text{290-295K}]{\text{Dry ether}} CH = NH.\,HCl$$

benzonitrile benzaldimine hydrochloride

$$\xrightarrow[\Delta]{H_3O^+} CHO + NH_4Cl$$

benzaldehyde

This process is called **Stephen reduction.**

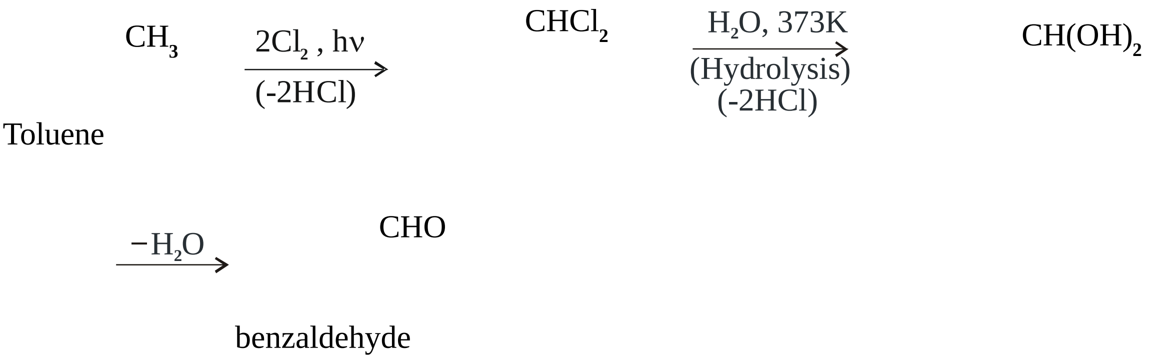
Nitrites can also be selectively reduced by diisobutylaluminium hydride (DIBAL – H) to imines followed by hydrolysis to aldehydes.

$$RCN \xrightarrow[\text{2. } H_2O]{\text{1. AlH (i-Bu)}_2} RCHO$$

$$CH_2 = CH - CH_2 - CN \xrightarrow[\text{2. } H_2O]{\text{1. AlH (i-Bu)}_2} CH_2 = CH - CH_2 - CHO$$

(4) By side chain halogenation followed by hydrolysis

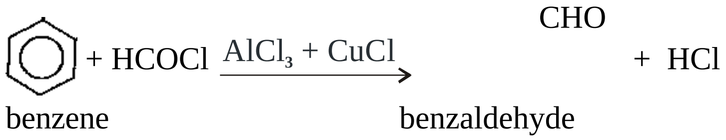
Side chain chlorination of toluene gives benzal chloride which upon hydrolysis gives benzaldehyde. This method is used for the manufacture of benzaldehyde.



(5) By Gattermann – Koch reaction

When a mixture of carbon monoxide and HCl gas is passed through a solution of benzene in nitrobenzene at 323K in presence of a catalyst consisting of anhydrous $AlCl_3$ and a small amount of CuCl, benzaldehyde is formed.

$$CO + HCl \longrightarrow \underset{\text{Formylchloride (unstable)}}{[HCOCl]}$$

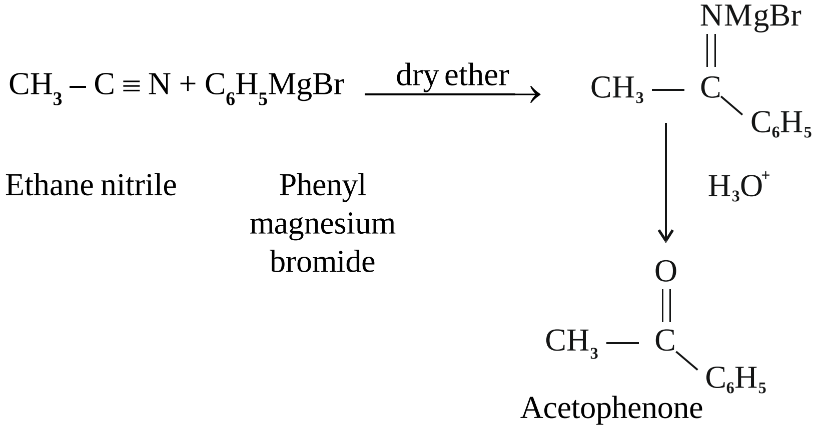


This reaction is known as **Gattermann - Koch reaction**.

B. Preparation of Aryl Ketones :

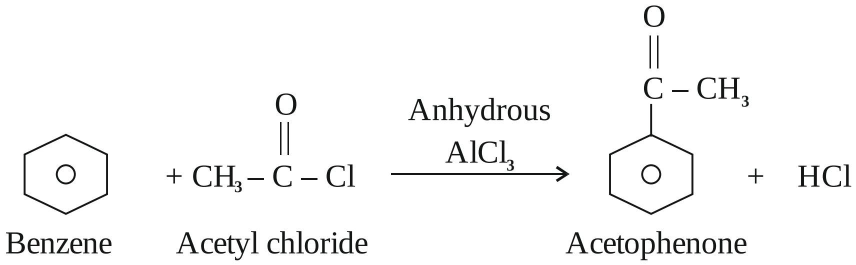
(1) From Nitriles :

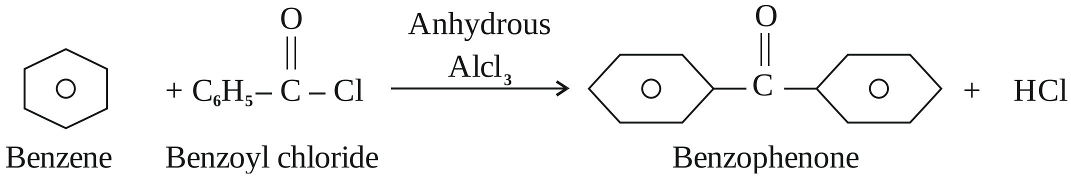
When phenyl magnesium bromide (Grignard reagent) reacts with an alkane nitrile in the presence of dry ether, an intermediate is formed which on acid hydrolysis produces aryl keton.

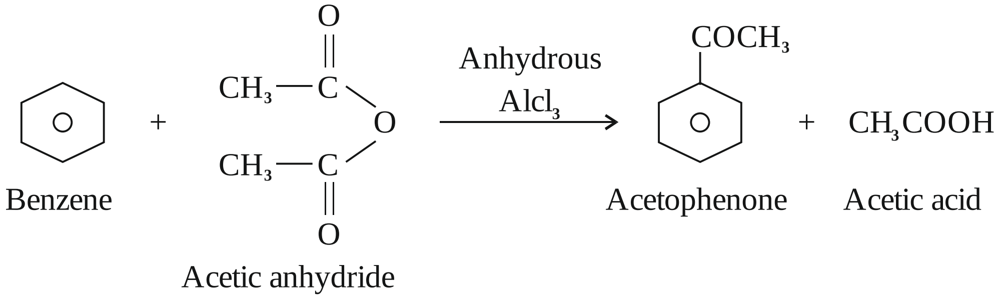


(2) From benzene or substituted benzene by Friedel-Crafts acylation reaction :

Friedel-Crafts acylation reaction involves the conversion of benzene or substituted benzene to aryl ketone on reaction with acid chloride or acid anhydride in the presence of a Lewis acid as catalyst like anhydrous aluminium chloride.





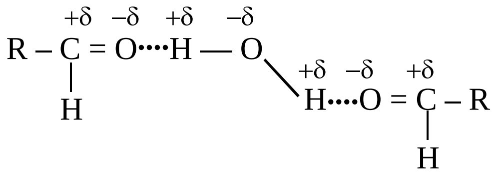


18.7 PROPERTIES OF ALDEHYDES AND KETONES :

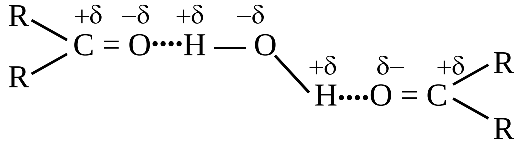
(a) Physical Properties:

1. **Physical State:** Formaldehyde is a gas at room temperature. Other aldehydes and ketones up to C_{11} are liquids and higher ones are solids.
2. **Odour:** Lower aldehydes have unpleasant odour whereas higher members have pleasant odour. Ketones are generally sweet smelling.
3. **Solubility:** Lower members are soluble is water, but solubility decreases with increase in molecular mass. However, all aldehydes and ketones are soluble is organic solvents like alcohol, ether etc.

   Explanation : The lower members are capable of forming hydrogen bond with water. So they are soluble in water.



Hydrogen bonding of aldehydes with water



Hydrogen bonding of ketones with water

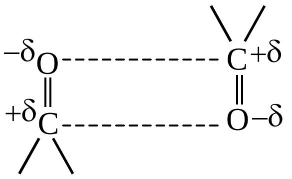
As the hydrocarbon portion of alkyl group increases with increase in molecular mass, the solubility rapidly decreases since the hydrogen bonding is prevented.

4. **Boiling poiont** : Boiling points of aldehydes and ketones are more than those of alkanes but less than those of alcohols of comparable molecular mass. The boiling points of ketones are slightly higher than those of isomeric aldehydes.

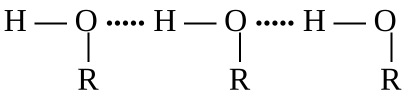
e.g	**Compound**	**Molecular mass**	**Boiling point(K)**
	$CH_3CH_2CH_2CH_3$	58	309
	CH_3CH_2CHO	58	322
	$CH_3CH_2CH_2OH$	60	371
	CH_3COCH_3	58	329

Explanation:

Boiling point depends upon molecular association. The stronger the intermolecular forces the more is the boiling point. In case of alkanes the molecules are held together by weak vander Waal's forces. But in case of aldehydes and ketones the association is due to electrostatic attraction between two opposite ends of carbonyl dipoles.



(Dipole-dipole interaction in case of aldehydes and ketones)



(Hydrogen bonding in case of alcohols)

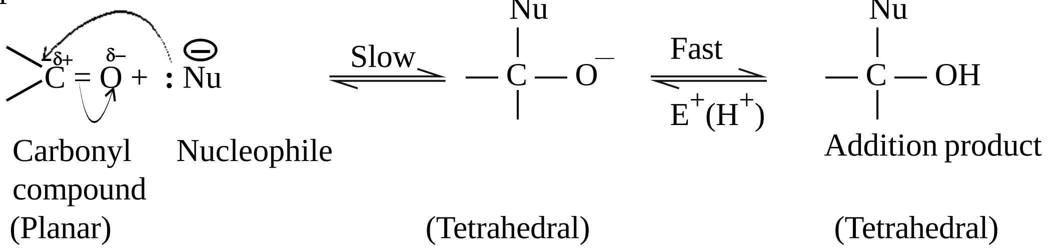
Thus, the boiling points of aldehydes and ketones are more than those of alkanes. In case of alcohols there is intermolecular hydrogen bonding which is stronger than dipole-dipole interaction. Hence, the boiling points of alcohols are more than those of aldehydes and ketones.

In case of ketones the carbonyl group is attached to two electron releasing alkyl groups. As a result the carbonyl group in ketones becomes more polar than in isomeric aldehyde. The more the polarity the more is the dipole-dipole interaction. Thus, ketones boil at comparatively higher temperature.

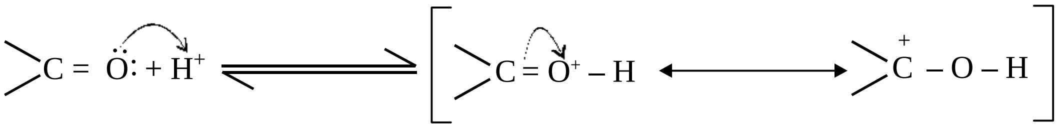
(b) Chemical Properties:

(1) Nucleophilic addition reactions: (AdN)

These reactions are due to the presence of a polar carbonyl group. The attacking agent is a nucleophile (*nucleus loving*) and the reaction is of addition type. Since oxygen atom is more electronegative, there develops an infinitesimal small positive charge over 'C' atom and a small -ve charge over 'O' atom of the carbonyl group. The nucleophile attacks at the +vely charged carbonyl carbon and as a result the double bond breaks in the direction of 'O' atom resulting in the formation of an anion. The anion thus formed takes up a proton from the solvent (usually water) or from the reagent forming the addition product. The reaction may be represented as follows.



Nucleophilic addition reactions are usually carried out in weakly acidic medium in case of weak nucleophiles like NH_3 or its derivatives. The protonation of 'O' atom of carbonyl group in presence of acids increases the positive charge on the carbon atom thereby facilitating the attack of the weak nucleophile.



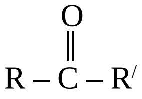
(2) Relative reactivities of Aldehydes and Ketones towards nucleophilic addition reactions.

Aldehydes are found to be more reactive than the ketones. This can be explained by two effects i.e. electronic effects (resonance effect and inductive effect) and steric effect.

A. Aliphatic aldehydes and ketones.

(i) Inductive effect:

Alkyl groups are electron releasing. The presence of alkyl group at the carbonyl carbon decreases the magnitude of the positive charge over 'C' atom thereby decreasing its tendency to accept the nucleophile. Thus, the more the number of alkyl groups attached to the carbonyl group the lesser is its reactivity towards nucleophilic addition reaction. The reactivity basing upon +I effect thus follows the order.

HCHO > RCHO > 
$R-\overset{\overset{O}{\|}}{C}-R'$

Formaldehyde Aldehyde Ketone

Again, presence of electron withdrawing groups at the carbonyl carbon (-I effect) increases the magnitude of the positive charge over 'C' atom thereby facilitating the nucleophilic attack. Thus, reactivity of substituted acetaldehyde follows the order,

$NO_2\,CH_2\,CHO$ > $ClCH_2\,CHO$ > CH_3CHO

Nitroacetaldehyde Chloroacetaldehyde Acetaldehyde.

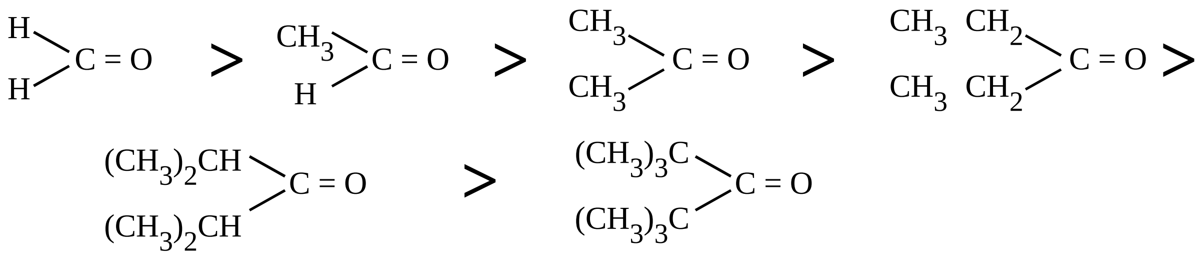
Further, the size of the alkyl groups also affects the reactivity. With increase in size of the alkyl group the reactivity decreases. Thus, the order of reactivity of various ketones is as follows.

CH_3COCH_3 > $CH_3\,COCH_2CH_3$ > $CH_3CH_2\,COCH_2CH_3$

Acetone. Ethylmethyl ketone Diethyl ketone.

(ii) Steric effect:

The approach of the nucleophile is prevented by the presence of bulky alkyl groups at the carbonyl carbon. This effect is known as *steric effect*. The attack of the nucleophile at the carbonyl carbon becomes more and more difficult as the number and size of the alkyl groups increase. Hence, the reactivity of aldehydes and ketones follows the following order,

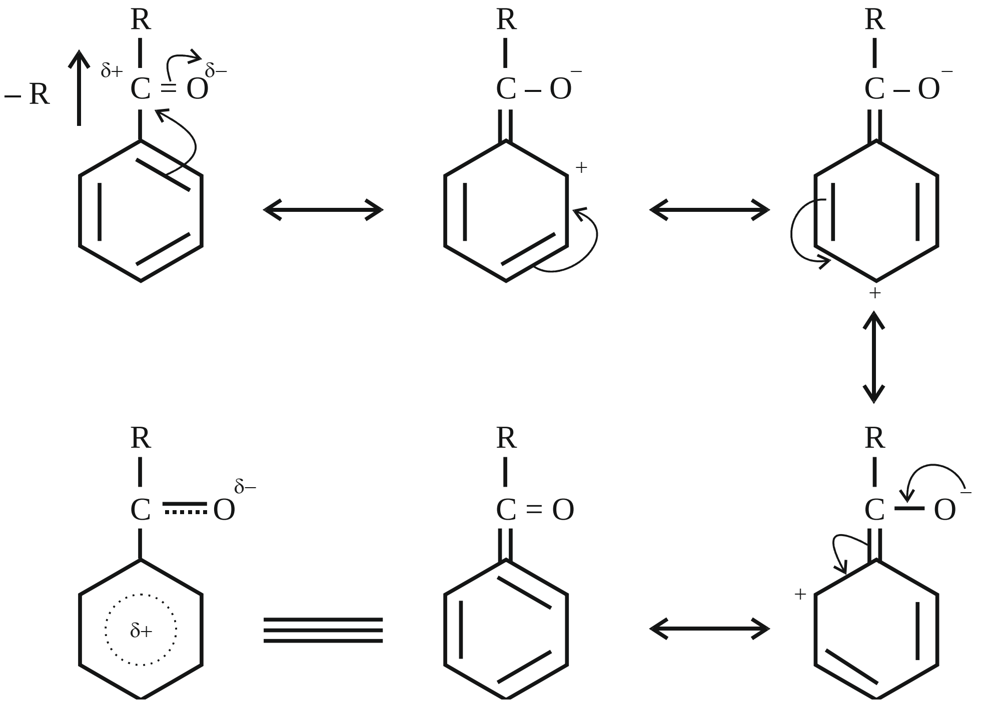


Di-isopropyl ketone

Ditert-butyl ketone

B. Aromatic aldehydes and ketone :

(i) Aromatic aldehydes and ketones are less reactive towards nucleophilic addition reactions than the aliphatic ones due to negative resonance effect (–R) decreasing the nucelophilic character of the carbonyl carbon atom as carbony group is an electron withdrawing group. This in turn decreases its tendency to be attacked by the nucleophile.



Resonance hybrid

Resonating structures

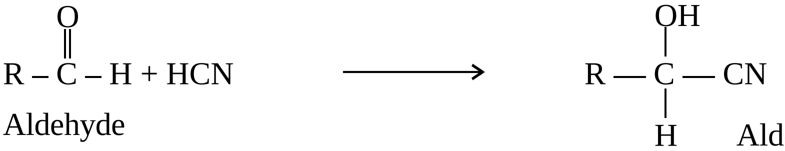
(ii) Again aromatic aldehydes are more reactive than aryl ketones due to +I effect of the alkyl group.

$$C_6H_5CHO \; > \; C_6H_5COCH_3 \; > \; C_6H_5COC_6H_5$$

3. Examples of Nucleophilic addition reactions :

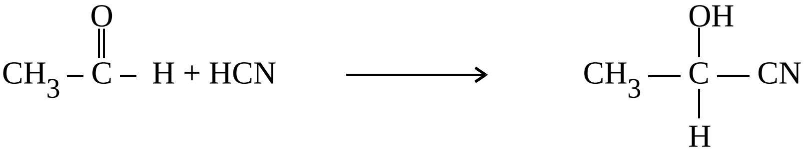
(a) Addition of HCN

Both aldehydes and ketones react with HCN forming the corresponding cyanohydrins.



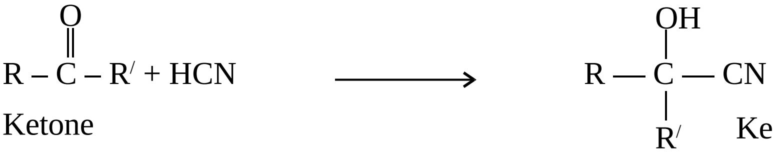
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \longrightarrow R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN$$

Aldehyde   Aldehyde cyanohydrin



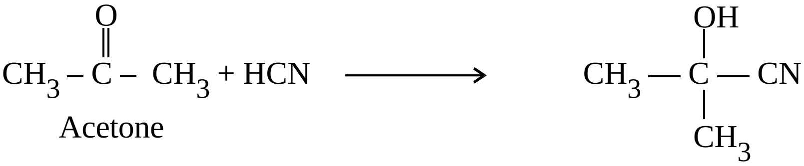
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \longrightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN$$

Acetaldehyde.   Acetaldehyde cyanohydrin.



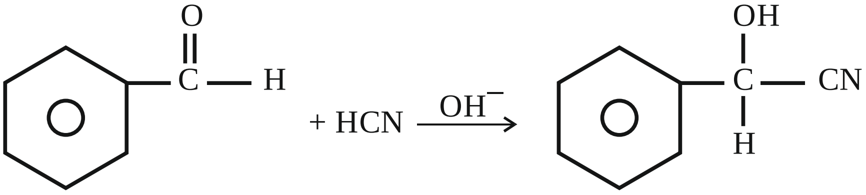
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + HCN \longrightarrow R-\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN$$

Ketone   Ketone cyanohydrin



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCN \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN$$

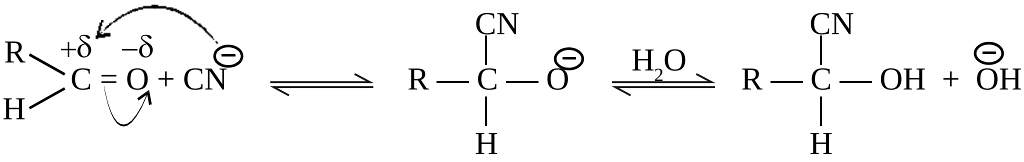
Acetone   Acetone cyanohydrin



Benzaldehyde   Benzaldehyde Cyanohydrin

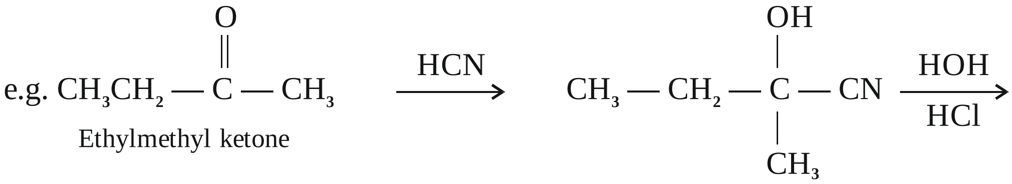
Since HCN is a poisonous substane the reaction is often carried out by mixing the carbonyl compound with aqueous sodium cyanide and then slowly acidifying the solution by adding mineral acid. This reaction is a base catalyzed reaction proceeding through the following mechanism.

$$HCN + OH^{\ominus} \rightleftharpoons CN^{\ominus} + H_2O$$



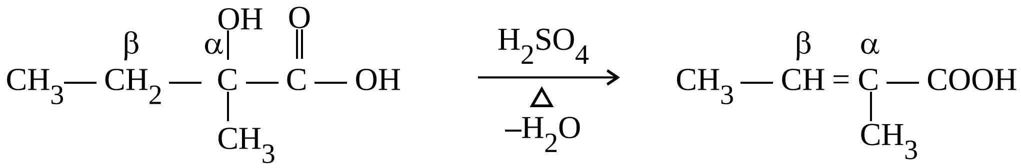
Aldehyde.   Nucleophile   Cyanohydrin

Cyanohydrins are nitriles. They, upon hydrolysis yield α-hydroxy acids which undergo subsequent dehydration forming α, β unsaturated acids.



$$\text{e.g. } CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{HCN} CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN \xrightarrow[HCl]{HOH}$$

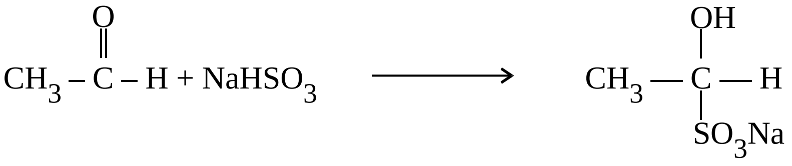
Ethylmethyl ketone



$$\underset{\alpha\text{- hydroxy acid}}{CH_3-\overset{\beta}{CH_2}-\overset{\overset{OH}{\alpha|}}{\underset{CH_3}{\underset{|}{C}}}-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\text{–}H_2O]{H_2SO_4,\ \Delta} \underset{\alpha,\ \beta\text{-unsaturated acid}}{CH_3-\overset{\beta}{CH}=\overset{\alpha}{\underset{CH_3}{\underset{|}{C}}}-COOH}$$

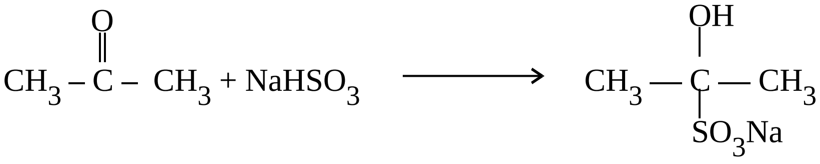
(b) Addition of $NaHSO_3$

Both aldehydes and ketones (specially methyl ketones) react with $NaHSO_3$ forming the corresponding crystalline bisulphite compounds.



$$CH_3-\overset{\overset{O}{\|}}{C}-H+NaHSO_3 \longrightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{SO_3Na}{|}}{C}}-H$$

Acetaldehyde sodium bisulphite

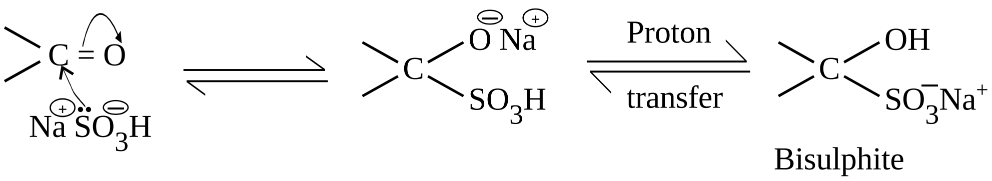


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+NaHSO_3 \longrightarrow CH_3-\overset{\overset{OH}{|}}{\underset{\underset{SO_3Na}{|}}{C}}-CH_3$$

Acetone sodium bisulphite

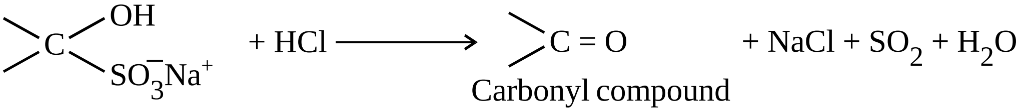
The reaction is carried out by adding carbonyl compound to a concentrated aqueous solution of sodium bisulphite when a crystalline solid bisulphite compound separates out.

Machanism: There is initial nucleophilic attack by bisulphite ion on carbonyl carbon followed by proton transfer.

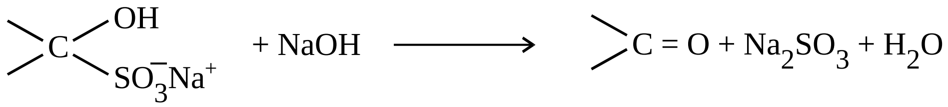


Bisulphite compound

The crystalline bisulphite addition product can be decomposed with dilute mineral acids or aqueous alkalies to regenerate the original aldehyde or ketone.



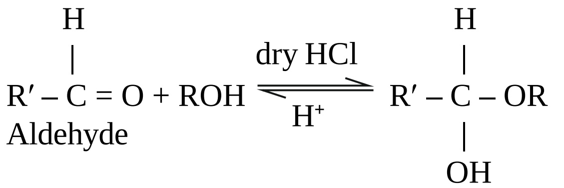
Carbonyl compound



The reaction is employed for separation and purification of carbonyl compounds from noncarbonyl impurities or compounds.

(c) Reaction with Alcohols

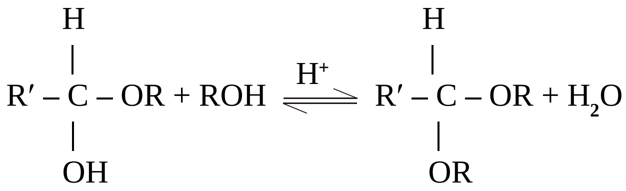
Alcohols add to the carbonyl group of aldehydes in the presence of dry HCl gas acid to yield hemiacetals, which further react with alcohols to give a gemdialkoxy compound known as acetal.



$$R'-\overset{\overset{H}{|}}{C}=O + ROH \underset{H^+}{\overset{\text{dry HCl}}{\rightleftharpoons}} R'-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-OR$$

Aldehyde

Hemi acetal (Unstable)



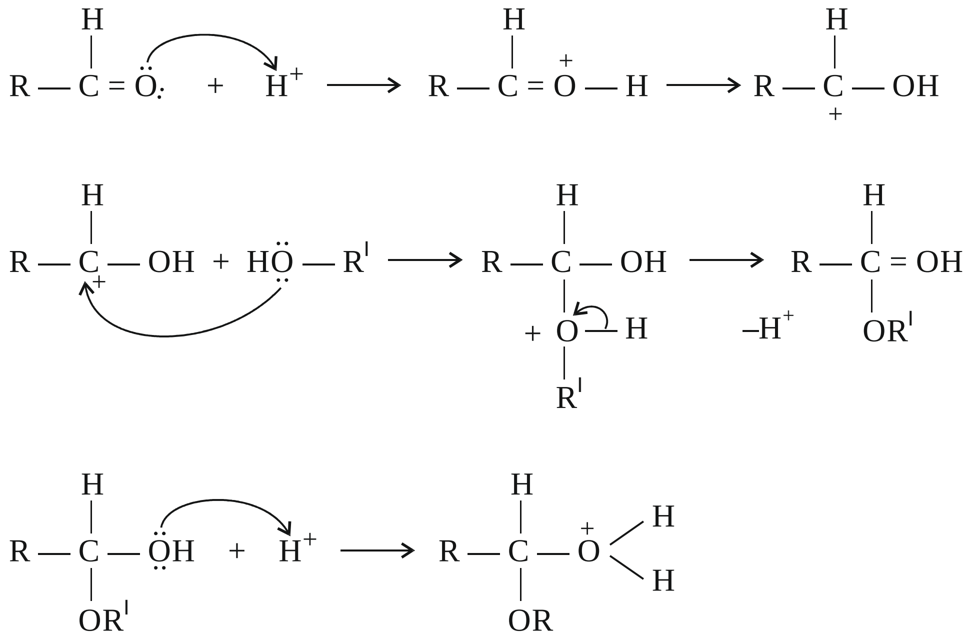
$$R'-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-OR + ROH \overset{H^+}{\rightleftharpoons} R'-\underset{\underset{OR}{|}}{\overset{\overset{H}{|}}{C}}-OR + H_2O$$

Hemiacetal (An alcohol)

Acetal (An ether)

MECHANISM

This reaction proceeds through the following steps.



(i)

$$R-\overset{\overset{H}{|}}{C}=\ddot{O}: + H^+ \longrightarrow R-\overset{\overset{H}{|}}{C}=\overset{+}{O}-H \longrightarrow R-\underset{+}{\overset{\overset{H}{|}}{C}}-OH$$

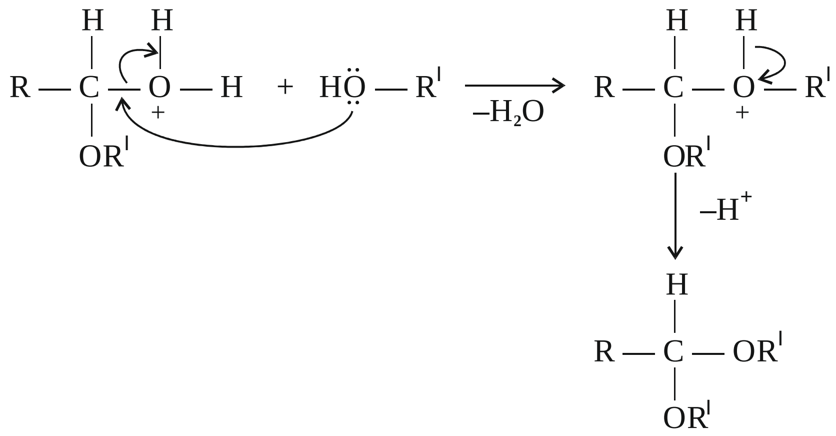
(ii)

$$R-\underset{+}{\overset{\overset{H}{|}}{C}}-OH + H\ddot{O}-R' \longrightarrow R-\underset{\underset{+\,O-H}{|}}{\overset{\overset{H}{|}}{C}}-OH \xrightarrow[-H^+]{} R-\underset{\underset{OR'}{|}}{\overset{\overset{H}{|}}{C}}=OH$$

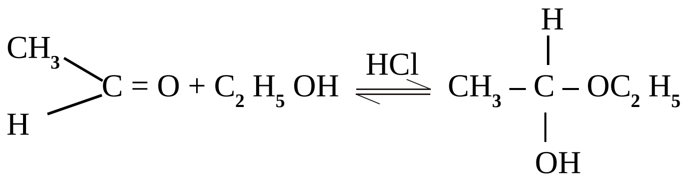
(iii)

$$R-\underset{\underset{OR'}{|}}{\overset{\overset{H}{|}}{C}}-\ddot{O}H + H^+ \longrightarrow R-\underset{\underset{OR}{|}}{\overset{\overset{H}{|}}{C}}-\overset{+}{O}\begin{matrix}H\\H\end{matrix}$$

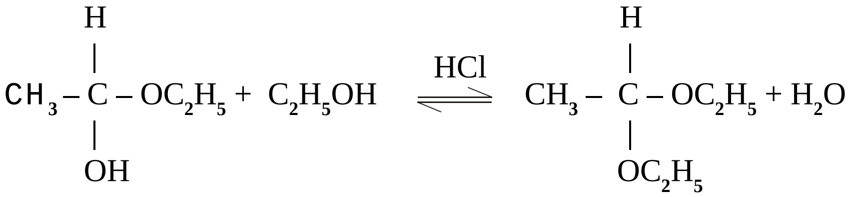
(iv)



For example, acetaldehyde is converted to acetal as follows. The forward reaction is catalysed by dry HCl, while the reverse reaction is catalysed by aqueous HCl.



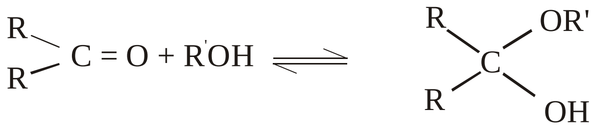
Acetaldehyde Hemiacetal



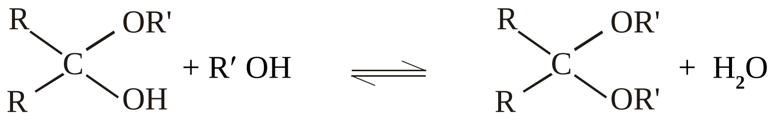
$$CH_3-\underset{OH}{\overset{H}{C}}-OC_2H_5 + C_2H_5OH \xrightleftharpoons{HCl} CH_3-\underset{OC_2H_5}{\overset{H}{C}}-OC_2H_5 + H_2O$$

Hemiacetal Acetaldehyde diethyl acetal

Ketones would react similarly to form **hemiketals** and **ketals**.

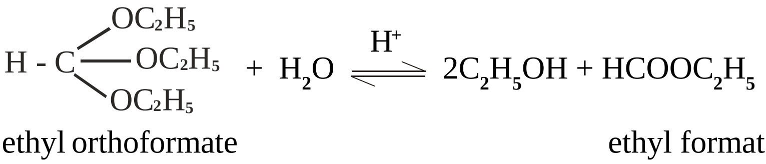


Hemiketal



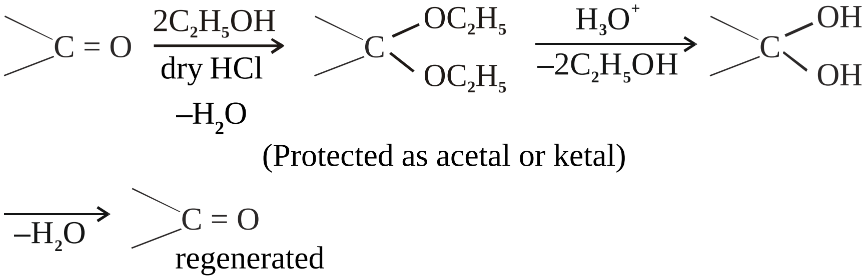
ketals

The above equilibria lie far to the left and are unfavourable to the formation of ketals. However, if the equilibria are tilted to the right by removing water produced during the reaction, ketals are prepared with better yield. This is done by the addition of orthoformic ester.

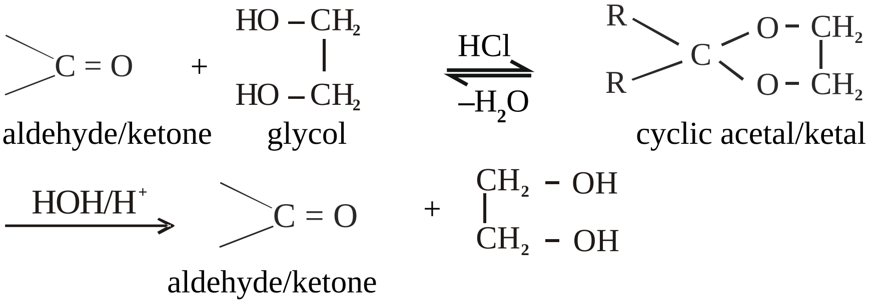


PROTECTION (BLOCKING) OF CARBONYL GROUP BY CYCLIC ACETAL FORMATION

In the course of organic synthesis it is sometimes necessary to protect or mask a carbonyl group in a molocule by preventing it from reacting during the course of a transformation of some other functional group in the molecule. This is done by converting the carbonyl group into an acetal or cyclic ketal which is regenerated by acid hydrolysis.

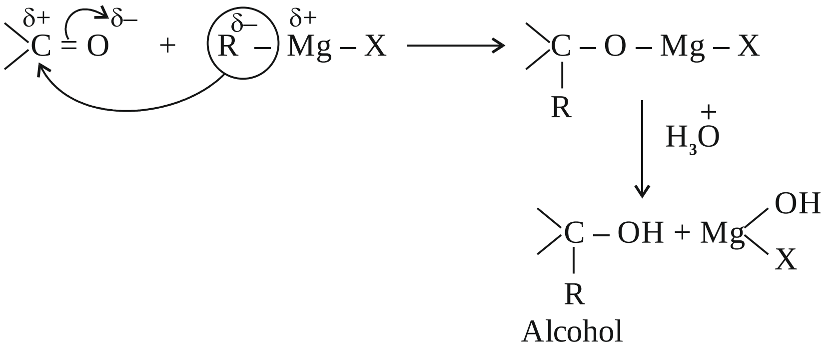


Cyclic acetals or ketals are obtained by reaction with glycol in the presence of acid and in the absence of alkyl formate. The carbonyl group is regenerated from the cyclic acetals or ketals by acid hydrolysis.

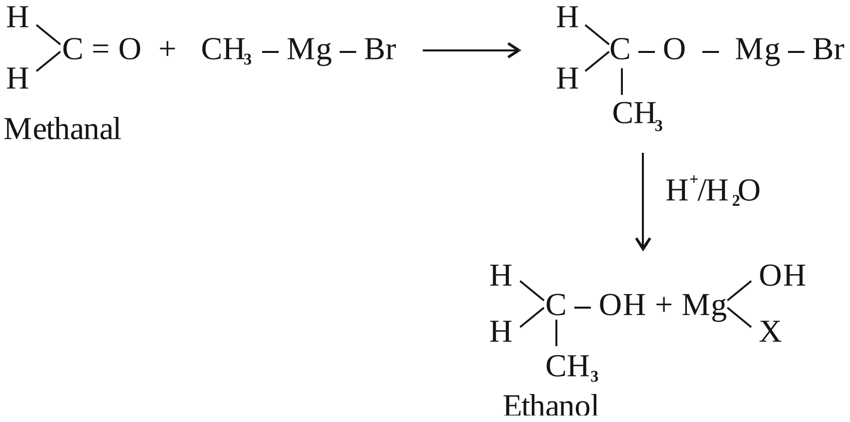


(d) Addition of Grignard reagents :

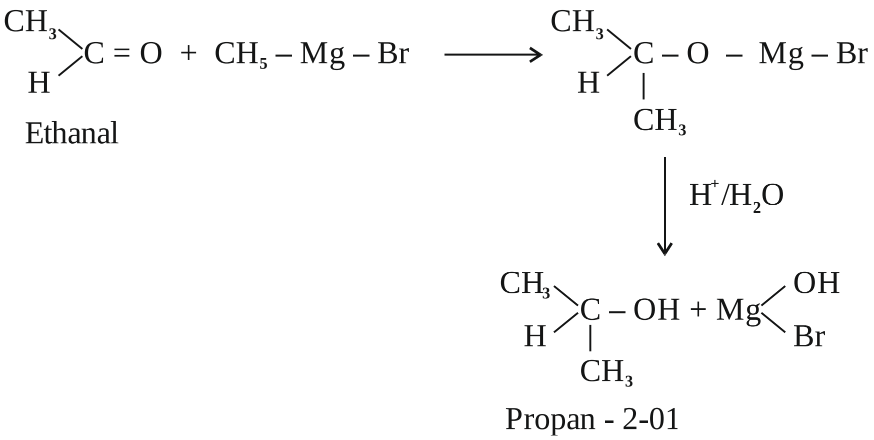
Grignard reagents add to the carbonyl group of aldehydes and ketones forming an adduct which on acid hydrolysis produce alcohols.



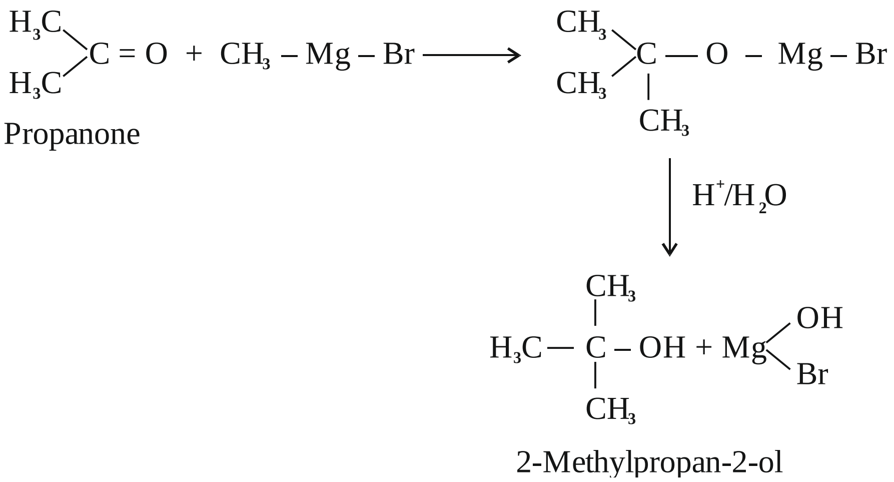
(i) Formation of primary (I°) alcohol on reaction with formaldehyde.

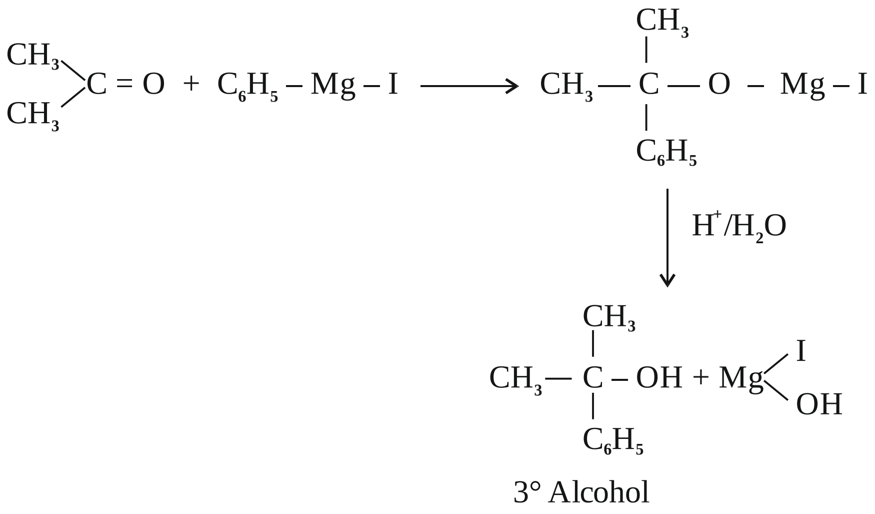


(ii) Formation of secondary (2°) alcohol on reaction with any aldehyde excepting formadehyde.



(iii) Formation of tertiary (3°) alcohol on reaction with a ketones.

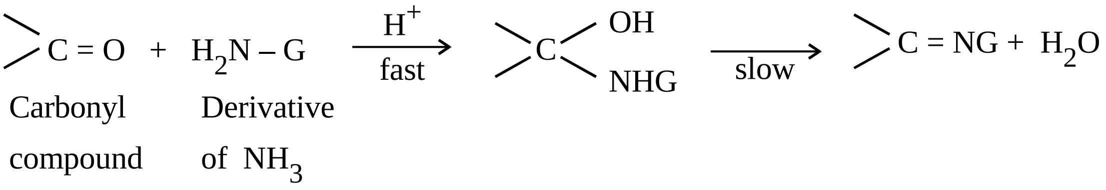




(e) Nucleophilic addition reactions followed by elimination of water (Addition of ammonia derivaties).

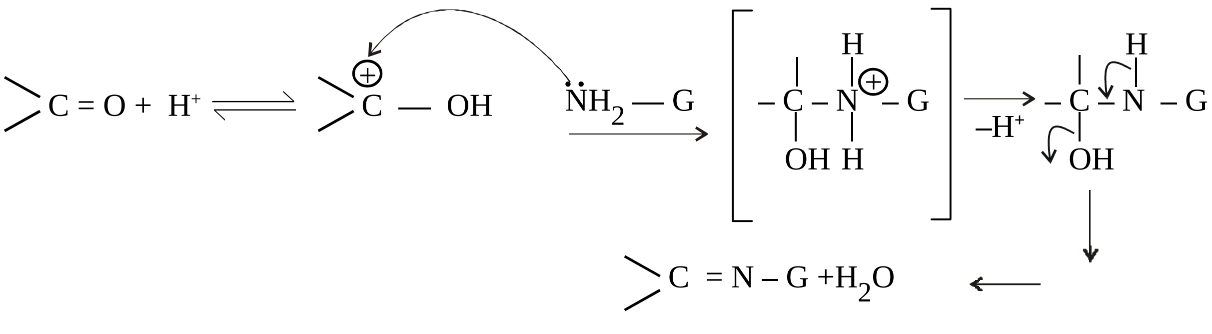
Derivatives of ammonia ($H_2N–G$) such as hydroxyl amine (NH_2OH), phenyl hydrazine ($C_6H_5NHNH_2$), semicarbazide ($NH_2NHCONH_2$) etc. react with carbonyl compounds in weakly acidic solution to form compound $>C = N – G$.

The reaction proceeds through the initial attack of nucleophile on the carbonyl group to form addition product, which subsequently loses a molecule of water to give a compound having a double bond between carbon and nitrogen. The reaction may be represented as follows:



The above reaction is very much helpful in identifying carbonyl compounds since the compound so formed as final product is an insoluble crystalline solid having sharp melting point.

The reactions of carbonyl compounds with ammonia derivatives are carried out at moderate acid strength or pH. The protonation of carbonyl oxygen takes place which makes the carbonyl carbon more prone to nucleophilic attack.



Although the reaction is acid catalysed, the solution should not be too much acidic. This is because the ammonia derivative gets protonated, thereby decreasing its nucleophilicity.

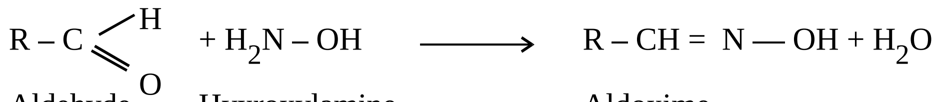
$$G-\ddot{N}H_2 + H^+ \longrightarrow G-\overset{\oplus}{N}H_3$$

Free base Salt

(i) Reaction with Hydroxylamine (NH_2OH)

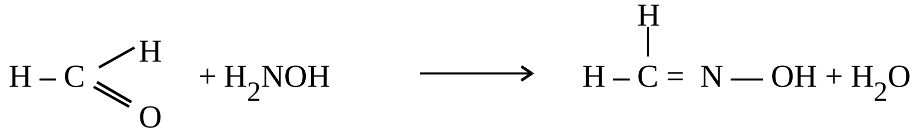
Aldehydes and ketones react with NH_2OH in presence of HCl to form corresponding oximes (aldoximes and ketoximes)

e.g.



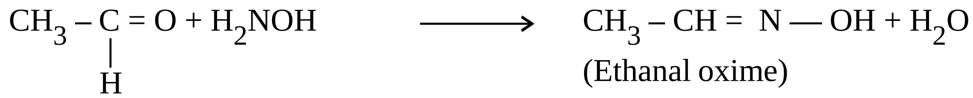
$$R-C\begin{array}{l}\diagup H\\ \diagdown\!\!\diagdown O\end{array} + H_2N-OH \longrightarrow R-CH=N-OH + H_2O$$

Aldehyde Hyxroxylamine Aldoxime



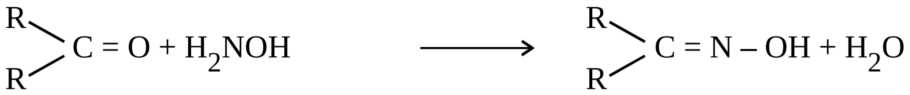
$$H-C\begin{array}{l}\diagup H\\ \diagdown\!\!\diagdown O\end{array} + H_2NOH \longrightarrow H-\overset{\overset{\displaystyle H}{|}}{C}=N-OH + H_2O$$

Methanal Methanaloxime



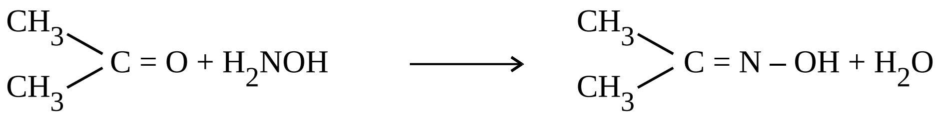
$$CH_3-\underset{\underset{\displaystyle H}{|}}{C}=O + H_2NOH \longrightarrow CH_3-CH=N-OH + H_2O$$

Ethanal (Ethanal oxime)



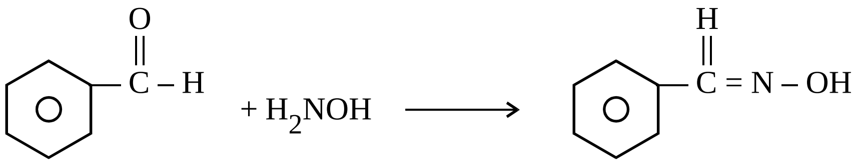
$$\begin{array}{l}R\diagdown\\ R\diagup\end{array}C=O + H_2NOH \longrightarrow \begin{array}{l}R\diagdown\\ R\diagup\end{array}C=N-OH + H_2O$$

Ketone Ketoxime



$$\begin{array}{l}CH_3\diagdown\\ CH_3\diagup\end{array}C=O + H_2NOH \longrightarrow \begin{array}{l}CH_3\diagdown\\ CH_3\diagup\end{array}C=N-OH + H_2O$$

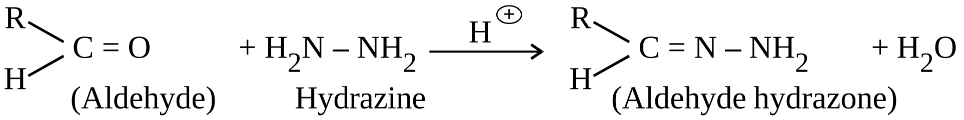
Propanone Propanoneoxime



Benzaldehyde Benzaldehydeoxime

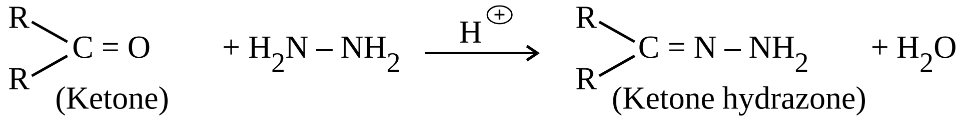
(ii) Reaction with hydrazine (NH_2-NH_2)

Aldehydes and ketones react with hydrazine in presence of dilute acid forming corresponding hydrazones.



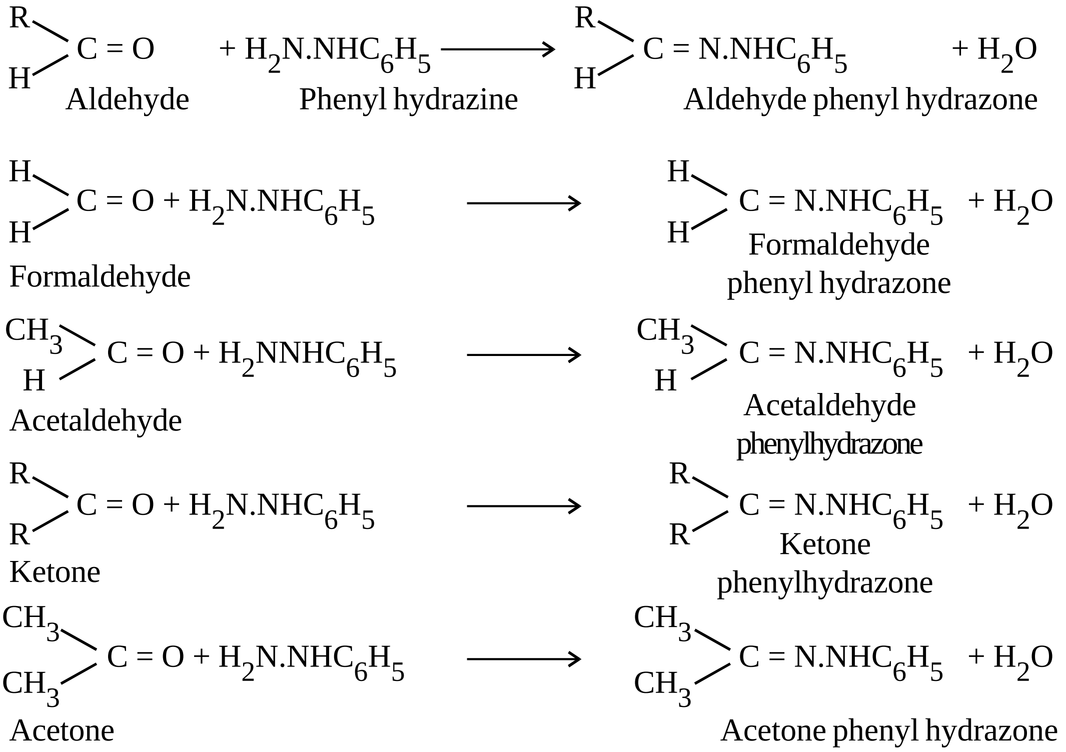
$$\begin{array}{l}R\diagdown\\ H\diagup\end{array}C=O + H_2N-NH_2 \xrightarrow{H^{\oplus}} \begin{array}{l}R\diagdown\\ H\diagup\end{array}C=N-NH_2 + H_2O$$

(Aldehyde) Hydrazine (Aldehyde hydrazone)



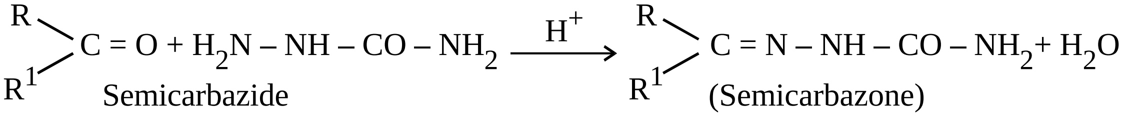
(iii) Reaction with phenylhydrazine ($C_6H_5NHNH_2$)

Aldehydes and ketones react with phenylhydrazine in presence of dilute mineral acid forming crystalline phenylhydrazones.



(iv) Reaction with semicarbazide ($H_2N - NH - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2$)

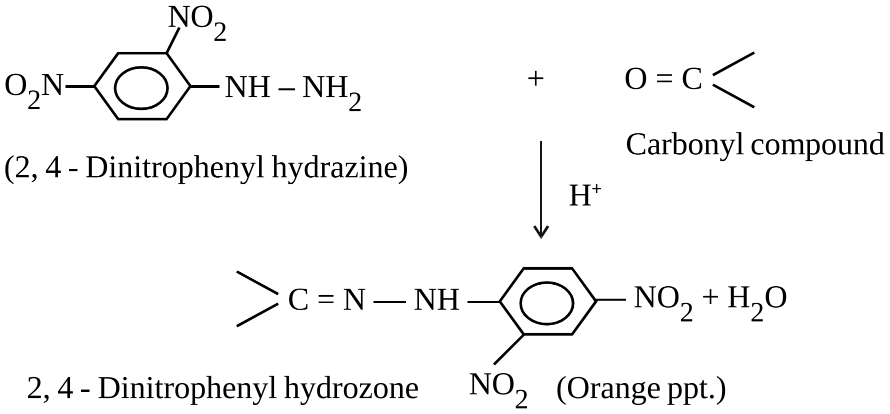
Aldehydes and ketones react with semicarbazide in acid medium to form the corresponding semicarbazones.



$R = R^1 = H$,	Formaldehyde semicarbazone
$R = H, R^1 = CH_3$,	Acetaldehyde semicarbazone
$R = R^1 = CH_3$,	Acetone semicarbazone
$R = H, R^1 = - C_6 C_5$	Benzaldehyde semicarbazone

Note:

The nitrogen derivatives of carbonyl compounds like oximes. hydrazones, phenyl hydrazones, and semicarbazones are used primarily to identify aldehydes and ketones. This is possible because these derivatives are mostly solids with characteristics melting points. 2, 4 - Dinitrophenyl hydrazine (DNPH) is more useful than phenyl hydrazine since the former forms yellow-orange or red precipitate easily with aldehydes and ketones.



(2, 4 - Dinitrophenyl hydrazine)

Carbonyl compound

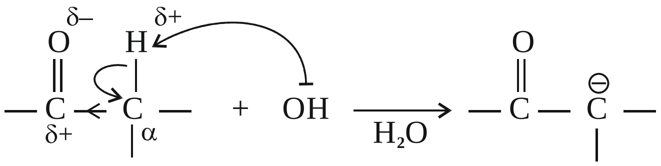
2, 4 - Dinitrophenyl hydrozone (Orange ppt.)

4. Reactions due to α - hydrogen

Acidity of α - hydrogens of aldehydes and ketones :

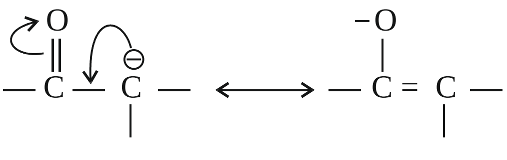
Hydrogen atom present on the carbon atom next to the carboxyl group, called α - hydrogen atom is acidic by nature due to the following factors.

(i) Carbonyl group is an electron withdrawing group (– I effect) thus decreasing the electron density from the adjacent carbon - carbon bond making Cα - carbon electron deficient. This in turn results with the decrease of electron density of α - H bond. Hence α - H atom becomes acidic by nature and can be easily abstracted by a base forming enolate anion.



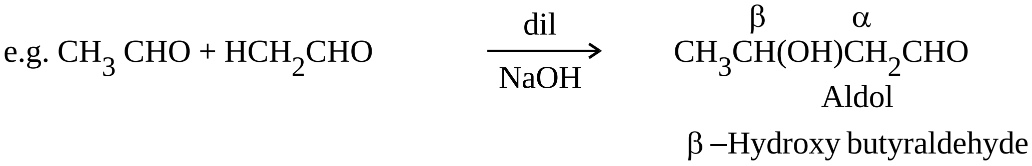
Enolate anion

(ii) Enolate anion i.e. conjugate base is resonancce stablilized.



Due to acidic nature of α - hydrogen atoms aldehydes and ketones undergo the following reactions.

A. **Aldol condensation:** Two molecules of same or different carbonyl compounds each containing α -H -atom, condense together in presence of dilute alkali like NaOH, KOH, $Ba(OH)_2$ or Na_2CO_3 to form a syrupy liquid known as **Aldol**. This aldol which shows the properties of alcohol, aldehyde or ketone is β-hydroxy aldehyde or β-hydroxy ketone.

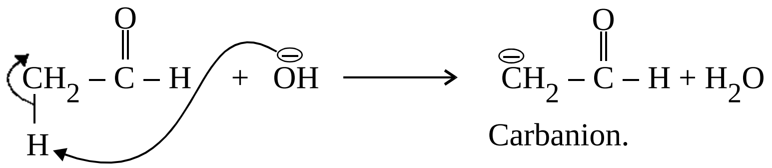


e.g. $CH_3\,CHO + HCH_2CHO \xrightarrow[NaOH]{dil} \underset{\text{Aldol}}{CH_3\overset{\beta}{C}H(OH)\overset{\alpha}{C}H_2CHO}$

β –Hydroxy butyraldehyde

Mechanism :

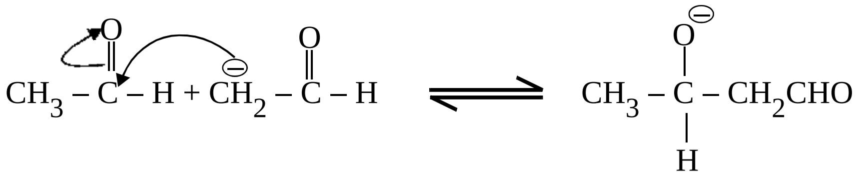
(i) Formation of carbanion due to the abstraction of α - hydrogen by $\bar{O}H$



$$\underset{H}{\overset{|}{CH_2}} - \overset{O}{\overset{\|}{C}} - H + \overset{\ominus}{O}H \longrightarrow \overset{\ominus}{C}H_2 - \overset{O}{\overset{\|}{C}} - H + H_2O$$

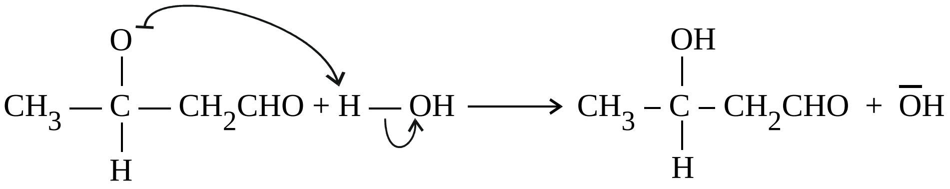
Carbanion.

(ii) Nucleophilic attack of carbanion on the electron deficient carbonyl carbon of other molecule of acetaldehyde to form an anion



$$CH_3 - \overset{O}{\overset{\|}{C}} - H + \overset{\ominus}{C}H_2 - \overset{O}{\overset{\|}{C}} - H \rightleftharpoons CH_3 - \underset{H}{\underset{|}{\overset{O^{\ominus}}{\overset{|}{C}}}} - CH_2CHO$$

(iii) The anion finally abstracts a proton from water to form aldol.



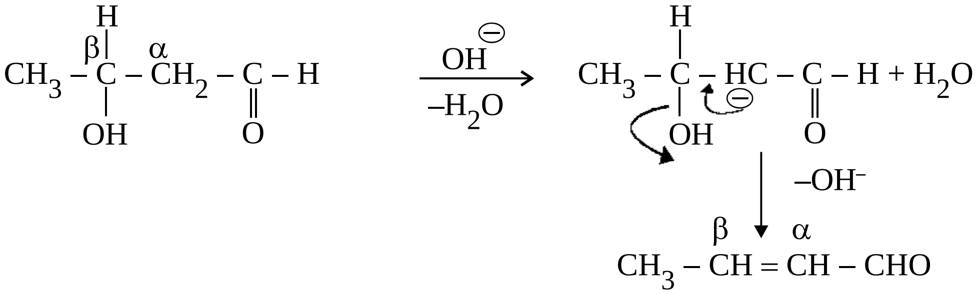
$$CH_3 — \underset{H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}} — CH_2CHO + H — OH \longrightarrow CH_3 - \underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - CH_2CHO + \bar{O}H$$

Aldol

Restrictions

(i) When concentrated alkali is used the aldol formed undergoes base catalysed dehydration forming α, β-unsaturated aldehyde.

e.g.

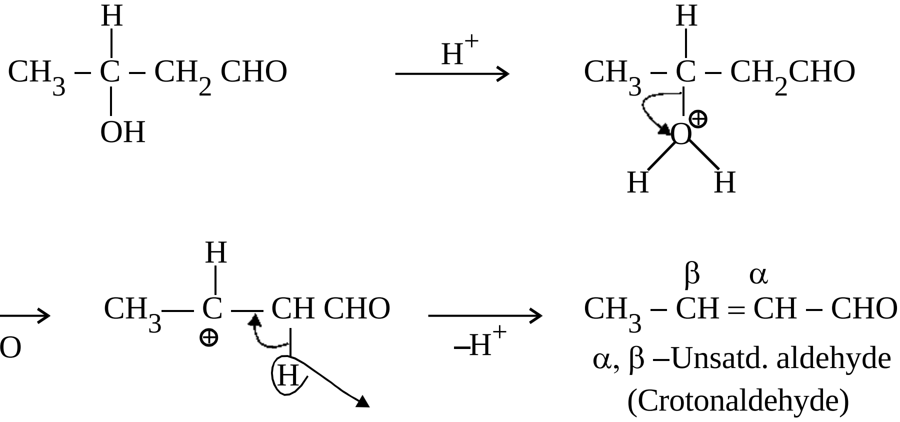


$$CH_3-\overset{\overset{H}{\beta|}}{\underset{\underset{OH}{|}}{C}}-\overset{\alpha}{CH_2}-\underset{\underset{O}{\|}}{C}-H \xrightarrow[-H_2O]{\overset{\ominus}{OH}} CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\ominus}{HC}-\underset{\underset{O}{\|}}{C}-H+H_2O \xrightarrow{-OH^-} CH_3-\overset{\beta}{CH}=\overset{\alpha}{CH}-CHO$$

α, β –Unsaturated aldehyde
(Crotonaldehyde)

(ii) When a trace of mineral acid is there the aldol formed is no longer stable. It undergoes acid catalysed dehydration to form α, β-unsaturated aldehyde.

e.g.

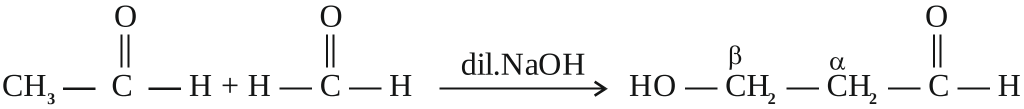


$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2\,CHO \xrightarrow{H^+} CH_3-\overset{\overset{H}{|}}{\underset{\underset{H\quad H}{\overset{\oplus}{O}}}{C}}-CH_2CHO \xrightarrow[-H_2O]{} CH_3-\overset{\overset{H}{|}}{\underset{\oplus}{C}}-\underset{\underset{H}{|}}{CH}\,CHO \xrightarrow[-H^+]{} CH_3-\overset{\beta}{CH}=\overset{\alpha}{CH}-CHO$$

α, β –Unsatd. aldehyde
(Crotonaldehyde)

(iii) When two different aldehydes each containing α -hydrogen atom condense together in presence of dilute alkali the product formed is a mixture of aldols. This is known as **Cross Aldol condensation or Cross Aldolisation.** Examples are :–

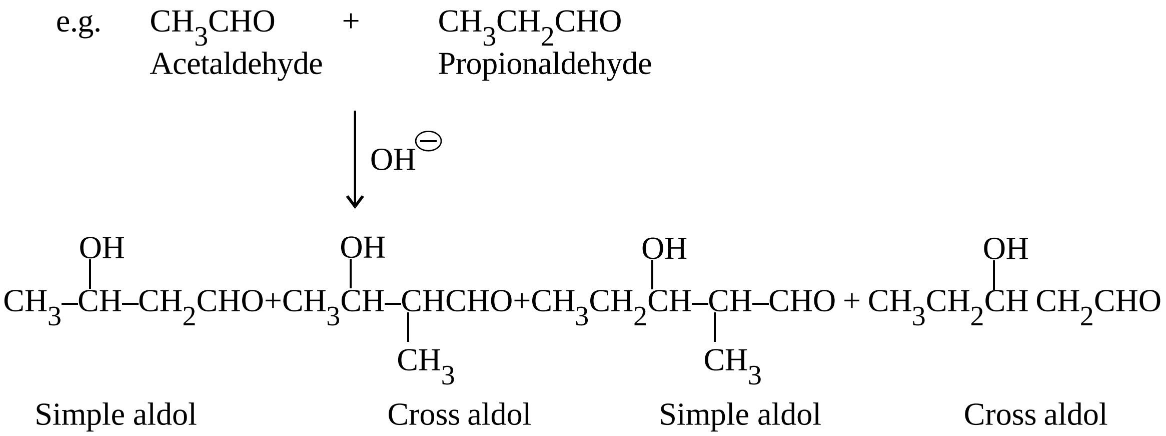
I.



$$CH_3-\overset{\overset{O}{\|}}{C}-H+H-\overset{\overset{O}{\|}}{C}-H \xrightarrow{dil.NaOH} HO-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-H$$

Acetaldehyde Formaldehyde (No α - hydrogen atom) β-hydroxypropionaldehyde

II. Here four different aldols are formed, two from condensation of the two aldehydes with like molecules and the other two from condensation of two different aldehydes in two different ways.

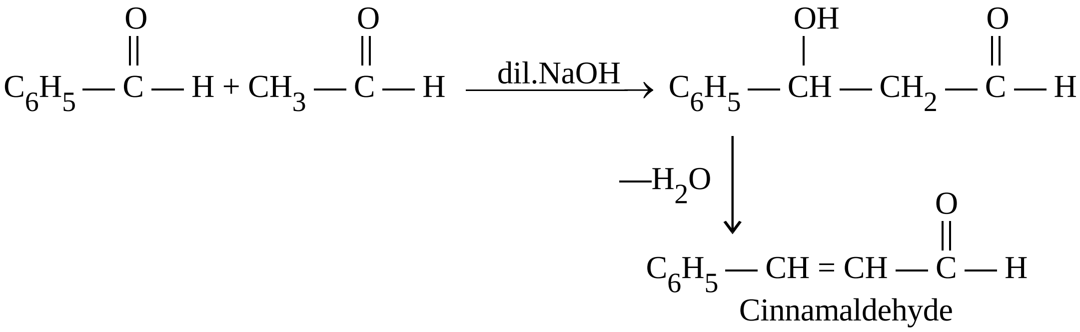


e.g. CH_3CHO (Acetaldehyde) + CH_3CH_2CHO (Propionaldehyde)

$$\xrightarrow{OH^{\ominus}}$$

$$\underset{\text{Simple aldol}}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_2CHO} + \underset{\text{Cross aldol}}{CH_3\overset{OH}{\overset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}HCHO} + \underset{\text{Simple aldol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}H-\underset{CH_3}{\underset{|}{C}}H-CHO} + \underset{\text{Cross aldol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}H\ CH_2CHO}$$

III.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{dil.NaOH}} C_6H_5-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

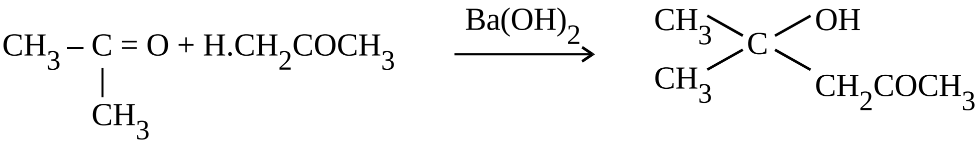
$$\xrightarrow{-H_2O} C_6H_5-CH=CH-\overset{O}{\overset{\|}{C}}-H$$

Cinnamaldehyde

Cross Aldol condensation is also possible in case of two different ketones and in case of condensation reaction between an aldehyde and a ketone.

Aldol condensation is case of Ketones:

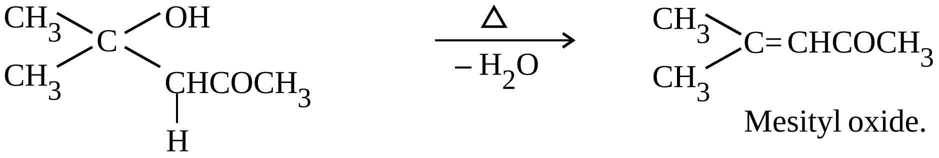
Two molecules of acetone condense together in presence of $Ba(OH)_2$ to produce diacetonealcohol (aldol of acetone)



$$\underset{CH_3}{\underset{|}{CH_3-C}}=O + H.CH_2COCH_3 \xrightarrow{Ba(OH)_2} (CH_3)_2C(OH)CH_2COCH_3$$

Acetone Acetone Diacetone alcohol

Diacetone alcohol upon heating loses a molecule of water to form mesityl oxide.

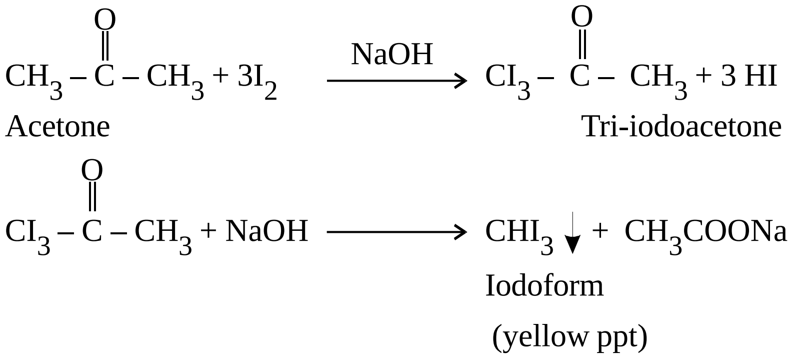


$$(CH_3)_2C(OH)\underset{H}{\underset{|}{C}}HCOCH_3 \xrightarrow[-H_2O]{\Delta} (CH_3)_2C=CHCOCH_3$$

Mesityl oxide.

B. Iodoform reaction:

Compounds which contain CH_3CO- group or which produce CH_3CO group on oxidation can undergo **iodoform** reaction. Methyl ketones or acetaldehyde when treated with sodium hypoiodite (alkaline solution of iodine), iodoform is formed as yellow precipitate along with an acid which contains one C atom less than the parent compound.

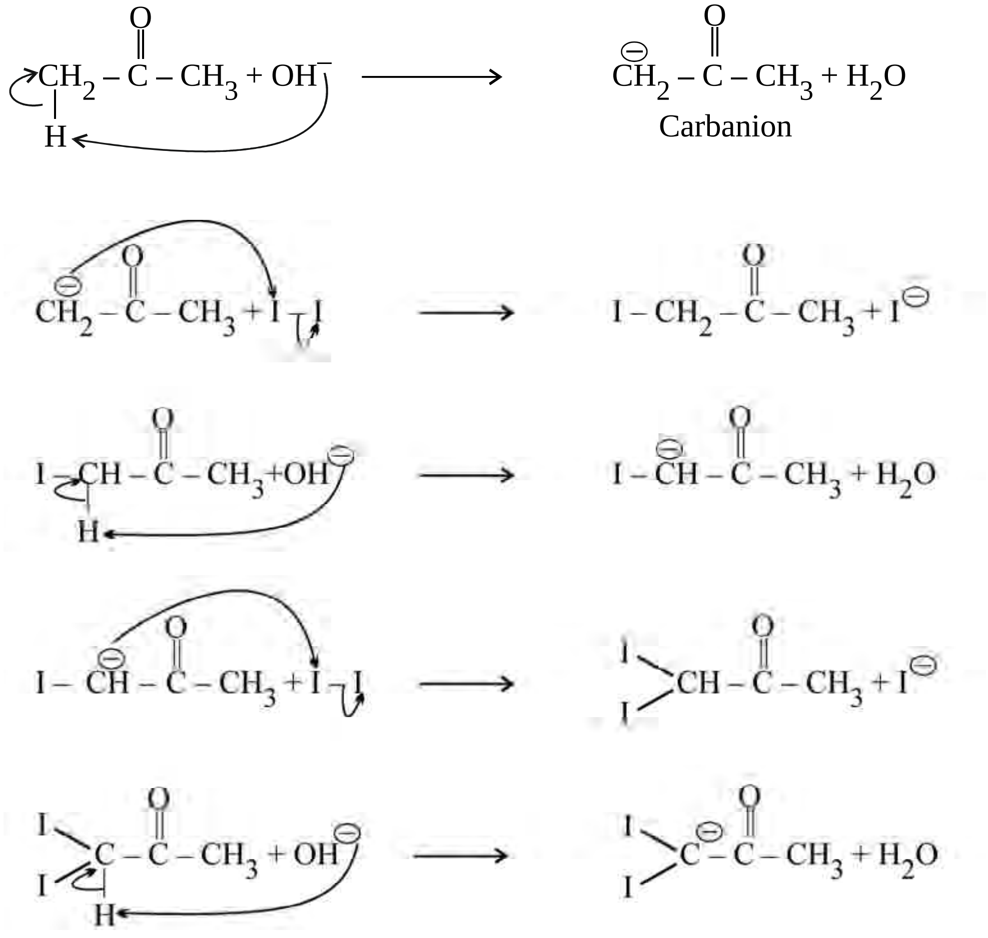


$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 3I_2 \xrightarrow{NaOH} \underset{\text{Tri-iodoacetone}}{CI_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + 3\,HI$$

$$CI_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + NaOH \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3\downarrow} + CH_3COONa$$

Mechanism:

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



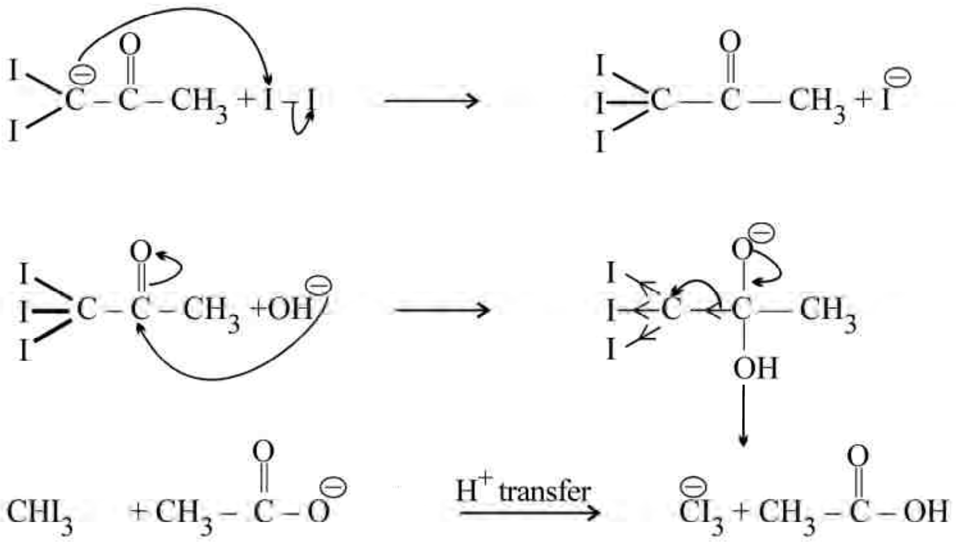
$$\underset{\displaystyle H}{\overset{|}{CH_2}}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + OH^- \longrightarrow \underset{\text{Carbanion}}{\overset{\ominus}{C}H_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + H_2O$$

$$\overset{\ominus}{C}H_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I-I \longrightarrow I-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I^{\ominus}$$

$$I-\underset{\displaystyle H}{\overset{|}{CH}}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + OH^{\ominus} \longrightarrow I-\overset{\ominus}{C}H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$

$$I-\overset{\ominus}{C}H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I-I \longrightarrow I_2CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I^{\ominus}$$

$$I_2\underset{\displaystyle H}{\overset{|}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + OH^{\ominus} \longrightarrow I_2\overset{\ominus}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2O$$



Iodoform

This test is used for identification of compounds containing CH_3 CO-group or any other group like $CH_3 - \underset{|}{CH} - OH$ which can be oxidised to CH_3 CO-group by sodiumhypoiodite.

5. Oxidation reactions

Aldehydes differ from ketones in oxidation reactions. It is a fact that aldehydes can be easily oxidised to carboxylic acids.

$$R - \overset{\overset{\displaystyle O}{\|}}{C} - H + [O] \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - OH$$

Aldehyde Carboxylic acid

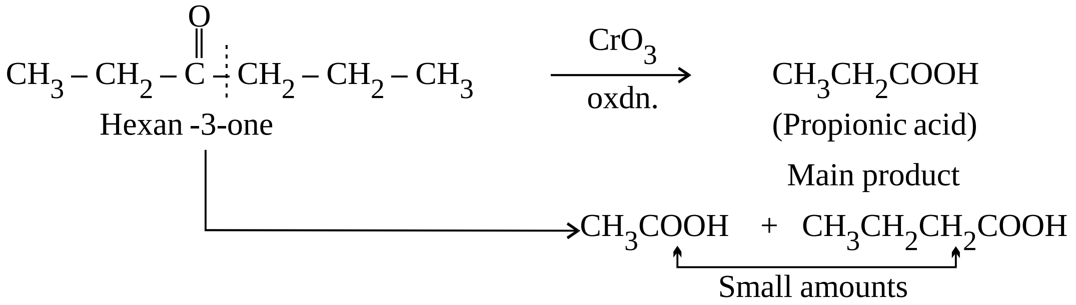
The easy oxidation of aldehydes is due to the presence of a H –atom attached to carbonyl group which on oxidation becomes –OH group without breaking any other bond. Aldehydes can also be oxidised with oxidising agents like Cu^{2+}, Ag^+ or bromine water to carboxylic acids. On the other hand, ketones can be oxidised to carboxylic acids with less number of carbon atoms under drastic conditions using powerful oxidising agents like acidified $KMnO_4$ or $K_2Cr_2O_7$. Thus, aldehydes are treated as good reducing agents. They can reduce Fehling's solution and Tollens' reagent whereas ketones can not.

Mixed ketones when oxidised under drastic conditions give rise to a mixture of carboxylic acids which involve cleavage of carbon-carbon bonds. When oxidised with acidified $KMnO_4$ or $K_2Cr_2O_7$ and conc.H_2SO_4, C–CO bond of the ketones breaks and the α- carbon atom containing least number of hydrogen atom is attacked preferentially (**Popoff's rule**). Thus,

$$CH_3-CO \,\vdots\, CH_2-CH_2-CH_3 \xrightarrow{\text{acid. }KMnO_4} CH_3COOH + CH_3\,CH_2COOH$$

Pentan -2-one (Acetic acid) (Propionic acid)

If the carbon atoms adjacent to carbonyl group have the same number of hydrogen atoms, the carbonyl group chiefly remains with the smaller alkyl group. Thus, the oxidation of hexan-3-one gives propionic acid as the main product with smaller amount of acetic acid and butyric acid.



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C} \,\vdots\, CH_2-CH_2-CH_3 \xrightarrow[\text{oxdn.}]{CrO_3} \underset{\substack{\text{(Propionic acid)}\\ \text{Main product}}}{CH_3CH_2COOH}$$

$$\longrightarrow \underbrace{CH_3COOH \quad + \quad CH_3CH_2CH_2COOH}_{\text{Small amounts}}$$

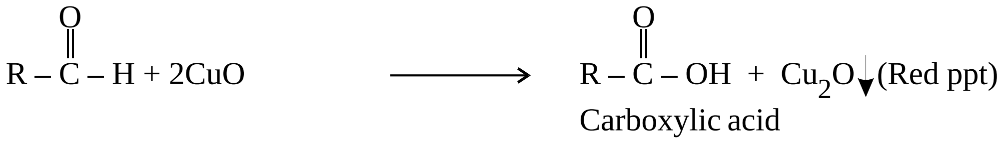
Hexan -3-one

(i) Reduction of Fehling's solution.

Aldehydes when boiled with Fehling's solution form a red precipitate of Cu_2O. Fehling's solution is alkaline Cu(II) ion complexed with sodium potassium tartrate. It is a mixture of Fehling A and Fehling B. Fehling A contains $CuSO_4$ whereas Fehling B contains NaOH and sodium potassium tartrate (Rochelle salt).

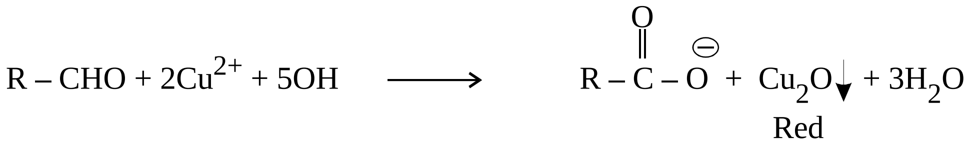
$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2CuO \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + Cu_2O\downarrow\text{(Red ppt)}$$

Aldehydes thus reduce Cu^{2+} ions to Cu^{+} ion and get oxidised to carboxylic acids. Ionically the same may be represented as



$$R-CHO + 2Cu^{2+} + 5OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O} + \underset{\text{Red}}{Cu_2O\downarrow} + 3H_2O$$

The function of Rochelle salt is to dissolve insoluble $Cu(OH)_2$ by complexing it with tartrate ion. i.e. it prevents the precipitation of $Cu(OH)_2$.

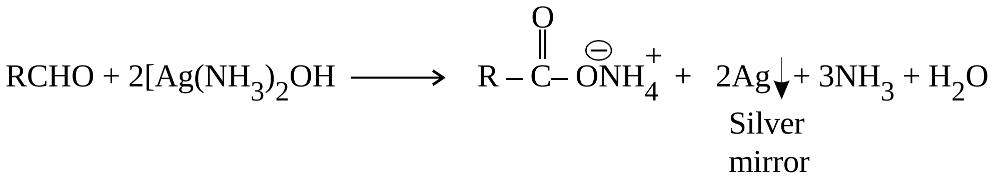
Aromatic aldehydes do not reduce Fehling's solution.

(ii) Reduction of Tollens' reagent :

When an aldehyde is warmed with Tollens' reagent a silver mirror is formed which appears on tha walls of the test tube in which the reaction is carried out. Tollens' reagent is ammoniacal solution of $AgNO_3$. It is prepared by adding NH_4OH solution to a solution of $AgNO_3$ till the precipitate AgOH formed first again redissolves.

$$AgNO_3 + NH_4OH \longrightarrow AgOH\downarrow + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow \underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]\,OH} + 2H_2O$$



$$RCHO + 2[Ag(NH_3)_2OH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\overset{+}{N}H_4 + \underset{\substack{\text{Silver}\\ \text{mirror}}}{2Ag\downarrow} + 3NH_3 + H_2O$$

Here also Ag^+ ion is reduced to metallic silver. The reaction is accompanied by oxidation of aldehydes to carboxylic acids. The silver thus deposited shines like a mirror for which this test is known as **silver mirror test**. This test is exhibited by both aliphatic and aromatic aldehydes.

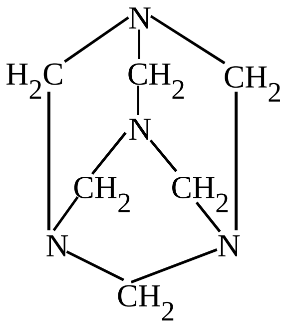
6. Miscellaneous reactions:

A. Reaction with NH_3:

(i) Formaldehyde reacts with NH_3 to form hexamethylenetetramine $[CH_2)_6N_4]$, known as **Urotropine** which is used as urinary antiseptic.

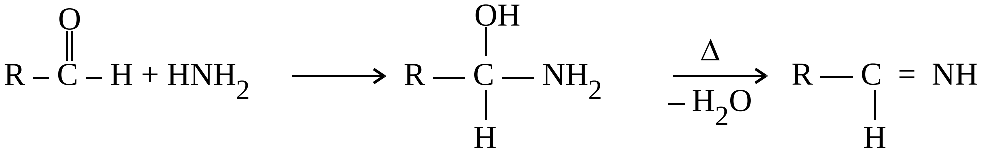
$$6HCHO + 4NH_3 \longrightarrow \underset{\text{Hexamethylenetetramine.}}{(CH_2)_6N_4} + 6H_2O.$$

Structure of Urotropine:



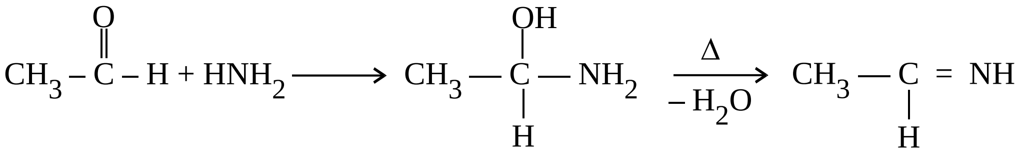
Nitration of urotropine under control conditions produces the explosive RDX (Research and Development Explosive)

(ii) Other aldehydes react with NH_3 to form aldehydeammonias which on heating undergo dehydration to form aldimine.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H+HNH_2 \longrightarrow R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-NH_2 \xrightarrow[-H_2O]{\Delta} R-\underset{\underset{\displaystyle H}{|}}{C}=NH$$

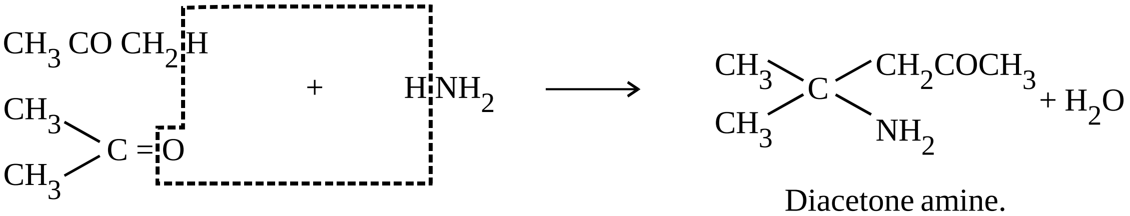
Aldehyde. Aldehydeammonia Aldimine



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H+HNH_2 \longrightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-NH_2 \xrightarrow[-H_2O]{\Delta} CH_3-\underset{\underset{\displaystyle H}{|}}{C}=NH$$

Acetaldehyde. Acetaldehydeammonia Acetaldimine

(iii) Acetone (2 molecules) react with NH_3 to form an addition product diacetone - amine, a complex ketonic amine.



Diacetone amine.

B. Cannizzaro's reaction:

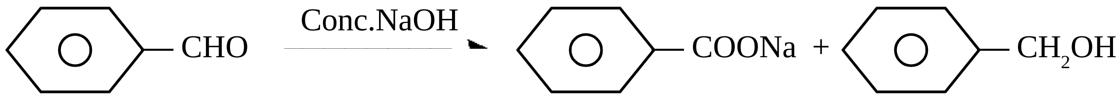
Aldehydes having no α-hydrogen atom when treated with concentrated alkali undergo disproportionation i.e. self oxidation-reduction reaction where one molecule of the aldehyde is oxidised to carboxylic acid and other molecule is reduced to alcohol. This reaction is termed as **Cannizzaro reaction**.

e.g. (i) HCHO upon reaction with conc. NaOH undergoes Cannizzaro's reaction. Out of two molecules of HCHO, one molecule is oxidised to HCOOH and other is reduced to CH_3OH.

$$2HCHO \xrightarrow{\text{Conc.NaOH}} HCOONa + CH_3OH$$

Formaldehyde Sodium formate Methyl alcohol

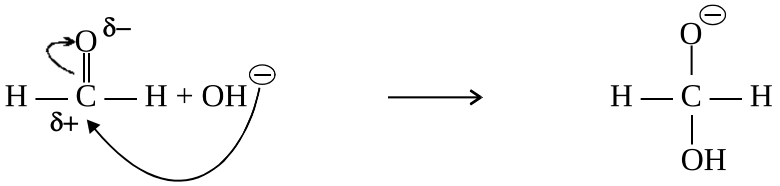
(ii)



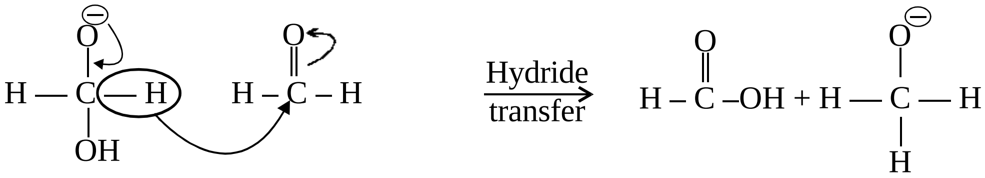
Benzaldehyde Sodium benzoate Benzyl alcohol

Mechanism:

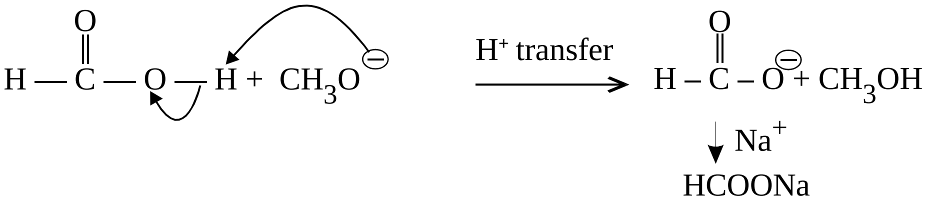
(i) Nucleophilic attack of OH^- at the electron deficient carbonyl carbon atom of one molecule of aldehyde.



(ii) This step involves the hydride transfer from the above intermdiate to the second molecule of aldeyde.

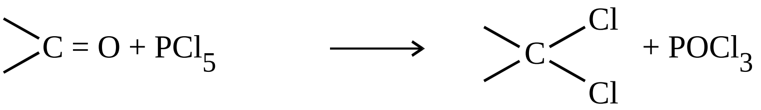


(iii) Since $HCOO^-$ ion is more stable than HCOOH, there will be H^+ ion shift and as a result formate ion is formed along with methyl alcohol.

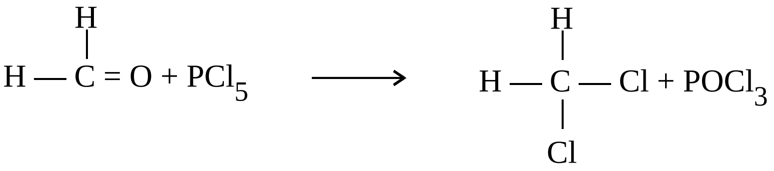


C. Reaction with Phosphorus pentachloride:

PCl_5 reacts with simple carbonyl compounds to form dichlorides.

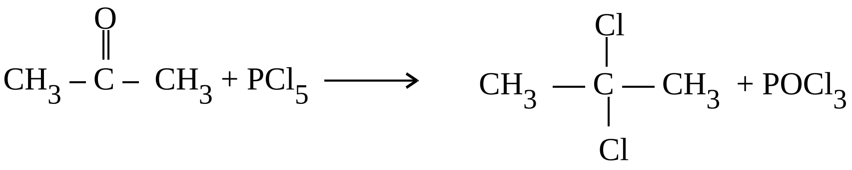


(carbonyl comp) (dichloroalkane)



$$H-\overset{\displaystyle H}{\overset{|}{C}}=O + PCl_5 \longrightarrow H-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle Cl}{|}}{C}}}-Cl + POCl_3$$

Formaldehyde Dichloromethane



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + PCl_5 \longrightarrow CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\underset{\displaystyle Cl}{|}}{C}}}-CH_3 + POCl_3$$

(Acetone) (2, 2 -Dichloropropane)

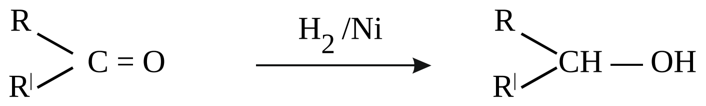
D. Reduction: Aldehydes and ketones yield a variety of products on reduction under different conditions.

(i) Catalytic reduction: When reduced with hydrogen in presence of a catalyst like Raney Ni, Pt or Pd, aldehydes give primary alcohols whereas ketones give secondary alcohols.

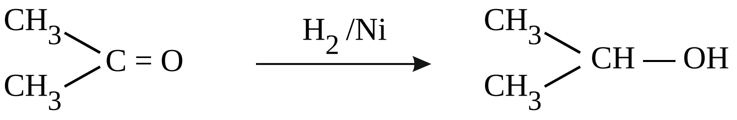
$$\underset{\text{Aldehyde}}{R-CHO} \xrightarrow{H_2/Ni} \underset{1^0\text{alcohol}}{RCH_2\,OH}$$

$$\underset{\text{Formaldehyde}}{H-CHO} \xrightarrow{H_2/Ni} \underset{\text{Methyl alcohol}}{CH_3\,OH}$$

$$\underset{\text{Acetaldehyde}}{CH_3-CHO} \xrightarrow{H_2/Ni} \underset{\text{Ethyl alcohol}}{CH_3\,CH_2\,OH}$$



$$\underset{\text{(Ketone)}}{\begin{matrix}R\\R^{|}\end{matrix}\!\!>C=O} \xrightarrow{H_2/Ni} \underset{2^0\text{-alcohol}}{\begin{matrix}R\\R^{|}\end{matrix}\!\!>CH-OH}$$



$$\underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O} \xrightarrow{H_2/Ni} \underset{\text{Isopropyl alcohol}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-OH}$$

(ii) Reduction by chemical reducing agents : Alcohols can also be obtained by reducing cacrbonyl compounds using lithium aluminium hydride ($LiAIH_4$) or sodium borohydride ($NaBH_4$) or sodium and ethyl alcohol.

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

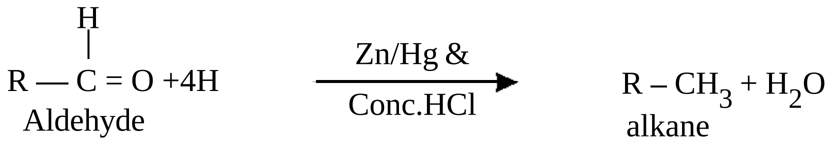
$NaBH_4$ is a mild and selective reducing agent, since it reduces only the carbonyl group without affecting the carbon-carbon double bonds in the molecule. Thus,

$$\underset{\text{But -2-en-1-al}}{CH_3-CH=CH-CHO} \xrightarrow{NaBH_4} \underset{\text{But -2-en-1-ol}}{CH_3-CH=CH-CH_2OH}$$

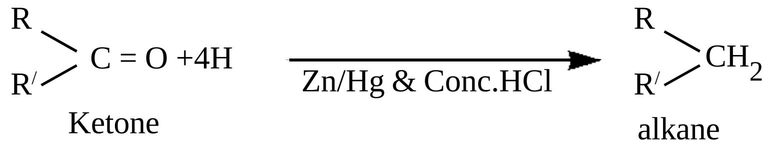
But, $CH_3-CH=CH-CHO \xrightarrow{H_2/Ni} \underset{\text{Butanal}}{CH_3-CH_2-CH_2-CHO}$

(iii) Reduction to hydrocarbons : The $>C=O$ group of aldehydes and ketones may be converted to $>CH_2$ by the following methods.

(I) Clemmensen reduction : This involves the reduction of aldehydes or ketone by zinc amalgam in the presence of Conc. HCl



$$\underset{\text{Aldehyde}}{R-\overset{\overset{H}{|}}{C}=O} + 4H \xrightarrow[\text{Conc.HCl}]{\text{Zn/Hg \&}} \underset{\text{alkane}}{R-CH_3} + H_2O$$



Acetaldehyde forms ethane whereas acetone forms propane on Clemmensen reduction.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 4[H] \xrightarrow{\text{Zn/Hg, Conc.HCl}} \underset{\text{Ethyl benzene}}{C_6H_5-CH_2CH_3} + H_2O$$

(II) Wolff - Kishner reduction : Carbonyl group of aldehydes and ketones can be reduced to $-CH_2-$ group on reaction with hydrazine followed by heating with sodium or potassium hydroxide in the presence of ethylene glycol.

$$>C=O \xrightarrow[-H_2O]{NH_2NH_2} >C=NNH_2 \xrightarrow[\Delta]{\text{KOH/Ethylene glycol}} >CH_2 + N_{2(g)}\uparrow$$

For example :

$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(ii) KOH, Glycol}\ \Delta]{\text{(i) }NH_2NH_2} \underset{\text{Ethane}}{CH_3CH_3}$$

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow[\text{(ii) KOH, Glycol}\ \Delta]{\text{(i) }NH_2NH_2} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3}$$

E. Reaction with primary amines : Aldehydes and ketones react with primary amines in the presence of acid as catalyst to form Schiff's bases.

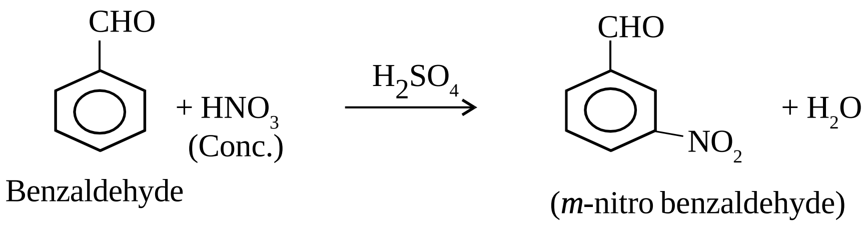
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Methylamine}}{H_2NCH_3} \xrightarrow[\Delta]{H^+} \underset{\text{Schiff's base}}{CH_3CH = NCH_3} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Aniline}}{H_2NC_6H_5} \xrightarrow[\Delta]{H^+} \underset{\substack{\text{Benzal aniline}\\\text{(A Schiff's base)}}}{C_6H_5CH = NC_6H_5} + H_2O$$

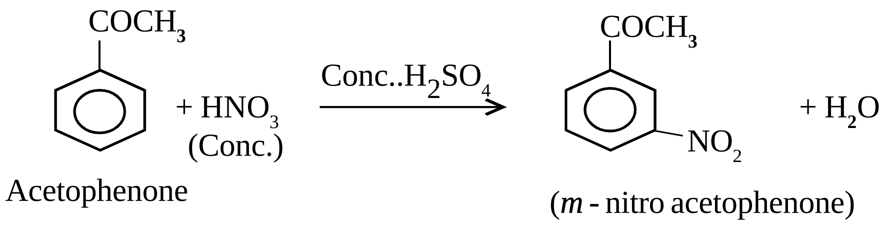
F. Electrophilic Substitution Reactions in aromatic aldehyde and ketones :

Aromatic aldehydes and ketones undergo electrophilic substitution reactions such as halogenation, nitration and sulphonation at the meta position. Since carbony group is an elctron withdrawing group, it is a a ring deactivating and m-directing group, it does not undergo Friedel-Craft's reaction.

I. Nitration : Benzaldehyde when treated with concentrated nitric acid in the presence of concentrated sulphuric acid undergoes nitration to form m-nitrobenzaldehyde. The reaction proceeds through electrophilic substitution reaction. The carbonyl group present in benzaldehyde behaves as a ring deactivator and meta-director, towards electrophilic substitution reaction.



With acetophenone, *m*-nitroacetophenone is formed.

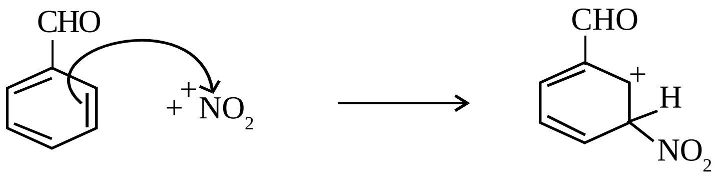


Mechanism:

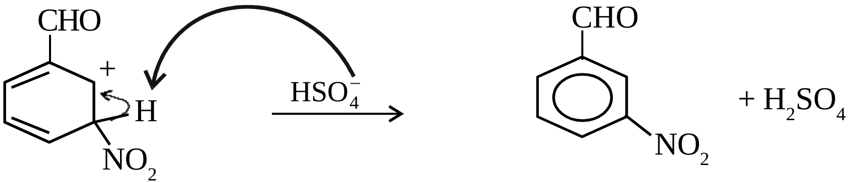
Step -1 : Formation of electrophile ($\overset{+}{NO_2}$)

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{NO_2} + 2HSO_4^- + H_3O^+$$

Step - 2 : The electrophilic attack and formation of carbocation :

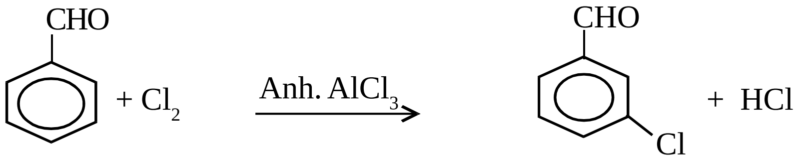


Step : 3 Loss of proton and formation of *m*-nitro benzaldehyde.



m-nitro benzaldehyde

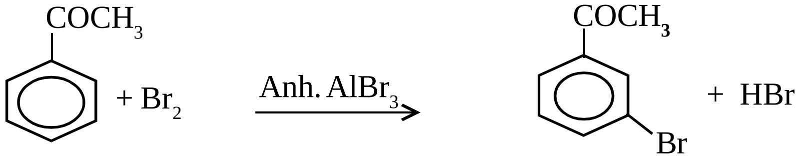
II. **Halogenation :** Like nitration, benzaldehyde and acetophenone undergo halogenation. For example, benzaldehyde reacts with chlorine in the presence of $FeCl_3$ or Anhy. $AlCl_3$ at room temperature, to form m-chlorobenzaldehyde. Here, Cl^+ ion acts as electrophile.



Benzaldehyde

m-chloro benzaldehyde

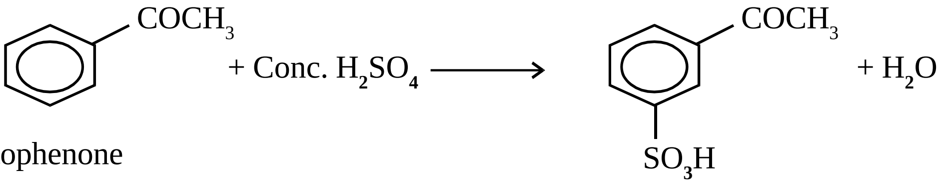
Similarly



Acetophenone

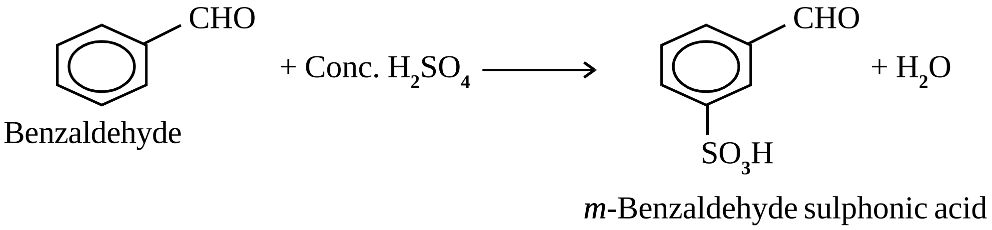
m-Bromoacetophenone

III. **Sulphonation :** Both aryl aldehydes and ketones undergo sulphonation giving m-derivative.



Acetophenone

m-acetylbenzenesulphonic acid



18.8 USES OF ALDEHYDES AND KETONES :

Aldehydes and ketones are used as solvents starting materials and reagents for the synthesis of other products in the chemical industry. Some of the important cases of aldehydes and ketones are :

(i) 40% aqueous solution of formaldehyde called **formalin** is used for the preservations of biological or anatomical specimens. It is also used as disinfectant and as a germicide.

(ii) Formaldehyde is used in the manufacture of bakelite, resins and other polymers.

(iii) Acetaldehyde is used in the preparation of a number of organic compounds such as acetic acid, ethyl acetate, n-butyl alcohol etc., and in the silvering of mirrors.

(iv) Benzaldehyde is mostly used as a flavouring agent in perfume industry in addition to its use for the preparation of a number of organic compounds like cinnamic acid, benzoyl chloride etc.

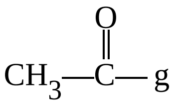
(v) Acetone is widely known for its use as one of the constituents of the liquid nail polish.

(vi) Compounds like vanillin, acetophenone, camphor etc. are well known for their use as flavouring and adouring agent.

18.9 SOLVED PROBLEMS :

1. A ketone 'A' which undergoes haloform reaction gives compound 'B' on heating with sulphuric acid gives compound'C' which forms monoozonide 'D'. 'D' on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B, C and write down the reactions involved.

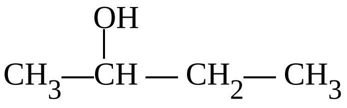
Solution : We know that the ketone which undergoes haloform reaction must contain a $CH_3—\overset{\overset{O}{\|}}{C}—$ group. So 'A' must be methyl ketone. Again since 'C' forms a monoozonide, it must contain a C=C bond. 'D' on hydrolysis in presence of zinc dust gives acetaldehyde. Hence the structure of 'C' will be



$$CH_3—CH = CH— CH_3$$

(C)

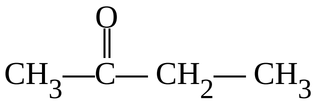
'B' on dehydration gives 'C'. So the structure of 'B' will be



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3$$

(B)

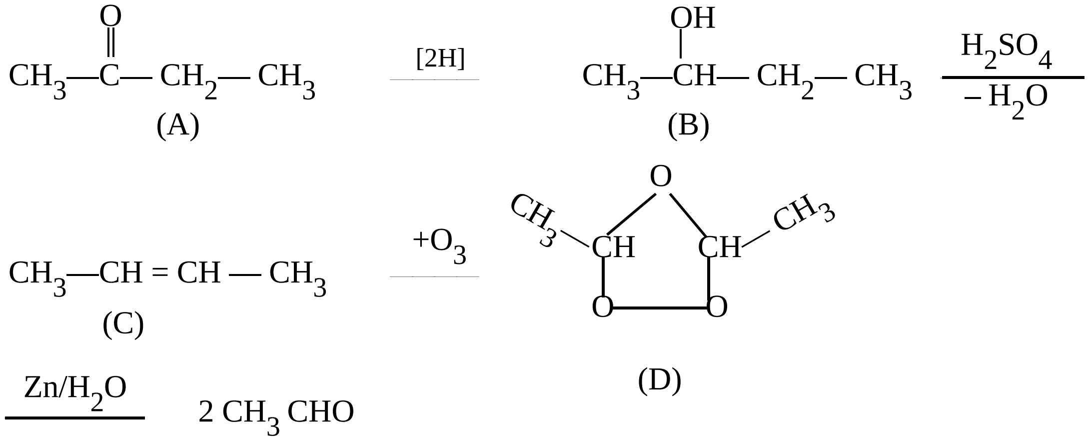
Again 'B' is obtained upon reduction of 'A'. So 'A' has the structure



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

(A) Butanone

The reactions involved may be represented as follows.

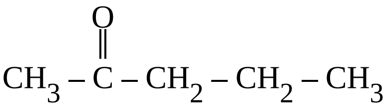


2. Compound 'A' with molecular formula $C_5H_{12}O$ on oxidation forms compound 'B' with molecular formula $C_5H_{10}O$. The compound 'B' gives iodoform test but does not reduce ammoniacal $AgNO_3$. 'B' on reduction with amalgamated zinc and HCl gives compound 'C' with molecular formula C_5H_{12}. Identify A, B and C. Write down the chemical reactions involved.

Solution:

'B' gives iodoform test but does not reduce ammoniacal $AgNO_3$ (Tollens' reagent) Thus

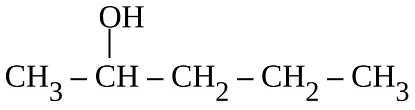
'B' is not an aldehyde, it must be a ketone having $CH_3-\overset{\overset{O}{\|}}{C}-$ group i.e. it must be a methyl ketone. So 'B' may be



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$$

(B) Pentan -2-one

Again ‘B’ is obtained from ‘A’ on oxidation. So ‘A’ is a secondary alcohol.



$$CH_3 - \overset{\overset{\textstyle OH}{|}}{C}H - CH_2 - CH_2 - CH_3$$

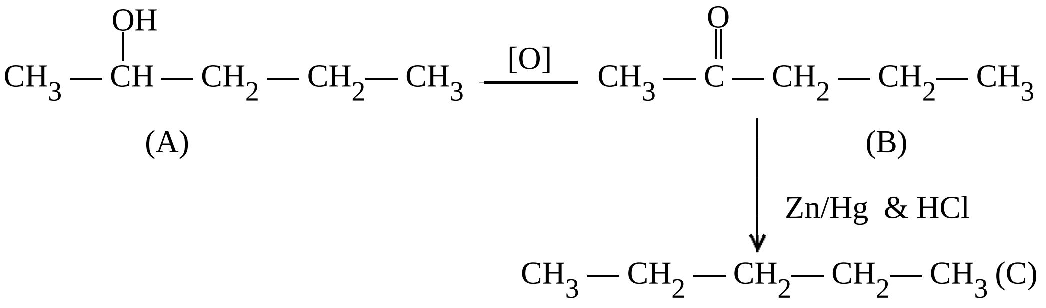
(A) Pentan -2-ol

‘B’ upon reduction with Zn/Hg and HCl gives ‘C’ having molecular formula C_5H_{12}. The $> C{=}O$ group is converted to $> CH_2$ group.

So it must be a hydrocarbon. $CH_3 — CH_2 — CH_2 — CH_2 — CH_3$

n — Pentane (C)

The reactions may be represented as



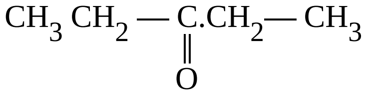
$$\underset{(A)}{CH_3 — \overset{\overset{\textstyle OH}{|}}{C}H — CH_2 — CH_2 — CH_3} \xrightarrow{[O]} \underset{(B)}{CH_3 — \overset{\overset{\textstyle O}{\|}}{C} — CH_2 — CH_2 — CH_3} \xrightarrow{Zn/Hg\ \&\ HCl} CH_3 — CH_2 — CH_2 — CH_2 — CH_3\ (C)$$

3. Compound (A) $C_5H_{10}O$ forms phenyl hydrazone and gives negative Tollens’ and iodoform tests. Compound ‘A’ on reduction gives n-pentane. Give the structure of (A). Explain the reaction.

Solution:

Compound (A) is a carbonyl compound (Aldehyde or a ketone) since it forms phenyl hydrazone. Again it gives negative Tollens’ and iodoform test, so it is a ketone but not methyl ketone. ‘A’ on reduction gives n-pentane, thus ‘A’ is a straight chain compound.

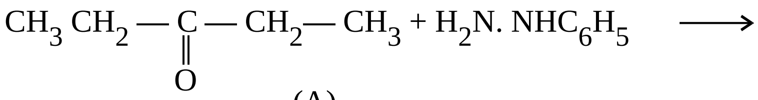
Keeping in view all the above, the formula of ‘A’ is



$$CH_3\,CH_2 — \underset{\underset{\textstyle O}{\|}}{C}.CH_2 — CH_3$$

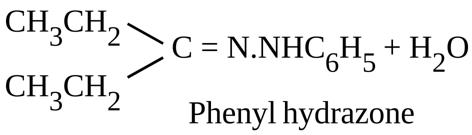
Pentan — 3 — one (A)

The reaction my be represented as

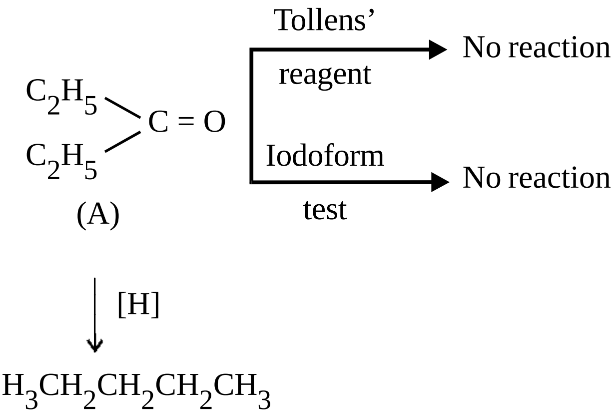


$$CH_3\,CH_2 — \underset{\underset{\textstyle O}{\|}}{C} — CH_2 — CH_3 + H_2N.\,NHC_6H_5 \longrightarrow$$

(A)



Phenyl hydrazone



n — Pentane

4. An unknown compound of C, H and O contains 69.77% C and 11.63% H and has a molecular weight of 86. It does not reduce Fehling's solution but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures?

Solution :

(i) For finding empirical formula

Element	%	Relative number of atoms	Simplest ratio
C	69.77	5.76	5
H	11.63	11.63	10
O	19.20	1.2	1

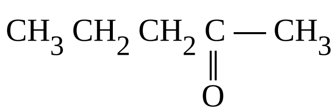
∴ Empirical formula = $C_5H_{10}O$

Empirical formula = $5 \times 12 + 1 \times 10 + 16 = 86$

Also molecular weight = 86

∴ Molecular formula = $C_5H_{10}O$

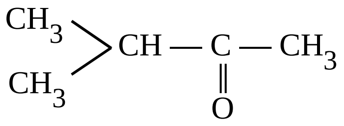
The compound forms a bisulphite compound indicates that it is an aldehyde or a ketone. It does not reduce Fehling's solution, which indicates it is a ketone. It gives +ve iodoform test which indicates that it must contain (CH_3–CO –) group. Keeping all the above facts in view, the structure of ketone may be



$CH_3CH_2CH_2\overset{O}{\underset{\|}{C}}—CH_3$ (O below C: $CH_3CH_2CH_2C(=O)—CH_3$)

Pentan — 2 — one

or



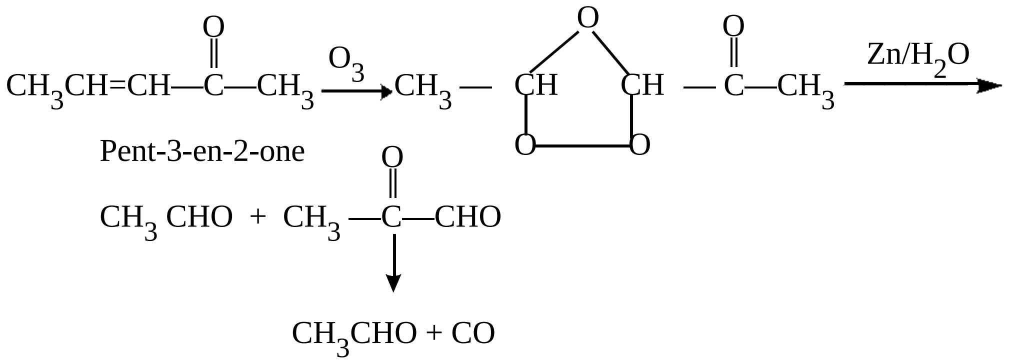
3 — Methyl butan — 2 — one

5. An organic compound ‘A’ C_5H_8O adds Br_2 to form $C_5H_8Br_2O$. It does not react with Tollens’ reagent but reacts with phenyl hydrazine. ‘A’ on ozonolysis gives acetaldehyde and $C_3H_4O_2$ which loses CO forming CH_3CHO. Identify ‘A’ and explain the reaction.

Solution

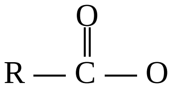
Compound ‘A’ adds one molecule of Br_2, therefore contains a double bond. It forms phenyl hydrazone, hence a carbonyl group is present. Further it does not react with Tollens’ reagent, hence the carbonyl group is ketone and not aldehyde.

‘A’ on ozonolysis gives CH_3CHO and $C_3H_4O_2$. Keeping in view the above facts the structure of ‘A’ is



6. Compound A ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave ‘C’. The compound D was oxidised further of give F which was a monobasic acid (mol. weight 60). Deduce the structures of A, B, C, D and E.

Solution

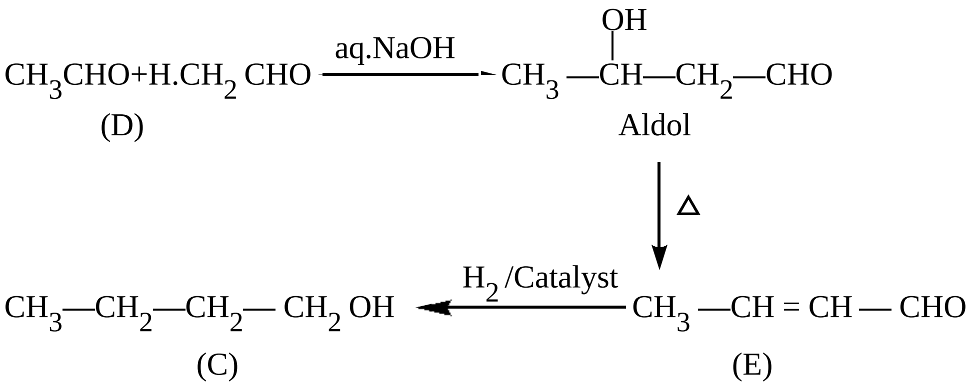


F is monobasic acid. The structure is $R — \overset{\overset{O}{\|}}{C} — OH$. Mol. wt. is 60 (given)

So, $M_R + 12 + 2 \times 16 + 1 = 60$

$\Rightarrow \quad M_R + 45 = 60$

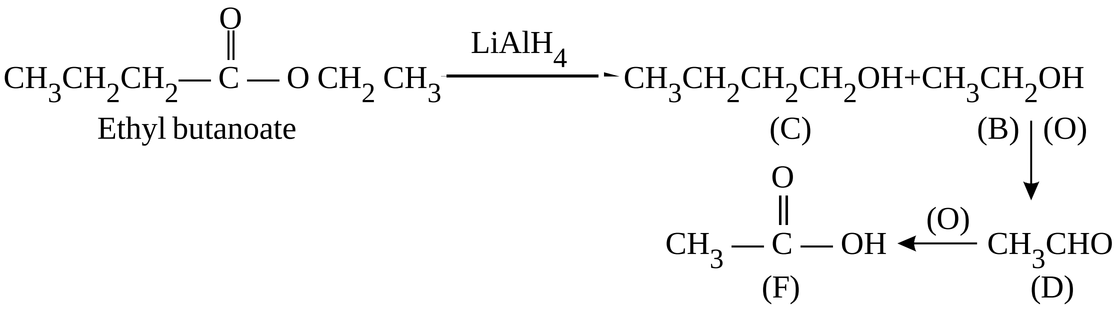
⇒ $M_R = 15$, So the alkyl group is CH_3. 'F' is obtained by oxidation of D. So 'D' must be CH_3CHO. 'D' on treatment with aq. alkali undergoes aldol condensation which on heating loses a molecule of water giving α, β– unsaturated aldehyde. So 'E' must be crotonaldehyde ($CH_3CH = CH\ CHO$)



$$\underset{(D)}{CH_3CHO}+H.CH_2\,CHO \xrightarrow{aq.NaOH} \underset{Aldol}{CH_3-\overset{OH}{\overset{|}{C}}H-CH_2-CHO}$$

$$\xrightarrow{\Delta} \underset{(E)}{CH_3-CH=CH-CHO} \xrightarrow{H_2/Catalyst} \underset{(C)}{CH_3-CH_2-CH_2-CH_2\,OH}$$

'D' is obtained on oxidation of 'B'. Since 'D' is $CH_3\,CHO$, 'B' must be CH_3CH_2OH. Basing on structure of B (CH_3CH_2OH) and that of C($CH_3-CH_2-CH_2-CH_2-OH$), the structure of 'A' may in deduced as follows.



$$\underset{\text{Ethyl butanoate}}{CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-O\,CH_2\,CH_3} \xrightarrow{LiAlH_4} \underset{(C)}{CH_3CH_2CH_2CH_2OH}+\underset{(B)}{CH_3CH_2OH}$$

$$\underset{(B)}{CH_3CH_2OH} \xrightarrow{(O)} \underset{(D)}{CH_3CHO} \xrightarrow{(O)} \underset{(F)}{CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

7. An organic compound (A) contains 40% carbon and 6.7% hydrogen. Its vapour density is 15. On reacting with a concentrated solution of KOH, it gives two compounds (B) and (C). When 'B' is oxidised, original compound 'A' is obtained. When 'C' is treated with conc. HCl it gives a compound D which reduces Fehling's solution and Tollens' reagent and also gives effervescence with $NaHCO_3$ solution. Write the structures of A, B, C and D and explain the reactions.

Solution

For empirical formula

Element	%	Relative number of atoms	Simplest ratio
C	40	3.33	1
H	6.7	6.70	2
O	53.3	3.33	1

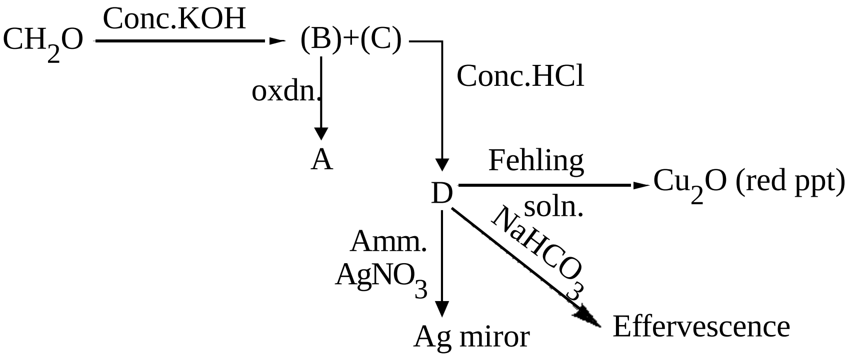
∴ Empirical formula of (A) = CH_2O

Empirical formula weight = 30

Molecular weight = 2 × vapour density = 2 × 15 = 30

Hence molecular formula = Empirical formula = CH_2O

The reaction path is:



(A) is HCHO, Upon treatment with conc. KOH it undergoes Cannizzaro's reaction forming CH_3OH and HCOOK. Since 'B' upon oxidation gives 'A', 'B' must be CH_3OH and 'C' is HCOOK. Upon treatment with conc. HCl 'C' forms HCOOH

$$HCOOK + HCl \longrightarrow \underset{(D)}{HCOOH} + KCl$$

'D' (HCOOH) reduces Fehling soln, Tollens' reagent and gives effervescence with $NaHCO_3$

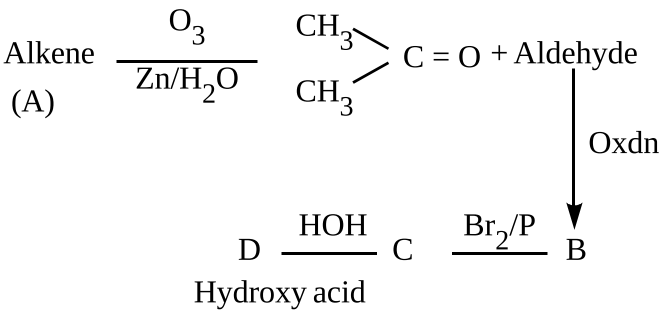
$$HCOOH + \underset{\text{Feh.soln}}{2CuO} \longrightarrow H_2O + CO_2 + \underset{\text{red}}{Cu_2O}\downarrow$$

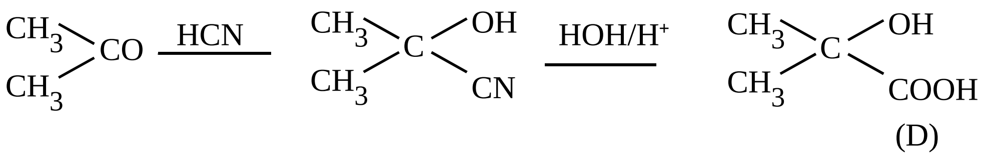
$$HCOOH + \underset{\text{Tollens' reagent}}{Ag_2O} \longrightarrow H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag}$$

$$HCOOH + NaHCO_3 \longrightarrow HCOONa + H_2O + CO_2\uparrow$$

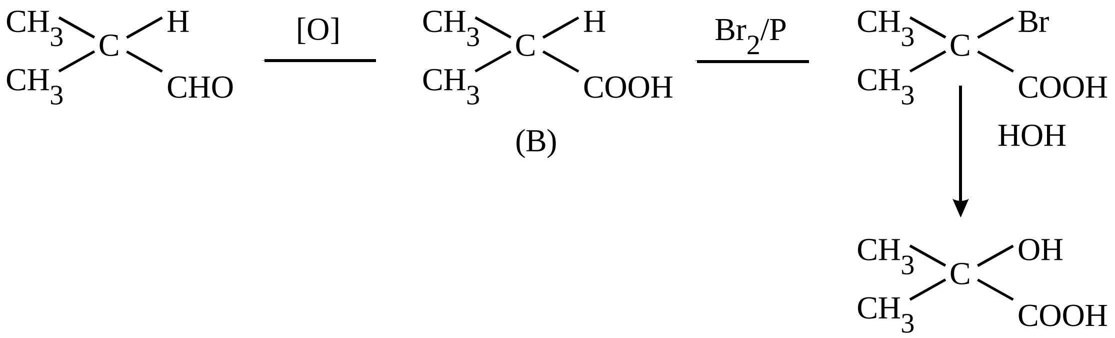
8. An alkene 'A' on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid (B). When 'B' is treated with Br_2 in presence of Phosphorus it yields compound 'C' which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with HCN followed by hydrolysis. Identify A, B, C and D.

Solution



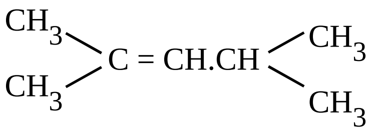


Thus ‘C’ is bromo acid, ‘B’ must be an acid formed by the oxidation of the aldehyde. Keeping all these things in view, the reactions may be represented as



(D)

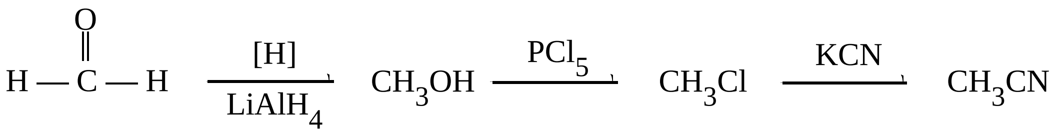
So, the structure of alkene (A) must be



(A)

18.9 IMPORTANT CONVERSIONS :

1. Formaldehyde → Acetaldehyde.



$$H-\overset{\overset{O}{\|}}{C}-H \xrightarrow[LiAlH_4]{[H]} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{KCN} CH_3CN$$

$$\begin{tikzcd}
 & & CH_3CN \arrow[d, "{[H]}"', "Na/Alc"] \\
CH_3CHO & CH_3CH_2OH \arrow[l, "{[O]}"', "K_2Cr_2O_7 / H_2SO_4"] & CH_3CH_2NH_2 \arrow[l, "HNO_2"']
\end{tikzcd}$$

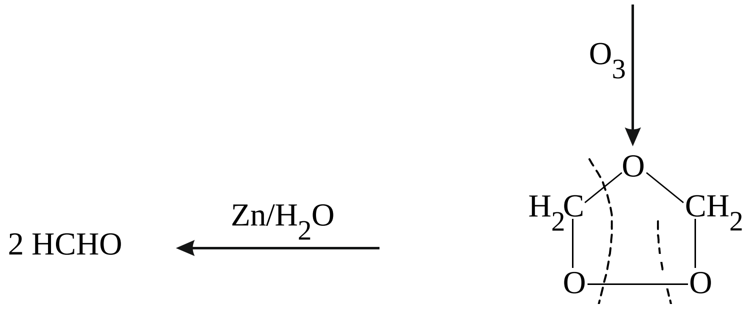
2. Acetaldehyde ⟶ Formaldehyde

(i)

$$\begin{tikzcd}
CH_3CHO \arrow[r, "{[O]}"] & CH_3COOH \arrow[r, "NaOH"] & CH_3COONa \arrow[r, "NaOH", "{CaO,\Delta}"'] & CH_4 \arrow[d, "Cl_2"', "h\nu"] \\
 & HCHO & CH_3OH \arrow[l, "{[O]}"'] & CH_3Cl \arrow[l, "aq.KOH"']
\end{tikzcd}$$

(ii)

$$CH_3CHO \xrightarrow[LiAlH_4]{[H]} CH_3CH_2OH \xrightarrow[170^0]{ConcH_2SO_4} CH_2 = CH_2$$



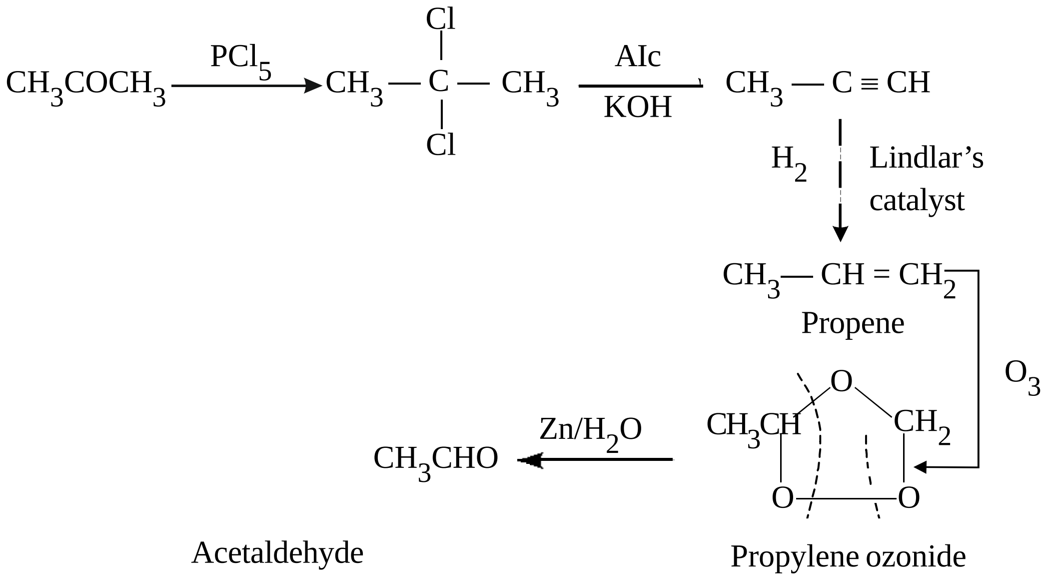
Formaldehyde

Ethylene ozonide

3. Acetaldehyde to Acetone :

$$CH_3CHO \xrightarrow{[O]} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\Delta} CH_3COCH_3$$

4. Acetone to Acetaldehyde :



5. Formaldehyde $\longrightarrow$ Acetone

$$HCHO \xrightarrow{\text{as above}} CH_3CHO \xrightarrow{\text{as above}} CH_3COCH_3$$

6. Acetone $\longrightarrow$ Formaldehyde

$$CH_3COCH_3 \xrightarrow{\text{as above}} CH_3CHO \xrightarrow{\text{as above}} HCHO$$

7. Ethylene $\longrightarrow$ Acetaldehyde

$$\begin{tikzcd}
CH_2 = CH_2 \arrow[r, "HBr"] & CH_3 — CH_2Br \arrow[r, "aqKOH"] & CH_2CH_2OH \arrow[d, "{[O]}", "K_2Cr_2O_7 / H_2SO_4"'] \\
 & & CH_3CHO
\end{tikzcd}$$

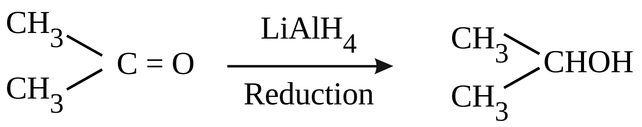
8. Acetaldehyde $\longrightarrow$ Ethylene

$$CH_3CHO \xrightarrow[\text{Na/Alc}]{[H]} CH_3—CH_2OH \xrightarrow[170^0]{ConcH_2SO_4} CH_2 = CH_2$$

9. Acetaldehyde $\longrightarrow$ Ethylalcohol

$$CH_3CHO \xrightarrow[\text{Na/Alc}]{[H]} CH_3CH_2OH$$

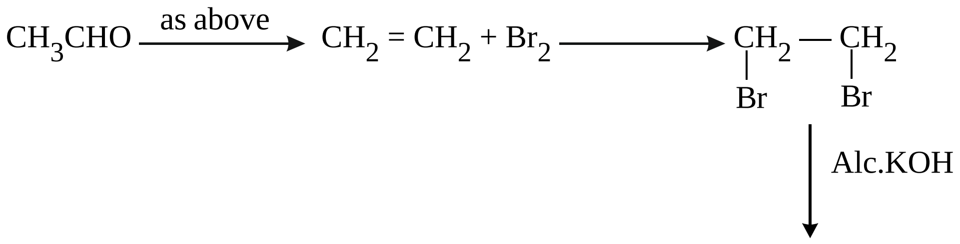
10. Acetone ⟶ Isopropyl alcohol



$$(CH_3)_2C=O \xrightarrow[\text{Reduction}]{LiAlH_4} (CH_3)_2CHOH$$

Isopropyl alcohol

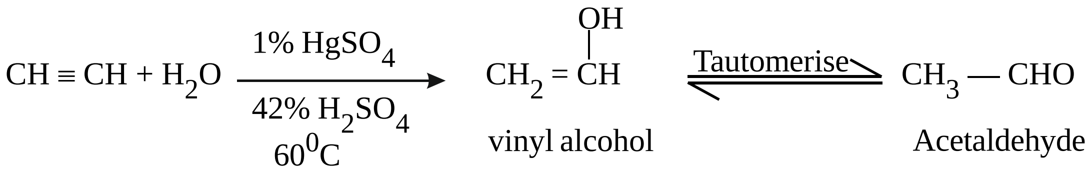
11. Acetaldehyde ⟶ Acetylene



$$CH_3CHO \xrightarrow{\text{as above}} CH_2=CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2}-\underset{Br}{CH_2} \xrightarrow{\text{Alc.KOH}} CH\equiv CH$$

CH≡CH
Acetylene

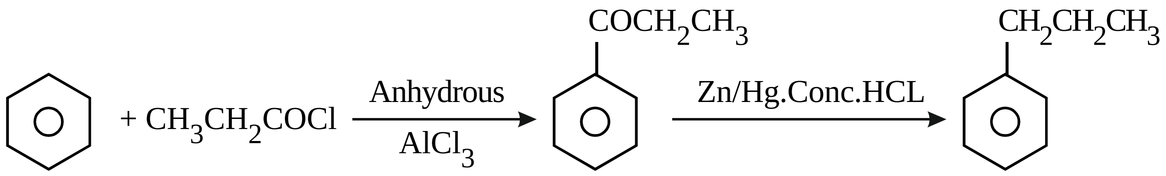
12. Acetylene ⟶ Acetaldehyde



$$CH\equiv CH + H_2O \xrightarrow[\substack{42\%\ H_2SO_4 \\ 60^0C}]{1\%\ HgSO_4} CH_2=\overset{OH}{CH} \xrightleftharpoons{\text{Tautomerise}} CH_3-CHO$$

vinyl alcohol Acetaldehyde

13. Benzene ⟶ n-propyl benzene



CHAPTER (18) AT A GLANGE

1. The general formula of an aldehyde is R — CHO ($R—\overset{\overset{O}{\|}}{C}—H$), whereas that of a ketone is RCOR/ ($R—\overset{\overset{O}{\|}}{C}—R'$). They are known as carbonyl compounds represented by the general formula $C_nH_{2n}O$.

2. Aldehydes show **chain, functional and position (only for aromatic aldehydes)** isomerism whereas ketones show **chain isomerism**, **functional isomerism** and **metamerism**.

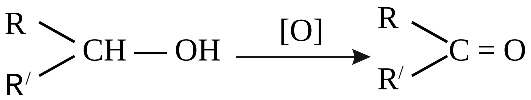
3. The carbon atom of the carbonyl group is sp^2 hybridised and the structure is **planar**.

4. **General Methods of Preparation**

(a) Oxidation of alcohols: Chemical ($K_2Cr_2O_7$ & H_2SO_4) and catalytic (reduced Cu)

$$R — CH_2OH \xrightarrow{[O]} R — CHO$$

(1^0alcohol)



$$\begin{matrix}R\\R'\end{matrix}\!\!>\!CH — OH \xrightarrow{[O]} \begin{matrix}R\\R'\end{matrix}\!\!>\!C = O$$

(Also by Oppenauer oxidation)

(2^0alcohol)

(b) From acids:

(i) Dry distillation of Ca-salt of the fatty acids —

$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

$$(RCOO)_2\ Ca + (HCOO)_2\ Ca \xrightarrow{\Delta} 2R — CHO + 2CaCO_3$$

$$(RCOO)_2\ Ca \xrightarrow{\Delta} R–CO–R + CaCO_3$$

(ii) Vapours of fatty acids passed over hot MnO or ThO_2 at 560K.

$$HCOOH \xrightarrow[560K]{MnO} HCHO$$

$$RCOOH + HCOOH \longrightarrow RCHO$$

$$RCOOH \longrightarrow RCOR$$

(c) From acid chlorides:-

Rosenmund reduction - Acid chlorides can be converted to aldehydes with hydrogen in boiling xylene using Pt or Pd as catalyst supported by $BaSO_4$, poisoned with sulphur.

$$R - COCl \xrightarrow[Pd/BaSO_4,\ S]{H_2} R - CHO$$

$$2R - CO - Cl + Cd\,R_2^1 \xrightarrow{\text{dry ether}} 2R - CO - R^1 + CdCl_2$$

(d) From alkynes :

$$\underset{\text{(Acetylene)}}{CH \equiv CH} \xrightarrow[1\%HgSO_4,\ 340K]{42\%\ H_2SO_4} CH_3CHO$$

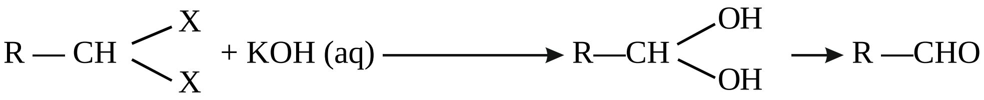
$$\underset{\text{(Propyne)}}{R - C \equiv CH} \longrightarrow \underset{\text{(Methyl ketone)}}{RCOCH_3}$$

(e) From alkenes: Ozonolysis

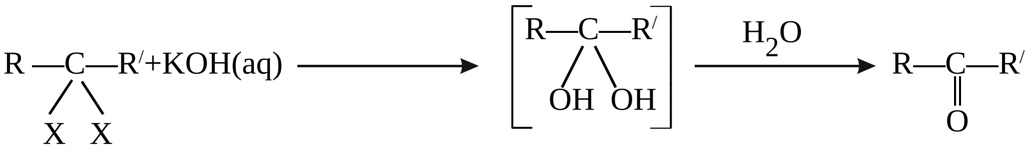
$$R - CH = CH_2 + O_3 \longrightarrow \text{Ozonide} \xrightarrow[H_2O]{\text{Zndust}} RCHO + HCHO$$

$$\begin{matrix} R \\ R' \end{matrix}\!\!>C = CHR'' + O_3 \longrightarrow \text{Ozonide} \xrightarrow[H_2O]{\text{Zndust}} \begin{matrix} R \\ R' \end{matrix}\!\!>C = O + R''CHO$$

(f) From gem-dihalides: Hydrolysis by **aq.KOH**



$$R - CH\!\!<\!\begin{matrix} X \\ X \end{matrix} + KOH\ (aq) \longrightarrow R-CH\!\!<\!\begin{matrix} OH \\ OH \end{matrix} \longrightarrow R-CHO$$



$$R-\underset{X\ \ X}{C}-R' + KOH(aq) \longrightarrow \left[R-\underset{OH\ \ OH}{C}-R' \right] \xrightarrow{H_2O} R-\underset{\underset{O}{\|}}{C}-R'$$

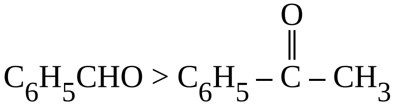
Physical Properties

5. HCHO is a gas at room temperature.
6. Lower members of carbonyl compounds are soluble is water, but the solubility decreases with increase in molecular mass.
7. Boiling points of aldehydes and ketones are less than these of the corresponding alcohols.

Reactions:

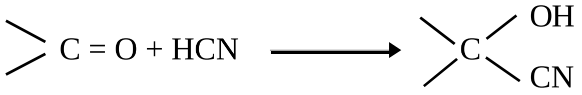
8. Carbonyl compounds undergo **nucleophilic addition** reactions. The order of reactivity follows the following sequence.

$HCHO > CH_3CHO > CH_3COCH_3 > CH_3CH_2COCH_2CH_3 >$



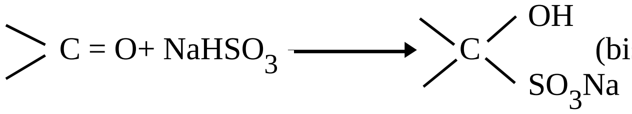
$C_6H_5CHO > C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$

(i) HCN :-



(Cyanohydrin)

(ii) $NaHSO_3$:-



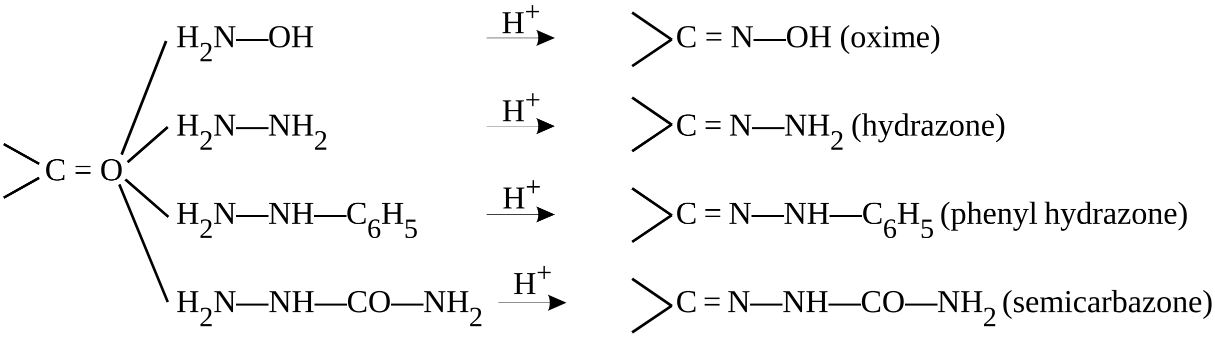
(bisulphite compound)

(employed for separation and purification of carbonyl compounds)

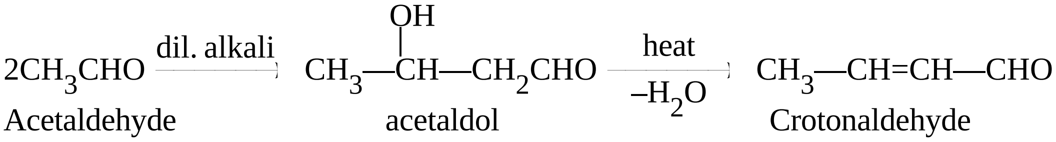
** Note that only methyl ketones undergo bisulphite addition reaction.*

9. **Nucleophilic addition followed by elimination of water.**

Reactent **Product**

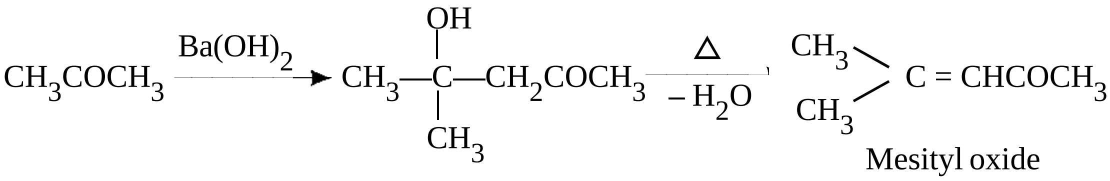


10. **Aldol condensation :-** Aldehydes & ketones having α-hydrogen atom undergo aldol condensation in presence of dilute alkali.



$$2CH_3CHO \xrightarrow{\text{dil. alkali}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CHO \xrightarrow[-H_2O]{\text{heat}} CH_3-CH=CH-CHO$$

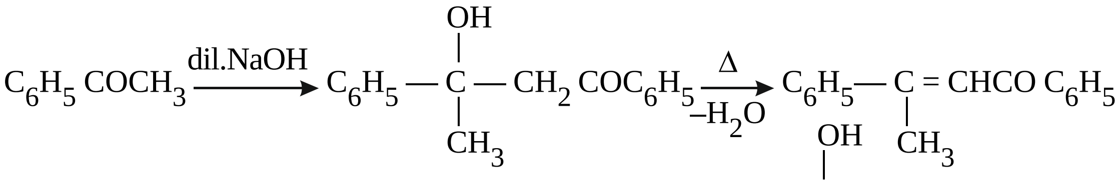
Acetaldehyde acetaldol Crotonaldehyde



$$CH_3COCH_3 \xrightarrow{Ba(OH)_2} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2COCH_3 \xrightarrow[-H_2O]{\Delta} (CH_3)_2C=CHCOCH_3$$

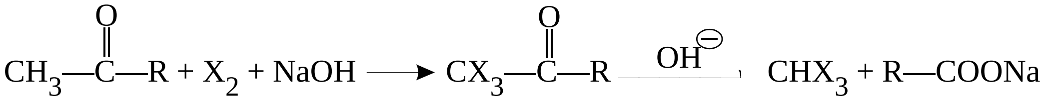
Mesityl oxide

Acetone Diacetone alcohol



$$C_6H_5\,COCH_3 \xrightarrow{\text{dil.NaOH}} C_6H_5-\underset{CH_3}{\overset{OH}{C}}-CH_2\,COC_6H_5 \xrightarrow[-H_2O]{\Delta} C_6H_5-\underset{CH_3}{C}=CHCO\,C_6H_5$$

11. **Haloform reaction:** Acetaldehyde, methyl ketones and $CH_3-\overset{OH}{CH}-R$ (R = H, alkyl or aryl) respond to haloform test.



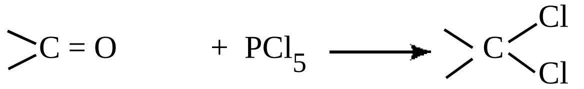
$$CH_3-\overset{O}{\overset{\|}{C}}-R + X_2 + NaOH \longrightarrow CX_3-\overset{O}{\overset{\|}{C}}-R \xrightarrow{OH^{\ominus}} CHX_3 + R-COONa$$

12. **Oxidation Reaction :** Aldehydes can reduce both Fehling's solution (Excepting aromatic aldehydes) and Tollens' reagent whereas ketones can not. Aldehydes form a red precipitate of Cu_2O when warmed with Fehling's solution and form a silver mirror when warmed with Tollens' reagent.

Fehling's solution is a mixture of Fehling A($CuSO_4$) solution and Fehling B (NaOH and sodium potassium tartrate) Sodium potassium tartrate is called Rochelle salt. Tollens' reagent is ammoniacal silver nitrate solution

13. **Reduction of Aldehydes and Ketones:-** Aldehydes and ketones can be catalytically reduced using Raney nickel or Pt.or by $LiAIH_4$ to alcohols. $NaBH_4$ can also be used for this purpose. $NaBH_4$ is a mild and selective reducing agent, since it reduces only the carbonyl group and leaves the carbon carbon double bond intact. Clemmensen and Wolff - Kishner reduction converts a > C = O group to $—CH_2$ group.

14. **PCl_5** reacts with simple carbonyl compounds forming dichlorides.



(Carbonyl comp) (Dichloride)

15. **Formaldehyde** reacts with **ammonia** forming hexamethylenetetramine or urotropine which is used as urinary antiseptic. And for the synthesis of RDX.

16. **Cannizzaro's Reaction :** Aldehydes having no α-hydrogen atom when treated with conc. alkali undergo Cannizzaro's reaction. Two molecules of an aldehyde participate in the reaction out of which one molecule is oxidised to a carboxylic acid and the other molecule is reduced to an alcohol.

$$2R-CHO \xrightarrow{\text{Conc.NaOH}} RCOONa + RCH_2OH$$

Aldehyde	Sod. salt of the carboxylic acid	alcohol

17. Methods of Preparation of Benzaldehyde

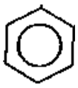
1\. (a) $CH_3 \xrightarrow{\text{Etard's Reaction}} CHO$

(b) $CH_3 \xrightarrow[\text{Oxidation}]{CrO_3} CHO$

2\. $COCl \xrightarrow{\text{Rosenmund Reduction}} CHO$

3\. $C \equiv N \xrightarrow{\text{Stephen Reduction}} CHO$

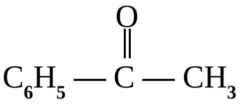
4\. $CH_3 \xrightarrow{Cl_2} CHCl_2 \xrightarrow[\text{(ii) -}H_2O]{\text{(i) Hydrolysis}} CHO$

5\. 

$\xrightarrow[\text{Gattermann - Koch Reaction}]{CO+HCl,(AlCl_3\text{ - }CuCl)} CHO$

18. Methods of preparation of Acetophenone.

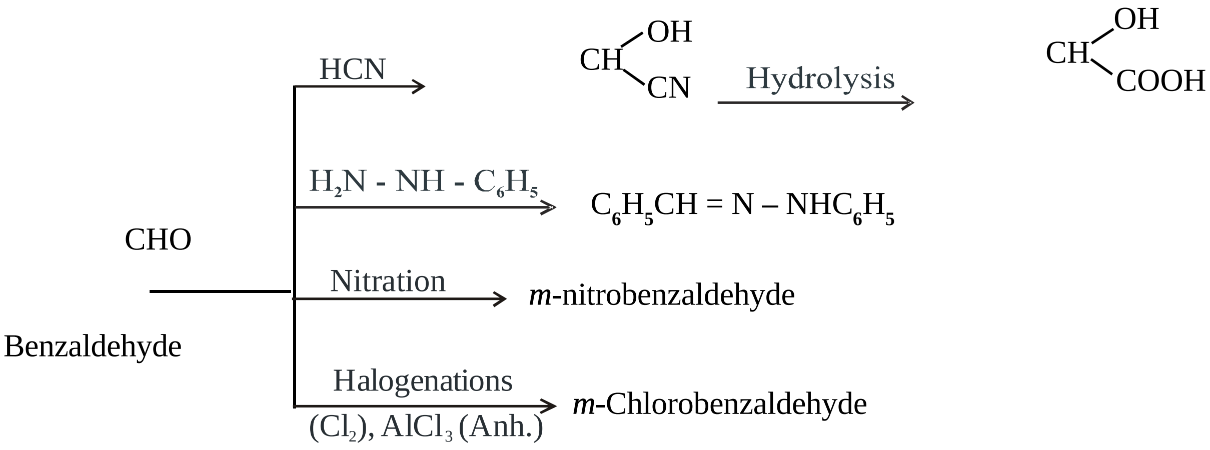
(a) $CH_3 — C \equiv N \xrightarrow[\text{(ii) }H_3O+]{\text{(i) }C_6H_5\text{ MgBr, dry ether}}$



$C_6H_5 — \overset{O}{\overset{\|}{C}} — CH_3$

(b) $+\ CH_3 — COCl \xrightarrow{\text{Anh. }AlCl_3} \overset{COCH_3}{|}\ +\ HCl$

19. Reactions of aryl aldehyde and ketone.



CHO

Benzaldehyde

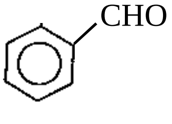
$\xrightarrow{HCN} CH\begin{matrix}OH\\CN\end{matrix} \xrightarrow{\text{Hydrolysis}} CH\begin{matrix}OH\\COOH\end{matrix}$

$\xrightarrow{H_2N\text{ - }NH\text{ - }C_6H_5} C_6H_5CH = N – NHC_6H_5$

$\xrightarrow{\text{Nitration}}$ *m*-nitrobenzaldehyde

$\xrightarrow[(Cl_2),\ AlCl_3\text{ (Anh.)}]{\text{Halogenations}}$ *m*-Chlorobenzaldehyde

Acetophenone undergoes the same reaction.

20. 2 

$\xrightarrow[\text{Cannizzaro Reaction}]{\text{Conc. NaOH}}$ CH_2OH + COONa

QUESTIONS

(A) Very short answer type (1 mark each)

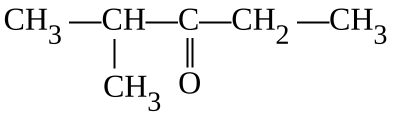
(i) What is Tollen's reagent ?

(ii) What is Fehling's solution ?

(iii) What is formed if calcium acetate is heated at 400^0C ?

(iv) To what state does ethanal reduce Cu(II) ?

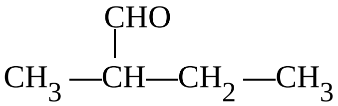
(v) What is the IUPAC name of



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$$

(vi) The Cannizzaro's reaction is given by ————

(vii) Write the IUPAC name of the compound



$$CH_3-\overset{CHO}{\overset{|}{CH}}-CH_2-CH_3$$

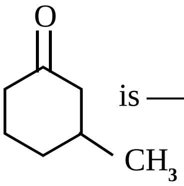
(viii) Write the structural formula of the compound 1-bromo-3-pentanone.

(ix) Aldehydes react with hydroxylamine to produce ————

(i) oxime (ii) alcohol (iii) hydrazone (iv) phenyl hydrazone.

(x) Name the functional isomer of propanone.

(xi) The precipitate formed when an aldehyde reacts with Fehling's solution is————

(xii) IUPAC name of compound  is ————

(xiii) Write the structure of the compound 4-Oxopentanal.

(B) Short answer type (2 marks each)

(i) How would you get oxime from acetaldehyde ? Give equation.

(ii) What is Fehling's solution ? How does it react with acetaldehyde ?

(iii) Write one reaction to distinguish between acetaldehyde and acetone. Give equation

(iv) What happens when acetaldehyde reacts with HCN ? Give equation.

(v) What happens when ethylene reacts with ozone ? Explain with equation.

(vi) What happens when formaldehyde reacts with HCN. ? Give equation.

(vii) Show the iodoform reaction in case of acetaldehyde with equation.

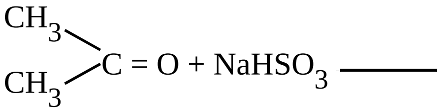
(viii) What is Tollens' reagent ? What happens when it reacts with benzaldehyde ?

(ix) What is Rosenmund's reduction ? Explain it giving an example.

(x) What happens when acetone is treated with HCN ? Give equation.

(xi) What happens when benzaldehyde is treated with Fehling's solution and why ? Explain.

(xii) Complete the following equation



$(CH_3)_2C = O + NaHSO_3 \longrightarrow$

(xiii) What happens when HCHO reacts with NH_3 ?

(xiv) How will you distinguish acetaldehyde and benzaldehyde.

(xv) Which compound can undergo Cannizzaro's reaction - Give one example

(xvi) What happens when acetaldehyde reacts with iodine in dilute NaOH solution ? Give equation.

(xvii) Write with equation what happens when acetone reacts with iodine in presence of sodium hydroxide.

(xviii) Identify X & Y in the series.

$$CH_3CHO \xrightarrow[KMnO_4]{Acidic} X \xrightarrow{SOCl_2} Y$$

(xix) How will you prepare phenyl hydrazone of acetone ? Indicate with equation.

(xx) Write with equation, how urotropine is formed

(xxi) Name the compound in IUPAC system having molecular formula C_3H_6O, which can reduce Tollens' reagent. What is Tollens' reagent ?

(xxii) Calcium acetate $\xrightarrow{\Delta}$ [A] $\xrightarrow{I_2 / KOH}$ [B] yellow ppt. Identify the products A & B. Name the reaction in Step-II.

(xiii) Explain why methanal in a gas, where as ethanal is liquid

(xiv) Explain why ethanal is having lower boiling point than ethanol.

(C) Short answer type questions (3 marks each)

(i) Distinguish between acetaldehyde and acetone.

(ii) Distinguish between formaldehyde and acetaldehyde.

(iii) Distinction between benzaldehyde and acetophenone

(iv) Name one primary alcohol which gives iodoform test and explain why?

(v) Distinguish between ethyl alcohol and acetone.

(vi) Distinguish between acetaldehyde and benzaldehyde.

(vii) Explain why aldehydes are more reactive than ketones.

(viii) Although both $>C=C<$ and $>C=O$ contain double bond, they differ in their characteristics. Explain.

(ix) Arrange the following compounds in increasing order of their boiling points with plausible explation.

CH_3CH_2OH, CH_3OCH_3, CH_3CHO, CH_3CH_3

(x) Explain Clemmensen's reduction giving one example.

(xi) Convert benzene to benzaldehyde.

(xii) Convert Benzoyl chloride to benzaldehyde.

(xiii) Convert benzaldehyde to m-chlorobenzaldehyde.

(D) Long answer type (7 marks each)

(i) Write notes on (a) Aldol condensation
(b) Cannizzaro reaction

(ii) How acetone is prepared ? What happens when acetone reacts with

(a) HCN (b) NH_2OH (c) $C_6H_5NH.NH_2$

(iii) Write notes on (a) Iodoform reaction
(b) Reduction of aldehydes and ketones.

(iv) Describe two general methods of preparation of ketones. State with equations how acetone reacts with

(a) Phenyl hydrazine
(b) Hydrocyanic acid
(c) Iodine in presence of sodium hydroxide.

(v) How can benzaldehyde be synthesized by the following reaction ?

(a) Etard reaction

(b) Rosenmund reduction

Explain why it is less reactive than CH_3CHO towards nucleophilic addition reaction.

(vi) How is acetaldehyde prepared ? With equation give its reaction with

(a) HCN (b) $C_6H_5NH.NH_2$ (c) NaOH solution

(vii) (a) What is Haloform reaction ? How will you prepare Iodoform from acetone ? Can you prepare Iodoform from Formaldehyde ?

(b) How will you prepare acetophenone by Friedel - Craft's reaction ?

(viii) How will you differentiate

(a) Ethyl alcohol and acetone

(b) Acetaldehyde and acetone

(ix) What happens when (give equation)

(i) C_2H_5OH is passed over hot reduced Cu at 300^0C

(ii) HCHO is treated with NH_3

(iii) Acetone is treated with I_2 and NaOH solution

(iv) CH_3CHO reacts with NH_2OH

(v) Calcium acetate is heated

(x) How is acetone prepared ? Give two methods. What happens when acetone reacts with:

(a) Phenyl hydrazine

(b) Hydroxylamine

(c) Sodium bisulphite

(xi) Explain with equation how aldehydes and ketones can be prepared from calcium salts of organic acids. What happens when acetaldehyde reacts with the following substances ?

(a) NH_2OH (b) Phenyl hydrazine (c) Hydrogen in presence of nickel catalyst.

(xii) How acetaldehyde can be prepared from the following ?

(a) Acetyl chloride (b) Acetylene

How does it react with (a) Fehling's solution, (b) Tollens' reagent ? Give equations. What is formalin ? How is it used ?

(xiii) How aldehydes and ketones are prepared from dry distillation of calcium salts ? How aldehydes react with (a) $NaHSO_3$ (b) Phenyl hydrazine ? Describe one test to distinguish between aldehydes and ketones.

(xiv) Give two methods for the preparation of ketones. How does acetone react with

(i) Iodine in NaOH solution and

(ii) Sodium bisulphite ?

(iii) Hydroxyl amine ?

(xv) How are ketones prepared from (a) salts of carboxylic acids (b) acid chlorides? How does acetone react with (i) ammonia (ii) barium hydroxide (iii) hydroxylamine?Explain with equation.

(xvi) Discuss briefly the structure and nature of the carbonyl group. In what respects the C = C and C = O bonds resemble and differ from each other.

ADDITIONAL QUESTIONS

I. Very short answer type (1mark each)

(i) What type of ketones undergo iodoform test ?

(ii) With which reagent can you distinguish between pentan-2-one and pentan-3-one?

(iii) What happens when calcium acetate is heated?

(iv) Which alkene on ozonolysis gives acetone?

(v) What is Rosenmund’s reduction ?

(vi) Why HCHO does not undergo aldol condensation ?

(vii) Which aldehyde can undergo iodoform test ?

(viii) What is the reagent used for conversion of acid chloride to aldehyde ?

(ix) Name one reagent used to distinguish between acetaldehyde & acetone.

(x) What is IUPAC name of Formaldehyde ?

II. Short answer type Questions (2 marks each)

(i) Explain why HCHO is more reactive than acetaldehyde.

(ii) Explain why diethyl ketone does not exhibit haloform reaction.

(iii) In what respect, the C = C and C = O bonds resemble each other?

(iv) Arrange HCHO, CH_3CHO and CH_3COCH_3 in order of increasing reactivity towards HCN.

(v) Explain why the boiling points of aldehydes and ketones are lower than those of alcohol.

(vi) Explain why the lower members of carbonyl compounds are soluble in water ?

(vii) How is acetaldehyde prepared from ethanol ?

(viii) What is the function of $BaSO_4$ in Rosenmund's reduction.

(ix) Explain why hydrazones of aldehydes & ketones are not prepared in highly acidic medium.

(x) Write the structure of Urotropine.

(xi) How will you detect carbonyl group in an organic compound ?

(xii) Explain why trichloroacetaldehyde does not undergo aldol condesation.

(xiii) Explain why benzaldehyde does not undergo aldol condensation whereas acetaldehyde does.

(xiv) Explain why the bond energy of $>C = O$ is higher than that of $>C = C<$

(xv) Oximes are more acidic than hydroxylamine. Why ?

(xvi) How does acetaldehyde react with Tollens' reagent? Give equation.

(xvii) How will you distinguish an aldehyde from a ketone? Give one chemical test.

(xviii) Which type of aldehydes show Cannizzaro reaction?

III. Long Answer type.

1. (a) Give four points of difference between acetaldehyde and acetone

   (b) How can you bring out the conversion of ethanol to 2-hydroxy -3-butanoic acid.

2. Explain the action of the following reagents on acetophenone

   (a) Hydrogen cyanide

   (b) I_2, aq.NaOH

   (c) Conc.HNO_3 in the presence of Conc.H_2SO_4

   (d) Phenylhydrazine.

3. How can you bring out the following conversions ?

   (a) Acetaldehyde to acetoxime

   (b) Methanal to ethanal

   (c) Ethanal to 2-hydroxybutanoic acid

   (d) Acetylene to acetone (4 steps)

4. What happens when

   (a) Formaldehyde is treated with NH_3?

   (b) Acetylene is pased through dilute H_2SO_4 in presence of $HgSO_4$.

   (c) Formaldehyde is treated with conc H_2SO_4.

   (d) Acetylchloride is treated with H_2 is presence of Pd/$BaSO_4$.

   (e) A mixture of calcium formate and calcium acetate undergoes dry distillation.

5. Discuss the reaction used to distinguish between aldehydes and ketones.

(F) Multiple Choice type Questions with answers.

1. The reagent with which both acetaldehyde and acetone react easily is

   (a) Fehling solution (b) Grignard reagent

   (c) Schiff's reagent (c) Tollens' reagent

2. Which of the following compounds is oxidised to prepare methyl ethyl ketone ?

   (a) 2-Propanol (b) 1-Butanol

   (c) 2-Butanol (d) Formaldehyde

3. Cannizzaro reaction is not given by

   (a) Trimethyl acetaldehyde (b) Acetaldehyde

   (c) Benzaldehyde (d) Formaldehyde

4. The formation of cyanohydrin from a ketone is an example of

   (a) Electrophilic addition (b) Nucleophilic addition

   (c) Nucleophilic substitution (d) Electrophilic substitution

5. When acetaldehyde is heated with Fehling's solution, it gives a precipitates of

   (a) Cu (b) CuO

   (c) Cu_2O (d) Cu + CuO + Cu_2O

6. Methyl ketones are usually characterised through

   (a) Tollens' reagent (b) Iodoform test

   (c) The Schiff's test (d) Benedict's reagent

7. Tollens' reagent is

   (a) Ammoniacal cuprous chloride (b) Ammoniacal cuprous oxide

   (c) Ammoniacal silver bromide (d) Ammoniacal silver nitrate

8. Aldehydes can be distinguished from ketones by using

(a) Schiff's reagent (b) Conc. H_2SO_4
(c) anhydrous $ZnCl_2$ (d) resorcinol

9. Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives

(a) acetic acid (b) acetaldyhyde
(c) formic acid (d) formaldehyde

10. Aldehydes can be oxidised by

(a) Tollens' reagent (b) Fehling's solution
(c) Benedict's solution (d) all

11. Isopropyl alcohol on oxidation forms

(a) Acetone (b) Ether
(c) Formalin (d) Hydrobenzamide

12. Formaldehyde reacts with NH_3 to give

(a) Hexamethylenetetramine (b) Formaldehyde ammonia
(c) Formalin (d) Hydrobenzamide

13. At room temperature formaldehyde is

(a) gas (b) liquid
(c) solid (d) all

14. Which of the following can reduce Tollens' reagent ?

(a) 2-hydroxy propane (b) Acetophenone
(c) Both (d) None

15. $RCH = O + H_2 \longrightarrow RCH_2OH$

For this reaction the catalyst is

(a) Ni only (b) Pd only
(c) Pt only (d) any of the above

16. Which of the following can reduce Tollens' reagent ?

(a) $CH_3 — CH = CH_2$ (b) CH_3COCH_3
(c) CH_3CHO (d) $CH_3 — O — CH_3$

17. Calcium acetate when dry distilled gives

(a) Formaldehyde (b) Acetaldehyde

(c) Acetone (d) Acetic anhydride

18. Formaldehyde when treated with conc. KOH gives

(a) CH_3CHO (b) C_2H_4

(c) CH_3OH, HCOOK (d) CH_3OH, CH_3CHO

19. Which compound undergoes iodoform reaction

(a) HCHO (b) CH_3CHO

(c) CH_3OH (d) CH_3COOH

20. Identify ‘Z’ in the series

$$CH = CH_2 \xrightarrow{\text{HBr}} X \xrightarrow{\text{Hydrolysis}} Y \xrightarrow[I_2\text{excess}]{\text{NaOH}} Z$$

(a) C_2H_5I (b) C_2H_5OH

(c) CHI_3 (d) CH_3CHO

21. Formaldehyde when treated with conc. KOH gives methanol and potassium formate. The reaction is known as

(a) Perkin’s reaction (b) Claisen’s reaction

(c) Cannizzaro’s reaction (d) Knoevenagel’s reaction

22. Formalin is an aqueous solution of

(a) Formic acid (b) Formaldehyde

(c) Fluorescein (d) Furfuraldehyde

23. Hexamethylene tetramine is used as

(a) analgesic (b) antipyretic

(c) Urinary antiseptic (d) all

24. Aldol condensation will not occur in

(a) HCHO (b) CH_3CH_2CHO

(c) CH_3COCH_3 (d) CH_3CHO

25. Propyne on hydrolysis in presence of HCl and $HgSO_4$ gives

(a) Acetaldehyde (b) Acetone

(c) Formaldehyde (d) None

26. When anhydrous acetaldehyde is brought in contact with a drop of conc. H_2SO_4 at ordinary temperature, the following compound is formed.

(a) Aldol
(b) Paraldehyde
(c) metaldehyde
(d) acetal

27. The reaction between formaldehyde and caustic soda to produce methyl alcohol is known as

(a) Cannizzaro reaction
(b) Kolbe's reaction
(c) Rosenmund's reduction
(d) Friedel Craft reaction

28. Rosaniline hydrochloride decolourised by SO_2 is called

(a) Benedict's solution
(b) Tollen's regent
(c) Schiffs reagent
(d) Magenta solution

29. Acetaldehyde reacts with phosphorus pentahalide to produce

(a) acetal
(b) ethyledene chloride
(c) alcohol
(d) chloral

30. Formaldehyde is a raw malerial for the manufacture of

(a) nylon
(b) terylene
(c) bakelite
(d) rayon

31. Which of the following reagents helps to distingish an aldehyde from a ketone ?

(a) Phenyl hydrazine
(b) $NaHSO_3$
(c) neutral $FeCI_3$
(d) Ammoniacal $AgNO_3$ solution

32. Which of the following does not show aldol condensation ?

(a) CH_3CHO
(b) CH_3CH_2CHO
(c) $(CH_3)_3\,C — CHO$
(d) $CH_3\,(CH_2)_2\,CHO$

33. In which of the following reactions, both the oxidised and reduced forms of the same compound are obtained ?

(a) Aldol condensation
(b) Cannizzaro reaction
(c) Reimer Tiemann reaction
(d) Kolbe's synthesis

34. In the Cannizzaro reaction given below

$2\,ArCHO \xrightarrow{OH^-} Ar\,CH_2OH + ArCOO^-$, the slowest step is

(a) The attack of OH^- at the carbonyl group
(b) The transfer of hydride ion to the carbonyl group
(c) The abstraction of a proton from the carboxylic acid
(d) The deprotonation of $Ar – CH_2OH$.

35. Which of the following statement is not true about benzaldehyde ?
    (a) Undergoes Cannizzaro reaction
    (b) Forms an addition compound with HCN
    (c) Undergoes aldol condensation
    (d) Reacts with phenylhydrazine

36. Cannizzaro reaction is given by :
    (a) C_6H_5CHO
    (b) CH_3 CHO
    (c) $C_6H_5CH_2CHO$
    (d) $C_6H_5CO\ CH_3$

37. Cannizzaro reaction is an example of :
    (a) Only oxidation
    (b) Only reduction
    (c) Disproportionation
    (d) None of these

38. Cyanohydrin of benzaldehyde on hydrolysis will give :
    (a) an optically active hydroxy acid
    (b) benzoic acid
    (c) benzyl alcohol
    (d) Acetophenone

39. In the given reaction 'X' will be **:**

$$C_6H_5COCl \xrightarrow[\text{Pd-BaSO}_4\text{,S}]{H_2} \text{'X'}$$

    (a) C_6H_5 COOH
    (b) $C_6H_5CH_2OH$
    (c) C_6H_5CHO
    (d) $C_6H_5CH_3$

(G) Fill in the blanks (with answers) (1 mark each)

1. Methanal + Ammonia ⟶ ________

2. Fehling A consists of an aqueous solution of copper suphate while Fehling 'B' consists of an alkaline solution of ________

3. Ethanol vapour is passed over heated copper and the product is treated with aq NaOH. The final product is ________

4. 40 % aqueous solution of HCHO is ________

5. Calcium formate on dry distillation gives ________

6. Carbon atom of carbonyl group is ________ hybridised.

7. When acetaldehyde is heated with Fehling solution a ________ precipitate of ________ is formed.

8. IUPAC name of acetaldehyde is ________

9. When vapour of isopropyl alcohol is passed over hot reduced copper ________ is formed.

10. Both aldehydes and ketones react with ________ reagent.

11. Silver mirror test is a test for ________

12. Acetaldehyde on treatement with ________ gives aldol.

13. Sodium potassium tartrate is ________ salt.

14. Magenta is ————

15. Conversion of hexan-1-ol to hexanal is carried out by the reagent ————.

16. The reagent ———— converts but-2-ene to ethanal.

H. Complete the following with answers (2 marks each)

1. $(A) \xrightarrow[\text{dil.}H_2SO_4]{Hg^{2+}} CH_3CHO \xrightarrow{(CH_3CO)_2O} (B)$

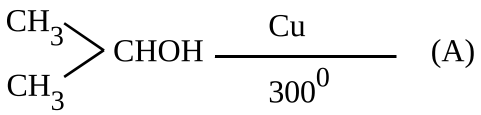
2. $CH_3COCl + H_2 \xrightarrow{Pd\ /\ BaSO_4,\ S} (A)$

3. $CH_3CHO \xrightarrow{\text{dilNaOH}} (A)$

4. $2HCHO + NaOH \longrightarrow$ ______ + ______

5. $HCHO + NH_3 \longrightarrow (A)$

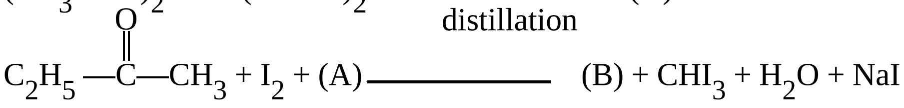
6.



$$(CH_3)_2CHOH \xrightarrow[300^0]{Cu} (A)$$

7. $(CH_3COO)_2\,Ca + (HCOO)_2\,Ca \xrightarrow[\text{distillation}]{\text{dry}} (A)$

8.



$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + I_2 + (A) \longrightarrow (B) + CHI_3 + H_2O + NaI$$

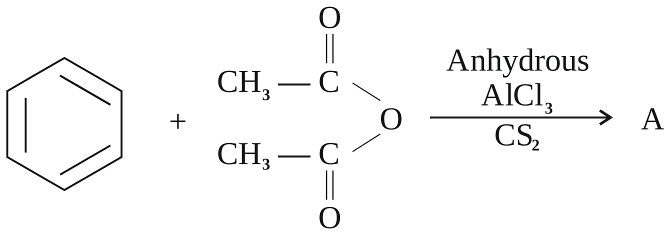
9. $CH_3CH_2OH \xrightarrow{(O)} A \xrightarrow{Cl_2} B \longrightarrow CHCl_3$

10. $HCHO + HCN \longrightarrow (A)$

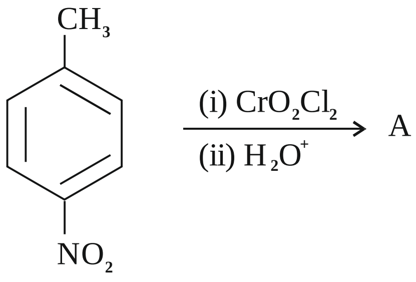
11. $CH_3CHO + I_2 \xrightarrow{NaOH} (A)$

12. $CH_3COCH_3 + H_2\,NOH \longrightarrow (A)$

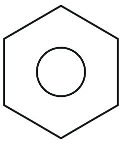
13.

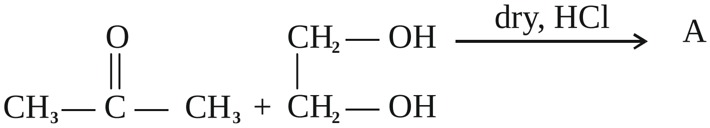


14.

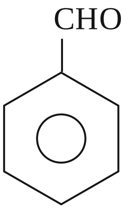


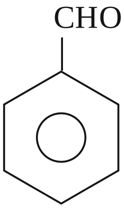
15. $(C_6H_5-CH_2)\,Cd + 2CH_3COCl \longrightarrow A$

16.  $\xrightarrow[\text{Anhydrous AlCl}_3]{\text{CO, HCl}}$ A

17. 
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \begin{array}{l}CH_2-OH\\ |\\ CH_2-OH\end{array} \xrightarrow{\text{dry, HCl}} A$$

18. $CH_3CHO + [Ag(NH_3)_2]\,OH \longrightarrow A$

19.  $\xrightarrow{\text{LiAlH}_4}$ A

20.  + Conc.NaOH $\xrightarrow{\Delta}$ A + B

21. $CH_3CO\,CH_2\,COO\,C_2H_5 \xrightarrow[\text{(ii) } H^+]{\text{(i) NaBH}_4} A$

22. $C_6H_5COCH_3 \xrightarrow{\text{Zn/Hg, Conc.HCl}} A$

ANSWERS

Multiple choice type question

1.b
2.c
3.b
4.b
5.c
6.b
7.d
8.a
9.b
10.d
11.a
12.a
13.a
14.d
15.d
16.c
17.c
18.c
19.b
20.c
21.c
22.b
23.c
24.a
25.b
26.b
27.a
28.c
29.b
30.c
31.d
32.c
33.b
34.b
35.c
36.a
37.c
38.a
39.c

Fill in the blanks

1. $(CH_2)_6N_4$
2. Sodium potassium tartrate
3.Aldol
4.Formalin
5. HCHO
6. sp^2
7.red, Cu_2O
8.Ethanal
9. CH_3COCH_3
10.Grignard
11.Aldehyde
12.dil.NaOH
13.Rochelle
14.Rosaniline hydrochloride
15.PCC
16. $O_3/Zn–H_2O$

Complete the following

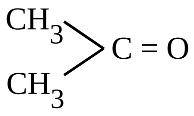
1. $CH \equiv CH$ (A) $CH_3CH(OCOCH_3)_2$ (B)

2. (A) is CH_3CHO

3. (A) is $CH_3CH(OH)\ CH_2CHO$

4. (A) = CH_3OH, (B) = HCOONa

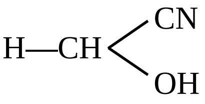
5. (A) = $(CH_2)_6N_4$

6. (A) = 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = O$

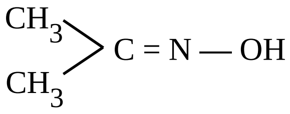
7. (A) = CH_3CHO

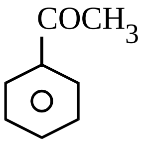
8. (A) = NaOH (B) = C_2H_5COONa

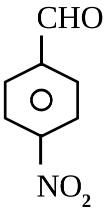
9. (A) = CH_3CHO (B)CCl_3CHO

10. (A) = 
$H—CH<\begin{matrix}CN\\OH\end{matrix}$

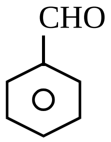
11. (A) CHl_3

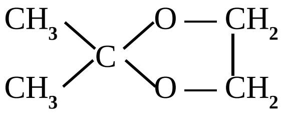
12. (A) = 
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C = N — OH$

13. 

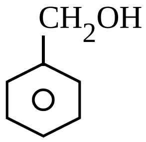
14. 

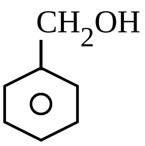
15. $C_6H_5CH_2COCH_3$

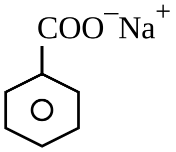
16. 

17. 

18. CH_3COONH_4

19. 

20. A = 

B = 

21. $CH_3CHOH\ CH_2\ COOC_2H_5$

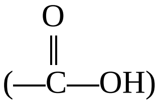
22. $C_6H_5CH_2CH_3$

❑❑❑

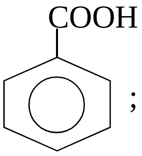
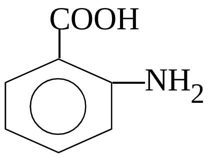
CHAPTER - 19

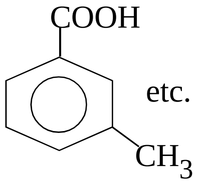
CARBOXYLIC ACIDS

19.1 GENERAL INTRODUCTION :

Organic compounds having carboxyl group ( $\text{—}\overset{\overset{\large O}{\|}}{C}\text{—OH}$) are called **carboxylic acids**. The carboxyl group is a combination of a *carbonyl* group ($>C=O$) and a *hydroxyl* group (—OH) and hence the name *carboxyl* (carb from *carbonyl* and *oxyl* from hydroxyl).

Carboxylic acids are classified as aliphatic or aromatic depending upon whether —COOH group is linked to aliphatic alkyl chain or aryl group respectively. For example, formic acid (HCOOH), acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH) etc. are aliphatic and

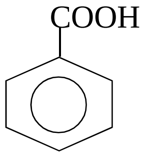
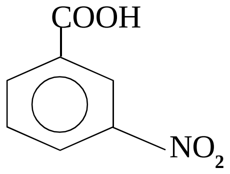
Benzoic acid,  ; 2-Amino benzoic acid,  ; 3-Methyl benzoic acid,

 etc. are aromatic acids.

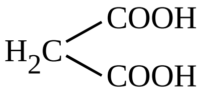
These acids are further classified as mono, di, tri carboxylic acids according to the number of carboxyl groups present in their molecules.

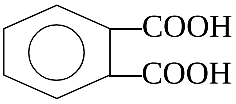
For example :

Monocarboxylic acids:

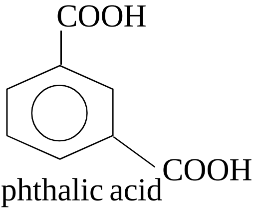
HCOOH	CH_3COOH		
Formic acid	Acetic acid	Benzoic acid	3-Nitrobenzoic acid

Dicarboxylic acid :

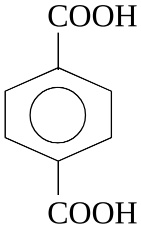
$\begin{array}{l}COOH\\ \mid\\ COOH\end{array}$		$\begin{array}{l}CH_2COOH\\ \mid\\ CH_2COOH\end{array}$
Oxalic acid	Malonic acid	Succinic acid



Phthalic acid
(1, 2 - Benzenedicarboxylic acid)



Isophthalic acid
(1, 3 - Benzenedicarboxylic acid)



Terephthalic acid
(1, 4 - Benzenedicarboxylic acid)

The aliphatic monocarboxylic acids are called fatty acids since many higher acids e.g. stearic ($C_{17}H_{35}$ COOH), palmitic ($C_{15}H_{31}COOH$), oleic ($C_{17}H_{33}COOH$) etc. are formed by the hydrolysis of natural fats. The general formula for aliphatic saturated monocarboxylic acids is C_nH_{2n+1} COOH or $C_nH_{2n}O$ or RCOOH where R stands for hydrogen or alkyl group. Lower members of monocarboxylic acids occur in various plants and animals.

19.2 NOMENCLATURE :

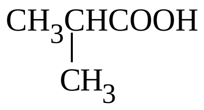
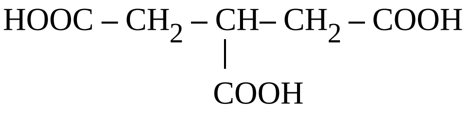
(1) **Common System :** According to common system, lower members are named after the source of the individual acids. For example, formic acid was so named because it was first obtained by the distillation of red ants (Latin: *formica* meaning *ant*). Similarly, acetic acid was so named because it was obtained from vinegar (Latin: *acetum* meaning *vinegar*). In this system, the positions of the substituents are indicated by Greek letters (α, β, γ, δ...). Carbon atom adjacent to the carboxyl group is assigned α and the next carbon atom β and so on.

(2) **IUPAC system:** (a) Aliphatic carboxylic acids according to IUPAC system are named as *alkanoic acids* by replacing the terminal ‘e’ of the corresponding alkane by ‘-oic acid’. The positions of the substituents are indicated by Arabic numerals according to the following rules:

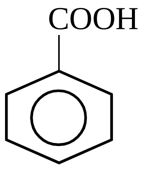
(i) The longest carbon chain containing –COOH group is selected.

(ii) The carbon atom of the carboxyl group is assigned the number 1.

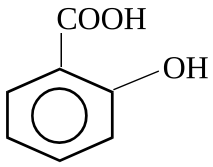
Table 19.1: Common and IUPAC names of some aliphatic carboxylic acids

Monocarboxylic acid	Common name	IUPAC name
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	n-Butyric acid	Butanoic acid
 $CH_3\underset{\displaystyle CH_3}{\underset{\mid}{C}}HCOOH$	Isobutryric acid or α-Methyl propionic acid	2-Methylpropanoic acid
 $(CH_3)_2CHCH_2COOH$	β-Methyl butyric acid	3-Methyl butanoic acid
$CH_3(CH_2)_3COOH$	n-Valeric acid	Pentanoic acid
$CH_3(CH_2)_4COOH$	n-Caproic acid	Hexanoic acid
$HOOC-COOH$	Oxalic acid	Ethanedioic acid
$HOOC-(CH_2)_2-COOH$	Succinic acid	Butanedioic acid
 $HOOC-CH_2-\underset{\displaystyle COOH}{\underset{\mid}{C}H}-CH_2-COOH$	—	Propane-1, 2, 3 – tricarboxylic acid

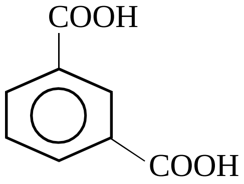
(b) **Aromatic acids** are named by common names or as derivatives of parent benzoic acid,which are also accepted by IUPAC. Examples of this family are :



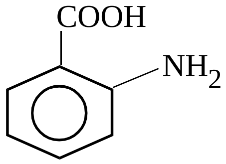
Benzenecarboxylic acid
(Benzoic acid)



2-Hydroxybenzoic acid
(Salicylic acid)

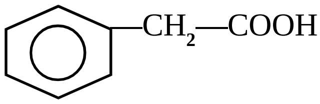


Benzene - 1, 3 - dicarboxylic acid
(Isophthalic acid)

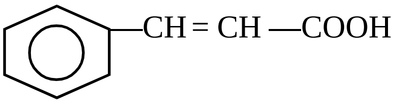


2-Aminobenzoic acid
(Anthranilic acid)

But the compounds where carboxyl group is present on the side chain of aromatic ring system as in phenyl acetic acid and cinnamic acid are called side-chain aromatic acids showing similar behaviour as aliphatic carboxylic acids.



Phenylacetic acid



Cinnamic acid

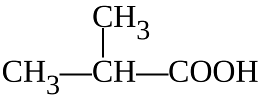
19.3 ISOMERISM :

A. Fatty acids exhibit *chain* and *functional* isomerism.

1. **Chain isomerism:** This type of isomerism occurs due to the difference in the nature of carbon chain. For example:

$CH_3CH_2CH_2COOH$ and

Butanoic acid

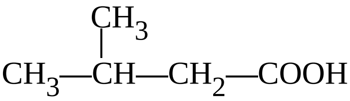


$$CH_3—\underset{}{\overset{\displaystyle CH_3 \atop |}{CH}}—COOH$$

2-Methyl propanoic acid

$CH_3CH_2CH_2CH_2COOH$ and

Pentanoic acid



$$CH_3—\overset{\displaystyle CH_3 \atop |}{CH}—CH_2—COOH$$

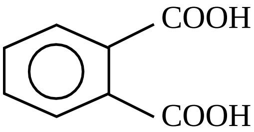
3-Methyl butanoic acid

2. **Functional isomerism:** This type of isomerism occurs due to the presence of different functional groups. Carboxylic acids are the functional isomers of esters. For example,

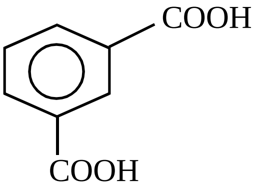
CH_3COOH	and	$HCOOCH_3$		
Acetic acid		Methyl formate		
$CH_3CH_2CH_2COOH$	and	$CH_3CH_2COOCH_3$		
Butanoic acid		Methyl propanoate		
CH_3CH_2COOH	and	CH_3COOCH_3	and	$HCOOC_2H_5$
Propanoic acid		Methyl ethanoate		Ethyl methanoate

B. Position Isomerism :

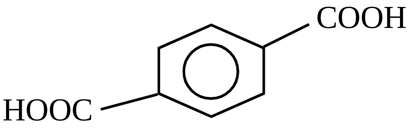
This type of isomerism is exhibited by aromatic acids. For example : Position isomers of benzene dicarboxylic acids are :



1, 2 Benzene
dicarboxylic acid
(Phthalic acid)



1, 3 Benzene
dicarboxylic acid
(Isophthalic acid)



1, 4 Benzene
dicarboxylic acid
(Terephthalic acid)

19.4 METHODS OF PREPARATION

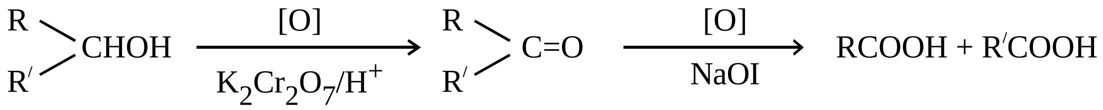
1. **By the oxidation of Alcohols, Aldehydes or Ketones:** Primary alcohols and aldehydes are readily oxidised to carboxylic acids by mild oxidizing agents like potassium permanganate solution in acid or alkaline medium or acidified potassium dichromate solution or chromium trioxide (CrO_3) in acidic medium.

$$\underset{\text{Primary alcohol}}{R\,CH_2OH} \xrightarrow[KMnO_4/H^+]{[O]} \underset{\text{Aldehyde}}{RCHO} \xrightarrow{[O]} \underset{\text{Acid}}{RCOOH}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

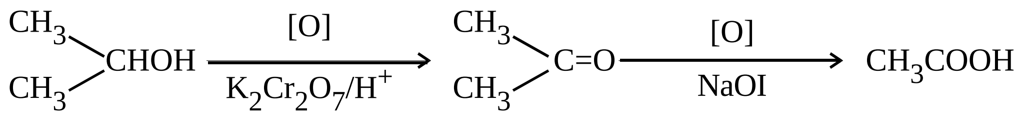
$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \underset{\text{Benzaldehyde}}{C_6H_5-CHO} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5\text{–}COOH}$$

Secondary alcohols on oxidation form ketones which on drastic oxidation gives acids, having less number of carbon atoms.



$$\begin{matrix}R \\ R'\end{matrix}\!\!>\!CHOH \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \begin{matrix}R \\ R'\end{matrix}\!\!>\!C{=}O \xrightarrow[NaOI]{[O]} RCOOH + R'COOH$$

Secondary alcohol ketone Acids



$$\begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>\!CHOH \xrightarrow[K_2Cr_2O_7/H^+]{[O]} \begin{matrix}CH_3 \\ CH_3\end{matrix}\!\!>\!C{=}O \xrightarrow[NaOI]{[O]} CH_3COOH$$

Isopropylalcohol Acetone Acetic acid

2. **By the hydrolysis of Alkyl cyanides:** Alkyl cyanides are hydrolysed to carboxylic acids in acidic or alkaline medium.

$$\underset{\text{Alkyl cyanide}}{R\text{—}C \equiv N} + 2H_2O \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Acid}}{RCOOH} + NH_3$$

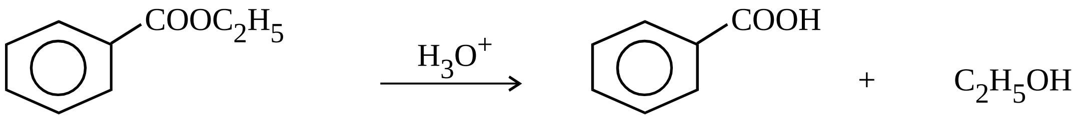
$$\underset{\text{Methyl cyanide}}{CH_3C \equiv N + 2H_2O} \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Acetic acid}}{CH_3COOH + NH_3}$$

$$\underset{\text{Benzonitrile}}{C_6H_5-CN + 2H_2O} \xrightarrow{H^+ \text{ or } OH^-} \underset{\text{Benzolic acid}}{C_6H_5-COOH + NH_3}$$

3. **By the hydrolysis of Esters, Acyl chlorides, Acid amides or Acid anhydrides:** Esters, acyl chlorides or acid anhydrides are easily hydrolysed to carboxylic acids by mineral acid or alkali.

$$\underset{\text{Ester}}{RCOOR'} + HOH \xrightarrow[H^+]{} \underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOCH_5} + HOH \xrightarrow[H^+]{} \underset{\text{Acetic acid}}{CH_3COOH} + C_2H_5OH$$



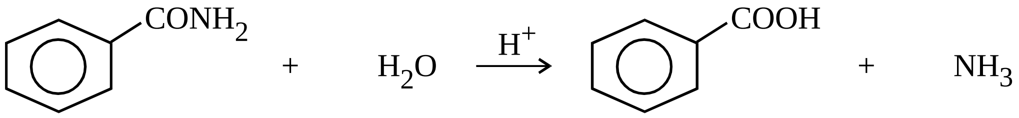
Ethyl benzoate Benzoic acid

$$\underset{\text{Acid chloride}}{RCOCl} + HOH \xrightarrow[H^+]{} \underset{\text{Acid}}{RCOOH} + HCl$$

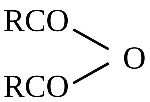
$$\underset{\text{Acetyl chloride}}{CH_3COCl} + HOH \xrightarrow[H^+]{} \underset{\text{Acetic acid}}{CH_3COOH} + HCl$$

$$\underset{\text{Acid amide}}{RCONH_2} + HOH \xrightarrow[H^+]{} \underset{\text{Acid}}{R—COOH} + NH_3$$

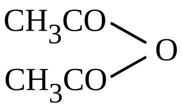
$$\underset{\text{Acetamide}}{CH_3CONH_2} + HOH \xrightarrow[H^+]{} \underset{\text{Acetic acid}}{CH_3—COOH} + NH_3$$



Benzamide Benzoic acid



$$\underset{\text{Acid anhydride}}{\begin{matrix}RCO\\RCO\end{matrix}\!>\!O} + HOH \xrightarrow{H^+} \underset{\text{Acid}}{2RCOOH}$$



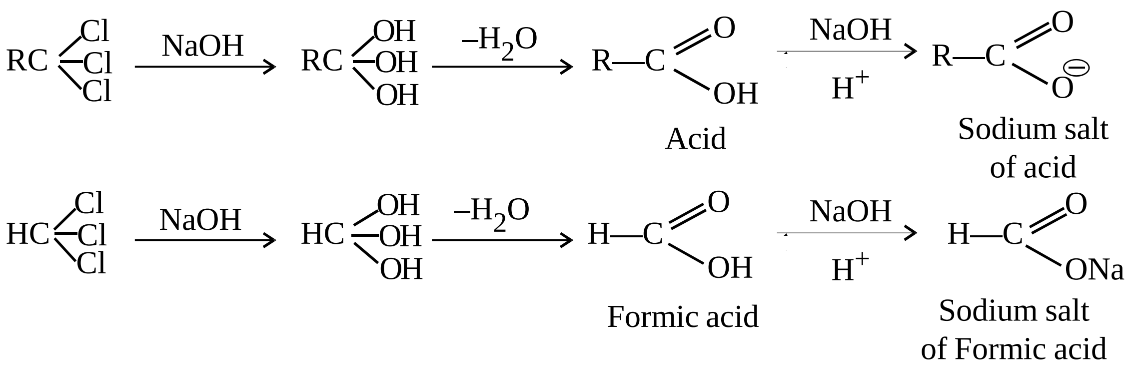
$$\underset{\text{Acetic anhydride}}{\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>\!O} + HOH \xrightarrow{H^+} \underset{\text{Acetic acid}}{2CH_3COOH}$$

$(C_6H_5CO)_2O + H_2O \longrightarrow 2C_6H_5COOH$

Benzoicanhydride Benzoic acid

4. **By the hydrolysis of Trichloroalkanes:**

Trichloroalkanes in which all the three chlorine atoms are linked to the same carbon atom are hydrolysed by alkali to carboxylic acids.



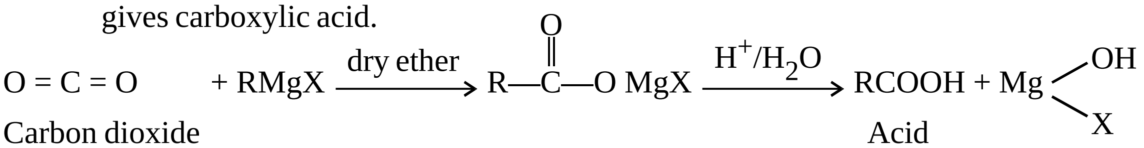
Acid

Sodium salt of acid

Formic acid

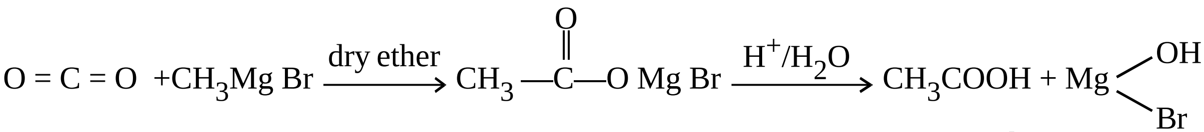
Sodium salt of Formic acid

5. **By Carbonation of Grignard reagent:** Alkyl or aryl magnesium halide (Grignard reagent) reacts with solid carbon dioxide in ether to form addition compound which on acidification gives carboxylic acid.

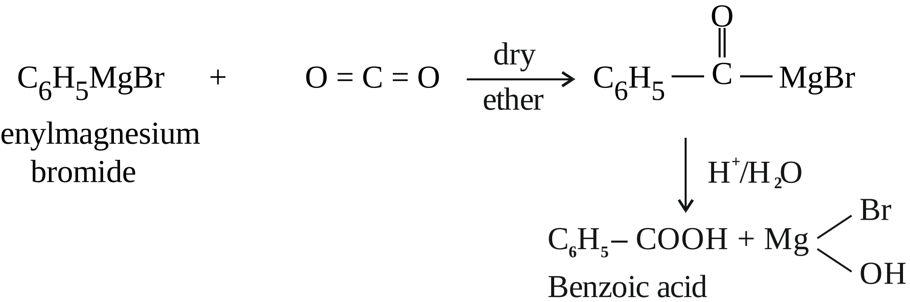


Carbon dioxide

Acid



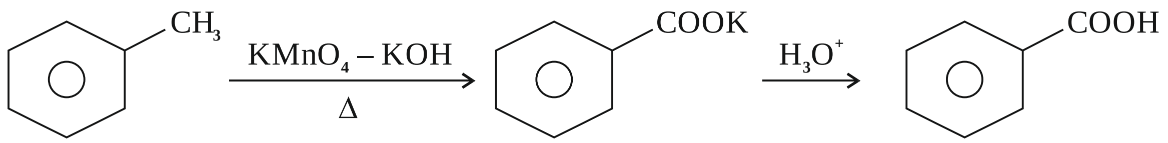
Acetic acid



Phenylmagnesium bromide

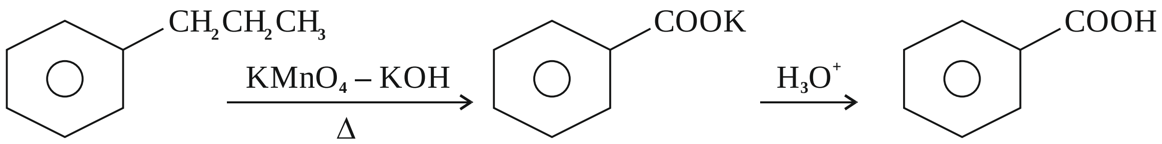
Benzoic acid

6. **Preparation of aromatic (Benzoic acid) by oxidation of alkylbenzenes (arenes) :** Benzoic acid is prepared by the oxidation of alkyl benzenes (irrespective of the length of the side chain) in the presence of strong oxidizing agent like acidified potassium dichromate or alkaline / acidic potassium permanganate or dil. HNO_3. Primary and secondary alkyl groups are oxidized, whereas tertiary group is not at all affected.



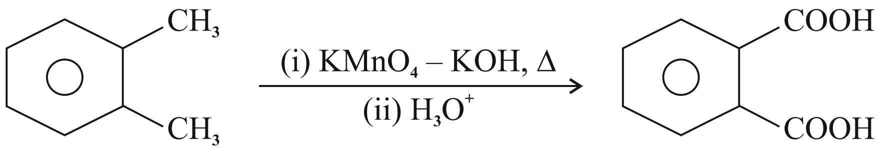
Tolune

Benzoic acid



1-Propylbenzene

Benzoic acid



o-xylene

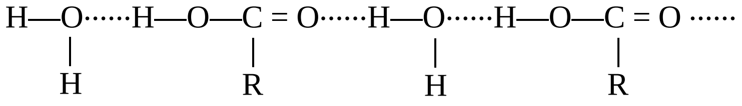
Phthalic acid

19.5 GENERAL PROPERTIES :

A. PHYSICAL PROPERTIES:

1. **Physical state:** The first three members are colourless liquids having pungent odour. The next six members are oily liquids having faint unpleasant odour. The higher members are colourless and odourless waxy solids.

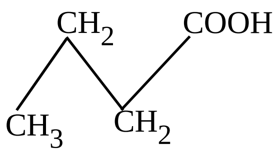
2. **Solubility:** The first four members are soluble in water due to intermolecular hydrogen bonding with water molecules.



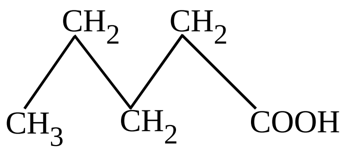
$$H—\underset{\displaystyle H}{\underset{|}{O}}\cdots\cdots H—O—\underset{\displaystyle R}{\underset{|}{C}}=O\cdots\cdots H—\underset{\displaystyle H}{\underset{|}{O}}\cdots\cdots H—O—\underset{\displaystyle R}{\underset{|}{C}}=O\cdots\cdots$$

The solubility of carboxylic acids gradually decreases with rise in size of the alkyl group. This is due to increase in nonpolar part of the molecule.

3. **Melting point:** For the first ten members of the homologous series, the melting points of carboxylic acids having even number of carbon atoms are higher than the nearest lower and next higher acids with odd number of carbon atoms.



(Acid with even number of carbon atoms)



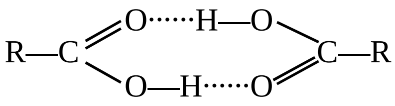
(Acid with odd number of carbon atoms)

The acids with odd number of carbon atoms have carboxyl group and terminal methyl group on the same side of zig-zag carbon chain and such unsymmetrical molecules fit poorly in the crystal lattice and hence have weaker intermolecular forces. The acids with even number of carbon atoms have carboxyl group and terminal methyl group on opposite side of zig-zag carbon chain and hence they fit better in the crystal lattice resulting in stronger intermolecular forces. This explains why the acids having even number of carbon atoms have melting points higher than the acids with odd number of carbon atoms.

Melting points of some Alkanoic acids.

Acid	Methanoic	Ethanoic	Propanoic	Butanoic	Pentanoic	Hexanoic
M.P(K)	281	289.6	251	265	238.5	270

4. **Boiling points :** The carboxylic acids have quite high boiling points due to the presence of intermolecular hydrogen bonding as shown below.



(Dimeric structure)

The carboxylic acids have relatively higher boiling points than the corresponding alcohols. This is because,

(i) O—H bond in carboxylic acid is more polar than O—H bond in alcohol due to electron withdrawing effect of carbonyl group on O—H bond.

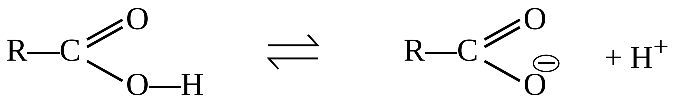
(ii) The molecules of carboxylic acids are held together by two hydrogen bonds forming cyclic dimers.

Table 19.2 : Boiling points of some Carboxylic acids and Alcohols.

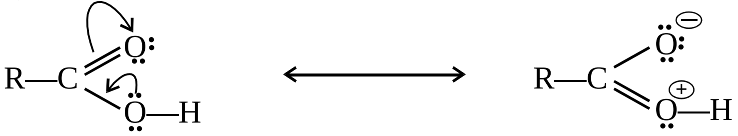
Acids/Alcohols	B.P(K)
HCOOH CH_3OH	373 338
CH_3COOH C_2H_5OH	391 351
C_2H_5COOH C_3H_7OH(Propanol)	424 370
C_3H_7COOH C_4H_9OH (Butan-l-ol)	437 391

B. ACIDIC NATURE OF CARBOXYLIC ACIDS

Carboxylic acids are relatively weaker acids as compared to mineral acids. The strength of the acid depends upon the extent of ionisation which mainly depends upon the stability of the carboxylate ion formed.



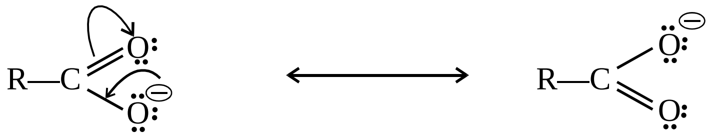
(i) A carboxylic acid molecule is a resonance hybrid of the following two resonating structures (I and II)



I II

The structure, II indicates that the oxygen atom of the hydroxyl group carries some positive charge. As a result, the electron pair of O—H is drifted towards oxygen atom. This displacement of electron pair causes the formation of a proton and a carboxylate ion.

The carboxylate ion which is formed is also a resonance hybrid of the following two resonating structures, III and IV.



III IV

Thus we observe that (i) carboxylic acid as well as the carboxylate ion both are stabilised by resonance.

(ii) The contributing structures of carboxylic acid (I & II) are not equivalent and the structure, II involves charge separation. As a result, the structure II contributes less to the stability of the carboxylic acid.

(iii) The resonating structures, III and IV are equivalent and contribute to the greater stability of the carboxylate ion.

Thus, the carboxylate ion being more stable than the undissociated carboxylic acid, the latter has a tendency to dissociate into proton and the carboxylate ion. Hence, the carboxylic acids show acidic character.

The strength of a carboxylic acid is expressed in terms of the dissociation constant (K_a)as:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

Higher the value of K_a, stronger is the acid and vice versa. As the numerical values of K_a vary by large magnitude, it is more convenient to express the acidic strength in terms of pK_a value, which is defined as

$$pK_a = -\log K_a$$

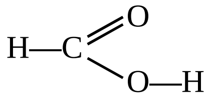
Smaller the value of pK_a, stronger is the acid and vice versa. The K_a and pK_a values of some acids are given below.

Table 19.3: K_a and pK_a values of some Carboxylic acids

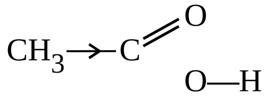
Acid	K_a	pK_a
HCOOH	17.7×10^{-5}	3.75
CH_3COOH	1.75×10^{-5}	4.76
FCH_2COOH	260×10^{-5}	2.59
$ClCH_2COOH$	136×10^{-5}	2.87
$BrCH_2COOH$	125×10^{-5}	2.90
$I\,CH_2COOH$	67×10^{-5}	3.16
$Cl_2CHCOOH$	5530×10^{-5}	1.26
Cl_3CCOOH	23200×10^{-5}	0.63
Cl_3CH_2COOH	1.3×10^{-5}	4.87
C_6H_5COOH	6.3×10^{-5}	4.20

1. **Effect of substituents on acid strength of aliphatic acids :** The substituents affect appreciably the acid strength of carboxylic acids.

(i) **Effect of electron releasing groups (+I effect) :** An electron releasing group attached to carboxyl group tends to release electrons towards the carbon atom to which it is attached and this effect is transmitted throughout the carbon chain. This increases the electron density on the oxygen atom of the – O – H group and as a result the release of H^+ becomes difficult. This explains why formic acid is a stronger than acetic acid.



Release of H becomes easy due to absence of electron releasing group



Release of H becomes difficult due to presence of an electron releasing group ($-CH_3$)

Acid strength decreases with increase in electron releasing nature (+I effect) of the substituents. The +I effect of alkyl groups increases in the following order:

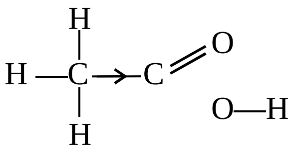
$$CH_3- < C_2H_5- < (CH_3)_2CH- < (CH_3)_3C-$$

Therefore, the acid strength of carboxylic acids decreases in the following order:

$HCOOH$	$> CH_3COOH$	$> CH_3CH_2COOH$	$> (CH_3)_2CHCOOH$
Formic acid	Acetic acid	Propionic acid	Isobutyric acid.

(ii) **Effect of electron withdrawing groups (–I effect):**

An electron withdrawing group attached to carboxyl group tends to withdraw electrons from the carbon atom to which it is attached and their effect is transmitted throughout the chain. As a result, the electron pair forming the O – H bond is displaced more towards oxygen of O – H group and the release of H^+ becomes more easier. Therefore, chloroacetic acid is a stronger acid than acetic acid.



Acetic acid

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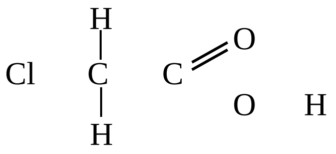
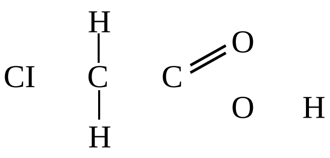


Chloroacetic acid

(a) ***Effect of number of halogen atoms:*** –I effect increases with increase in number of electron withdrawing atoms and hence acid strength increases.

For example,



(Monochloroacetic acid)

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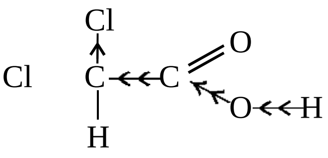

(Dichloroacetic acid)

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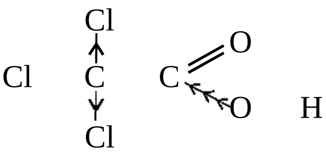


(Trichloroacetic acid)

(b) ***Effect of nature of halogen atoms:*** The strength of carboxylic acid depends upon nature of electron withdrawing substituent. Greater the electron withdrawing power of the substituent stronger is the acid. The electron withdrawing effect (– I effect) of halogen decreases in the order:

$$F > CI > Br > I.$$

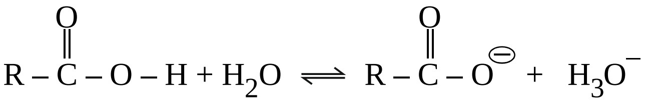
Hence the acid strength of halogen substituted monocarboxylic acids decreases in the order.

$$FCH_2COOH > CICH_2COOH > Br\ CH_2COOH > I\ CH_2COOH.$$

(c) ***Effect of position of halogen atoms:*** The electron withdrawing effect of halogen atom decreases as its distance from the – COOH group increases. The electron withdrawing effect of halogen is maximum when the halogen atom is linked to α - carbon atom of the carboxylic acid. Thus, α- chloropropionic acid is a stronger acid than β- chloropropionic acid.

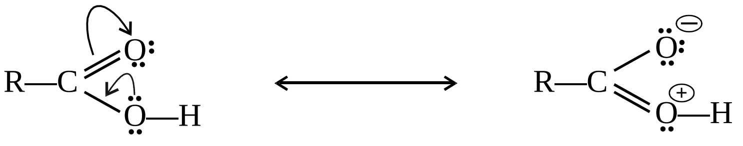
2. Comparison of Relative Acid Strength of Monocarboxylic acid and Alcohol

Both carboxylic acid and carboxylate ion are stabilised by resonance and the carboxylate is more stabilised by resonance as compared to carboxylic acid. Hence the carboxylic acids have tendency to release H^+ ions with the formation of stable carboxylate ions. However, resonance is not possible for alcohols and also alkoxide ions. Therefore, carboxylic acids are stronger acids than monohydric alcohols.

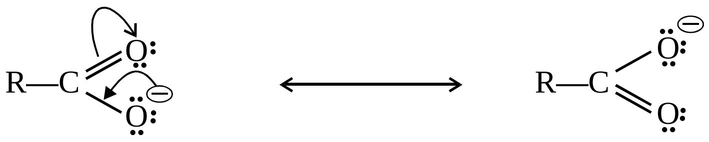


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + H_3O^-$$

Conjugate base



Less stable

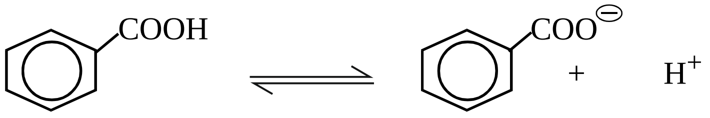


$$R-OH + H_2O \rightleftharpoons R-O^{\ominus} + H_3O^+$$

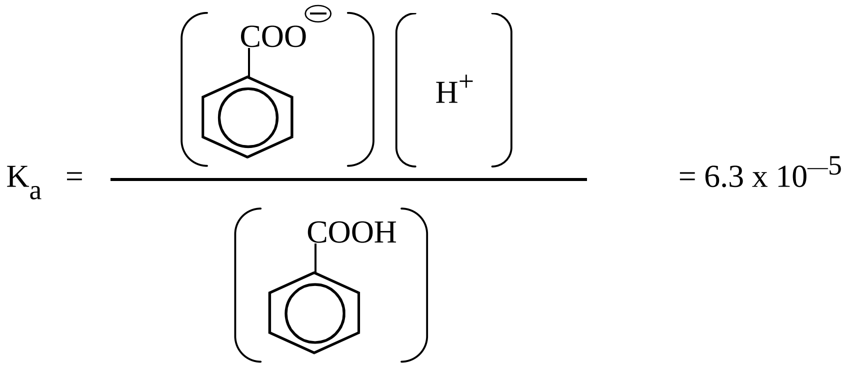
Not resonance stabilized

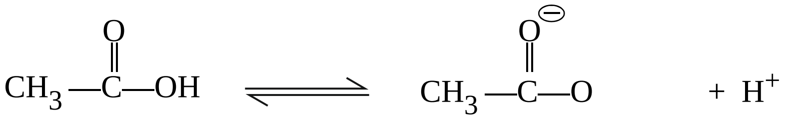
3. Acidity of Benzoic acid

Aromatic acids are slightly stronger acids than aliphatic acids because of greater value of K_a. For example, benzoic acid is a stronger acid than acetic acid, because benzoate ion is more resonance stabilized than acetate ion.



Benzoic acid Benzoate ion





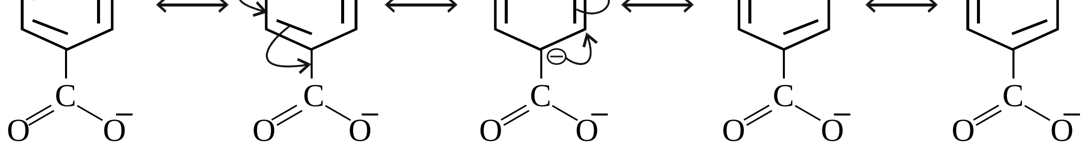
$$CH_3-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons CH_3-\overset{O^-}{\overset{\|}{C}}-O \quad + \ H^+$$

$K_a = 1.75 \times 10^{-5}$

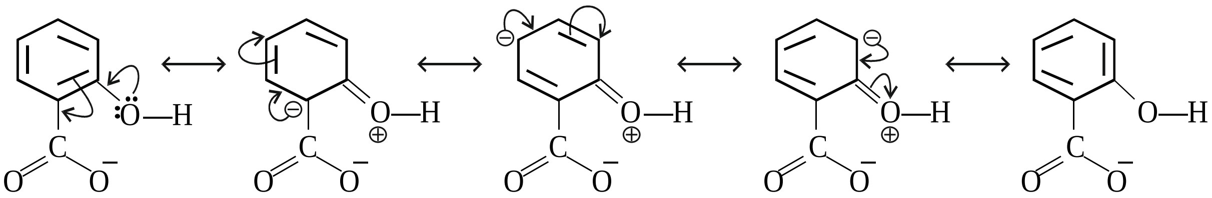
Effect of substitutents on acid strength:

Acidity of carboxylic acids is determined by both inductive effect and the resonance effect.

(i) Electron releasing substitutents (ortho-para directing groups) tend to decrease the strength of the acid. This is due to intensification of -ve charge on the carboxylate ion making it unstable. Thus with –OH group at the ortho or para position the benzene ring is incapable of delocalising the negative charge on the carboxylate anion.

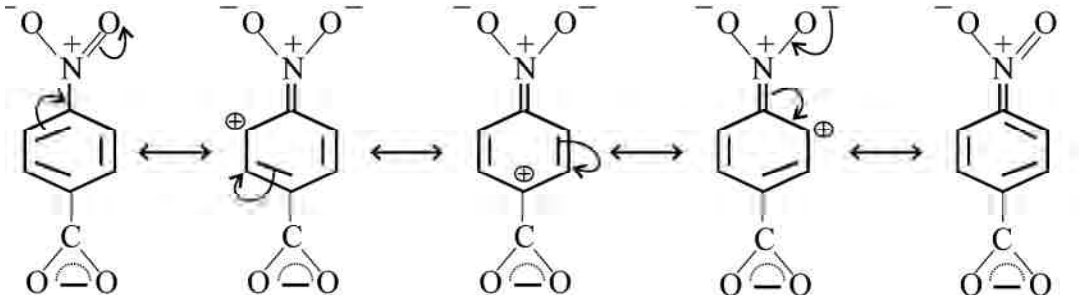


p — Hydroxy benzoate



o — Hydroxy benzoate

On the other hand electron withdrawing groups like —NO_2, –CN etc. tend to increase the strength of the acid. This is due to dispersal of the –ve charge on carboxylate ion making it more stable. In otherwords due to delocalisation of –ve charge on the carboxylate anion it gets stabilised.



Thus, *p*-nitrobenzoic acid (K_a=40 x10^{-5})is a stronger acid than benzoic acid.

(ii) The + I or –I effect of the substituents is more pronounced if the substituents are present at the para positions rather than at meta positions.

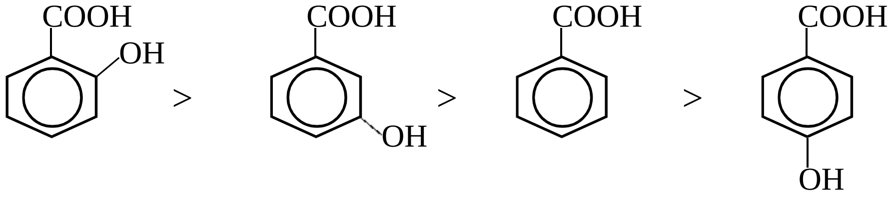
(iii) Irrespective of the nature of the substituents (+I or – I), ortho substituted benzoic acids are found to be stronger than benzoic acid. This is called **ortho effect.** This is probably due to resultant of steric and electronic factor. However, amino benzoic acids are exceptions. All of them are weaker than benzoic acid. Acidity of amino benzoic acids is in the order.

m— > *o* — > *p* —.

From the above discussion it can be concluded that the effect of substituents on acidity depends not only on the nature of the group but also on its position with respect to the position of the —COOH group.

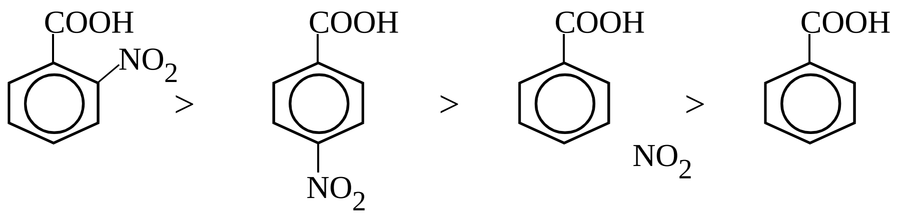
Some important observations

(i) Strength of *o* —, *m* — & *p* — hydroxy benzoic acids relative to benzoic acid follows the order,



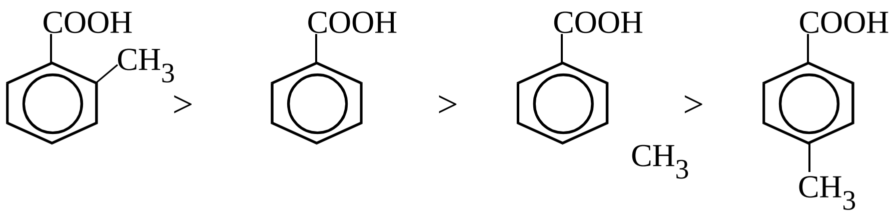
o-Hydroxy benzoic acid > *m*-Hydroxy benzoic acid > Benzoic acid > *p*-Hydroxy benzoic acid

(ii) Strength of *o* —, *m* — & *p* — nitrobenzoic acids relative to benzoic acid follows the order.



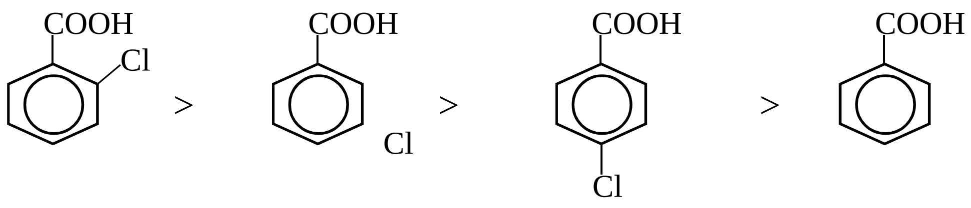
o-Nitrobenzoic acid > *p*-Nitrobenzoic acid > *m*-Nitrobenzoic acid > Benzoic acid

(iii) Strength of *o* —, *m* — & *p* — toluic acids relative to benzoic acid follows the order,



o-Toluic acid > Benzoic acid > *m*-Toluic acid > *p*-Toluic acid

(iv) Strength of *o* —, *m* — & *p* — chlorobenzoic acid reative to benzoic acid follows the order,



o-Chloro benzoic acid > *m*-Chloro benzoic acid > *p*-Chloro benzoic acid > Benzoic acid

4. Comparison of acid strength of aliphatic and aromatic acids (unsubstituted)

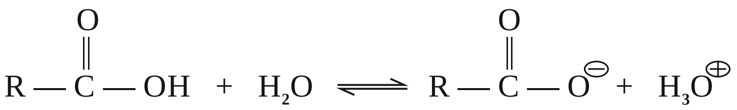
It is a fact that electron releasing groups tend to decrease the acid strength. Let us compare the acid strength of HCOOH, CH_3 COOH & C_6H_5 COOH. CH_3 —group is electron releasing. When it is attached to —COOH group the release of H^+ becomes comparatively difficult. So it is a weaker acid than HCOOH, where —COOH group is attached to a H atom. In case of benzoic acid the phenyl group (C_6H_5—) is attached to —COOH group, phenyl group has an over all electron donating effect when it is attached to a —COOH group. But this effect is weaker than +I effect of alkyl group. Thus, benzoic acid is a stronger acid than acetic acid. The acid strength follows the order,

$HCOOH > C_6H_5COOH > CH_3COOH$

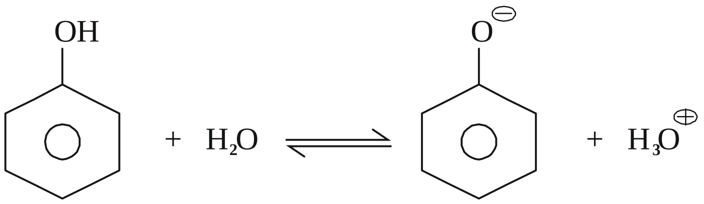
But when the phenyl group is attached to —COOH group through one or more CH_2— groups, it causes a slight electron withdrawing (—I) effect. Therefore phenyl acetic acid ($C_6H_5CH_2COOH$) is slightly stronger than benzoic acid i.e. $C_6H_5CH_2COOH > C_6H_5COOH$.

5. Comparison of acid strength of Carboxylic acids and Phenols

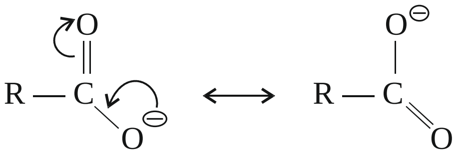
Though phenols are acidic due to the resonance stabilized conjugate base phenoxide ion, they are less acidic than the carboxylic acids.



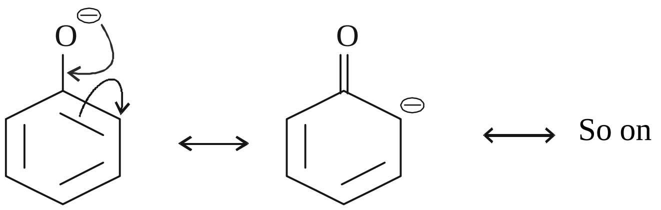
$$R-\overset{O}{\overset{\|}{C}}-OH + H_2O \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_3O^{\oplus}$$



The higher strength of carboxylic acid in comparision to phenols can be explained on the basis of higher stability of its conjugate base carboxylate ion which is having two equivalent resonating structures because of the presence of two electronegative oxygen atoms.



(Two equivalent resonating structures of carboxylate ion making it highly stable)



(Not equivalent though resonance stabilized.)

C. Chemical properties

The chemical properties of carboxylic acids may be discussed under the following heads:

(a) Reaction due to **H** atom of – COOH group.

(b) Reaction due to – **OH** part of – COOH group.

(c) Reaction due to – **CO** – part of – COOH group.

(d) Reaction due to – **COOH** group as a whole.

(e) Reactions due to **alkyl** group.

(a) Reaction due to H atom of – COOH group (acidic property)

1. Reaction with metals: Carboxylic acids react with strong electropositive metals like Na, Zn, Mg etc. to liberate hydrogen gas with the formation of salts.

$$2RCOOH + 2Na \longrightarrow 2\,RCOONa + H_2$$

Acid Sodium of acid

$$2HCOOH + 2Na \longrightarrow 2\,HCOONa + H_2$$

Formic acid Sodium formate

$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2\,Zn + H_2$$

Acetic acid Zinc acetate.

2. Reaction with alkali: Carboxylic acids react with alkali (NaOH or KOH) to form salts and water.

$$RCOOH + OHNa \longrightarrow RCOONa + H_2O$$

$$HCOOH + OHNa \longrightarrow HCOONa + H_2O$$

Foomic acid Sodium formate

$$CH_3COOH + OHNa \longrightarrow CH_3COONa + H_2O$$

$$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$$

3. Reactions with carbonates and bicarbonates:

Carboxylic acids react with carbonates or bicarbonates to liberate carbondioxide.

$$2RCOOH + Na_2CO_3 \longrightarrow 2RCOONa + CO_2 + H_2O$$

$$2HCOOH + Na_2CO_3 \longrightarrow 2HCOONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

Acitic acid Sodium acetate

This reaction is used to distinguish between carboxylic acids and phenols because phenols do not produce effervescence (evolution of CO_2) with aqueous solution of $NaHCO_3$ or Na_2CO_3.

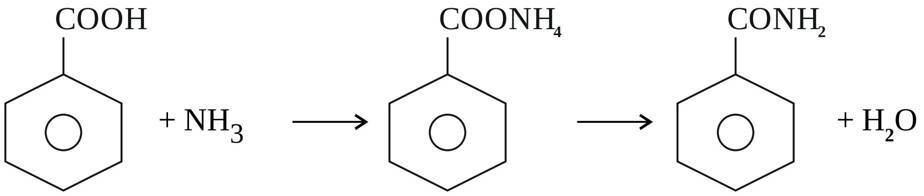
(b) Reaction due to – OH part of – COOH group.

1. **Formation of amides -** Carboxylic acids react with ammonia to form ammonium salts which when heated decompose to give amides.

$$\underset{\text{Acid}}{RCOOH + NH_3} \longrightarrow \underset{\text{Ammonium salt}}{RCOONH_4} \xrightarrow{\triangle} \underset{\text{Acid amide}}{RCONH_2 + H_2O}$$

$$\underset{\text{Formic acid}}{HCOOH + NH_3} \longrightarrow \underset{\text{Ammonium formate}}{HCOONH_4} \xrightarrow{\triangle} \underset{\text{Formamide}}{HCONH_2 + H_2O}$$

$$\underset{\text{Acetic acid}}{CH_3COOH + NH_3} \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\triangle} \underset{\text{Acetamide}}{CH_3CONH_2 + H_2O}$$



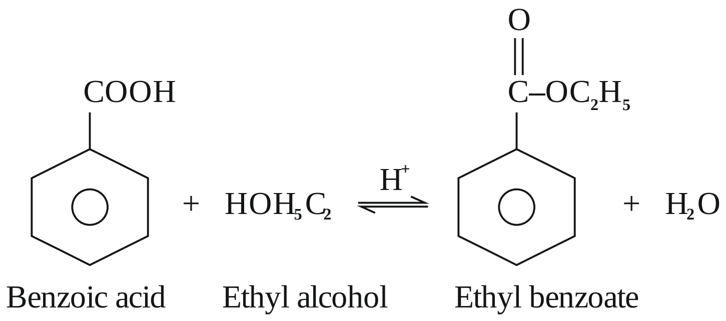
Benzoic acid　　Ammonium benzoate　　Benzamide

2. **Formation of esters (Esterification) -** Carboxylic acids react with alcohols in presence of a dehydrating agent like anhydrous zinc chloride or concentrated sulphuric acid to form esters.

$$\underset{\text{Acid}}{RCO}\boxed{OH + H}\underset{\text{Alcohol}}{OR'} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

$$\underset{\text{Formic acid}}{HCO}\boxed{OH + H}\underset{\text{Ethyl alcohol}}{OH_5C_2} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl formate}}{HCOOC_2H_5} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3CO}\boxed{OH + H}\underset{\text{Methyl alcohol}}{OCH_3} \overset{H^+}{\rightleftharpoons} \underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O$$

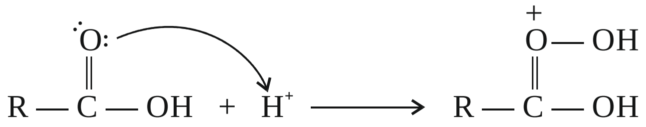


This reaction is reversible and is known as **esterification**. In order to shift the equilibrium in forward direction water formed has to be removed immediately. The dehydrating agent takes away water.

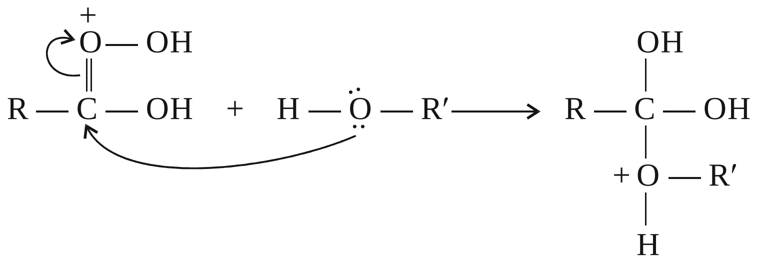
Mecanism :

The esterification of carboxylic acid with alcohol is one type of nucleophilic acyl substitution. It involves the following steps.

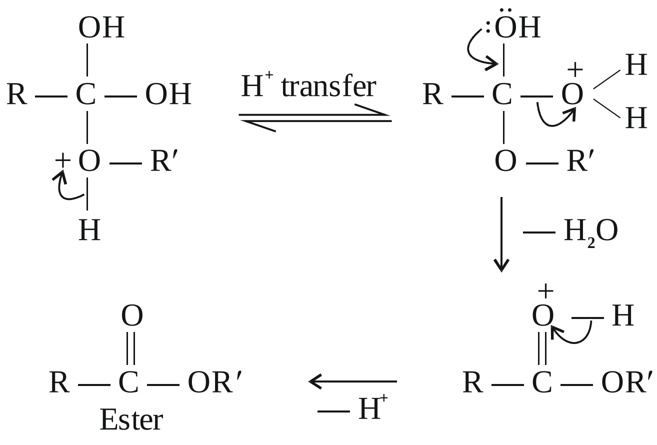
Step-1 : Protonation of the carboxyl oxygen.



Step-2 : Nucleophilic attack by the alcohol molecule



Step-3 : Loss of a molecule of water and a proton resulting with an ester.



3. **Formation of acid chlorides :** Carboxylic acids react with phosphorus halides (PCl_5, PCl_3) and thionyl chloride ($SOCl_2$) to form acid halides.

$$3RCOOH + PCl_3 \longrightarrow \underset{\text{Acid chloride}}{3RCOCl} + H_3PO_3$$

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

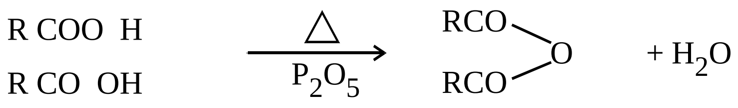
$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

$$\underset{\text{Acetic acid}}{3CH_3COOH + PCl_3} \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + H_3PO_3$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

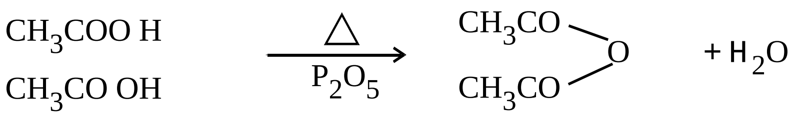
$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

4. **Formation of anhydrides :** Carboxylic acids on heating with a dehydrating agent like phosphorus pentoxide form acid anhydrides.



$$\begin{matrix} R\,COO\ H \\ R\,CO\ OH \end{matrix} \xrightarrow[P_2O_5]{\triangle} \begin{matrix} RCO \\ RCO \end{matrix}\!\!>O + H_2O$$

Acid anhydride



$$\begin{matrix} CH_3COO\ H \\ CH_3CO\ OH \end{matrix} \xrightarrow[P_2O_5]{\triangle} \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O + H_2O$$

Acetic acid Acetic anhydride

(c) **Reaction due to – CO – part of – COOH group:**

Reduction of carboxylic acids: These are reduced to primary alcohols when heated with lithium aluminium hydride ($LiAlH_4$) or with hydrogen and copper chromite ($CuCr_2O_4$) (in case of higher fatty acids).

$$R\text{–}COOH \xrightarrow[\text{or } CuCr_2O_4 \\ +H_2]{LiAlH_4} \underset{\text{Primary alcohol}}{RCH_2OH}$$

$$CH_3COOH + 4H \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + H_2O$$

(d) Reaction due to – COOH group as a whole:

1. Reduction :

(a) Reaction with HI and red phosphorus (Reduction to alkanes) :

Carboxylic acids when heated with red phosphorus and hydrogen iodide at 500K are reduced to alkanes. In this reaction – COOH group is reduced to – CH_3 group

$$RCOOH + 6\,HI \xrightarrow[\text{at 500K}]{\text{red P}} \underset{\text{Alkane}}{RCH_3} + 2H_2O + 3I_2$$

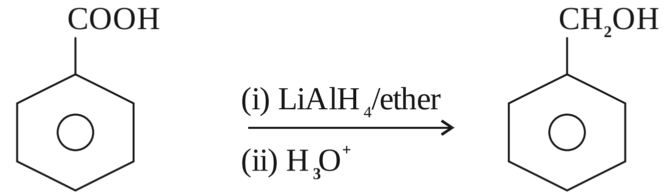
$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow[\text{at 500K}]{\text{red P}} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$$

(b) Reduction to alcohols :

Carboxylic acids can be reduced to alcohols on reaction with lithium aluminium hydride ($LiAlH_4$) or with diborane (B_2H_6).

$$RCOOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4\text{/ether}} \underset{\text{Primary alcohol}}{RCH_2OH}$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4\text{/ether}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$



Benzoic acid Benzyl alchol

2. **Decarboxylation on Reaction with soda lime:** Sodium or potassium salt of a carboxylic acid when heated with dry sodalime (NaOH + CaO) forms alkane with one carbon atom less than the parent acid. NaOH takes part in the reaction and calcium oxide helps in fusion of NaOH.

$$\boxed{R}\,COONa + \boxed{H}\,ONa \xrightarrow{CaO/\Delta} \underset{\text{Alkane}}{RH} + Na_2CO_3$$

$$\underset{\text{Sodium acetate}}{CH_3COONa + HONa} \xrightarrow{CaO/\Delta} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

3. **Kolbe's Electrolytic reaction (Electrolytic decarboxylation) :** Aqueous solution of sodium or potassium salt of a fatty acid on electrolysis gives alkane.

$$2RCOONa \rightleftharpoons 2RCOO^- + 2Na^+$$

$$H_2O \rightleftharpoons 2OH^- + 2H^+$$

At anode: $2RCOO^- \longrightarrow R - R + 2CO_2 + 2e$

At cathode: $2H^+ + 2e \longrightarrow H_2$

At cathode both Na^+ and H^+ are present, but H^+ ions are discharged preferentially due to their lower discharge potential thant Na^+ ions. Hence hydrogen gas is evolved at the cathode.

For examples :

$$\underset{\text{Sod.acetate}}{2CH_3COONa} \rightleftharpoons 2CH_3COO^- + 2Na^+$$

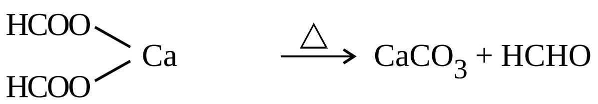
$$2H_2O \rightleftharpoons 2OH^- + 2H^+$$

At cathode: $2H^+ + 2e \longrightarrow H_2$

At anode: $2CH_3COO^- - 2e \longrightarrow \underset{\text{Ethane.}}{CH_3 - CH_3} + 2CO_2$

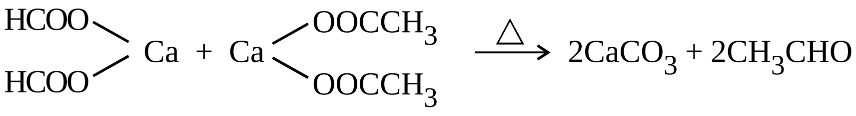
4. **Decomposition of Calcium salts of carboxylic acids :** Dry distillation of calicum salts of fatty acids results in the formation of carbonyl compounds.

Calcium formate when distilled gives formaldehyde.



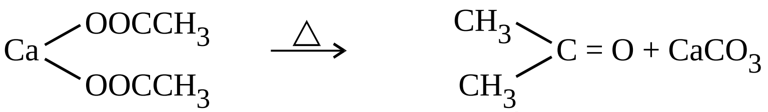
$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \xrightarrow{\triangle} CaCO_3 + \underset{\text{Formaldehyde.}}{HCHO}$$

Calcium formate when distilled with calcium acetate gives acetaldehyde.



$$(HCOO)_2Ca + Ca(OOCCH_3)_2 \xrightarrow{\triangle} 2CaCO_3 + 2CH_3CHO$$

Calcium acetate when distilled alone forms acetone.

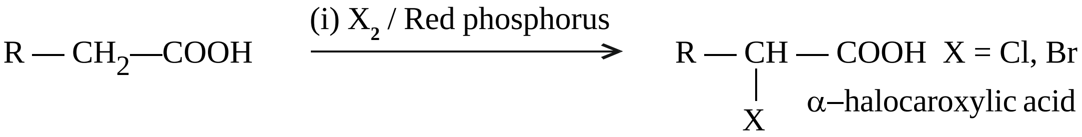


$$Ca(OOCCH_3)_2 \xrightarrow{\triangle} (CH_3)_2C = O + CaCO_3$$

Acetone.

(e) Reactions due to alkyl or aryl group.

1. **Reaction with halogens :** Carboxylic acids having an α–hydrogen atom react with chlorine or bromine in the presence of small amount of red phosphorus to form α-halocarboxylic acids.



$$R - CH_2 - COOH \xrightarrow{\text{(i) } X_2 \text{ / Red phosphorus}} R - \underset{\displaystyle X}{\underset{|}{CH}} - COOH \quad X = Cl, Br$$

α–halocaroxylic acid

When more than one mole of Cl_2 or Br_2 is used, the second and third hydrogen atoms are replaced.

$$\underset{\text{Acetic acid}}{CH_3COOH + Cl_2} \xrightarrow[-\,HCl]{\text{Red P}} \underset{\text{Monochloroacetic acid}}{ClCH_2\ COOH} \xrightarrow[-\,HCl]{Cl_2/\text{Red P}} \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH}$$

$$\xrightarrow[-HCl]{Cl_2 \text{ Red P}} \underset{\text{Trichloroacetic acid}}{Cl_3CCOOH}$$

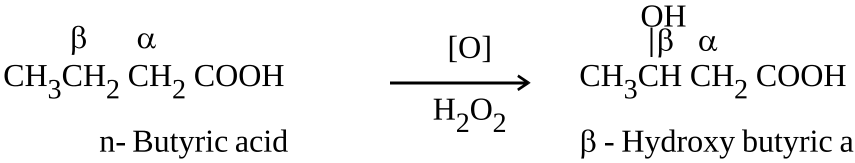
$$CH_3CH_2COOH \xrightarrow[-HBr]{Br_2\text{ /Red P}} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCOOH \xrightarrow[-HBr]{Br_2\text{ /Red P}} CH_3 - \overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}} - COOH$$

Propionic acid α- Bromo propionic acid α, α-Dibromo propionic acid

This reaction is known as **Hell - Volhard - Zelinsky (HVZ) reaction**

2. **Reaction with mild oxidising agent such as H_2O_2**

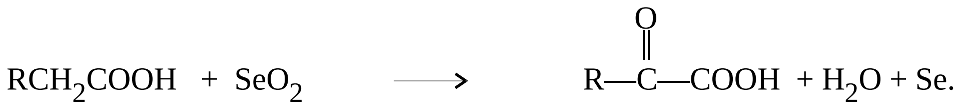
Carboxylic acids when heated with mild oxidising agent like hydrogen peroxide the alkyl group gets oxidised at the β- position. For example,



$$CH_3\overset{\beta}{CH_2}\ \overset{\alpha}{CH_2}\ COOH \xrightarrow[H_2O_2]{[O]} CH_3\overset{\displaystyle OH}{\overset{|\beta}{CH}}\ \overset{\alpha}{CH_2}\ COOH$$

n- Butyric acid β - Hydroxy butyric acid.

Carboxylic acids can also be oxidised at α - carbon by using oxidising agent such as selenium dioxide, SeO_2. Keto acids are obtained in this reaction.

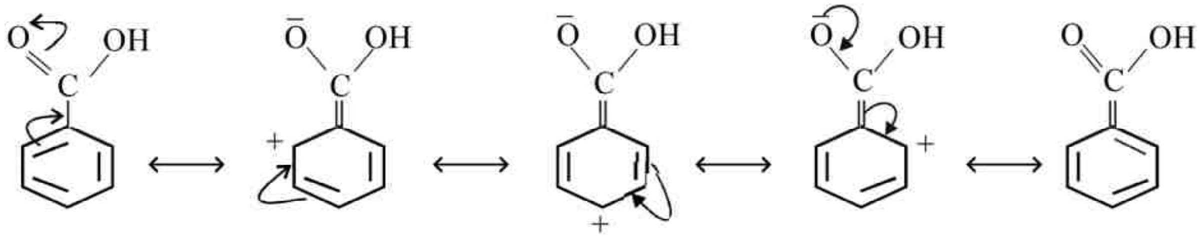


$$RCH_2COOH + SeO_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-COOH + H_2O + Se.$$

α - keto acid

3. Electrophilic substitution reaction

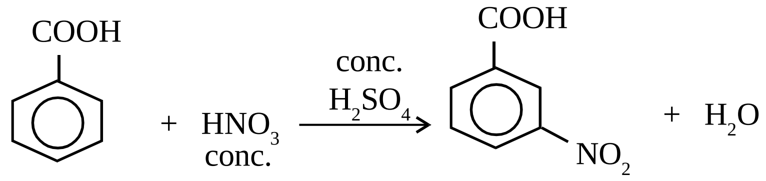
In benzoic acid, the carboxylic functional group is directly linked to the benzene ring and behaves as an electron withdrawing group. Due to the electron-withdrawing character (– R effect), the functional group behaves as a ring deactivator and makes the ortho and para- positions electron deficient.



Hence, the carboxylic acid group behaves as a ring deactivator and meta - director towards electrophilic substitution reactions, like, nitration, sulphonation and halogenation. But benzoic acid does not undergo Friedel crafts reation due to deactivations of the benzene ring by electron withdrawing effect of — COOH

(a) Nitration :

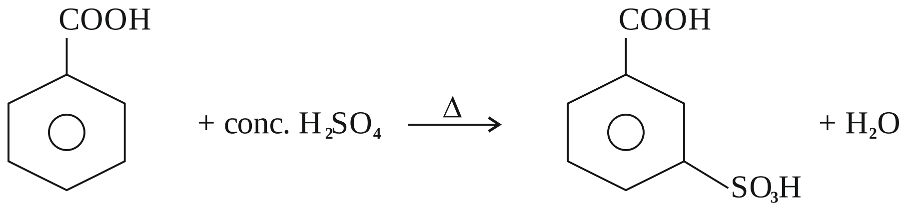
Benzoic acid reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form m-nitro benzoic acid.



Benzoic acid m- Nitrobenzoic acid

(b) Sulphonation :

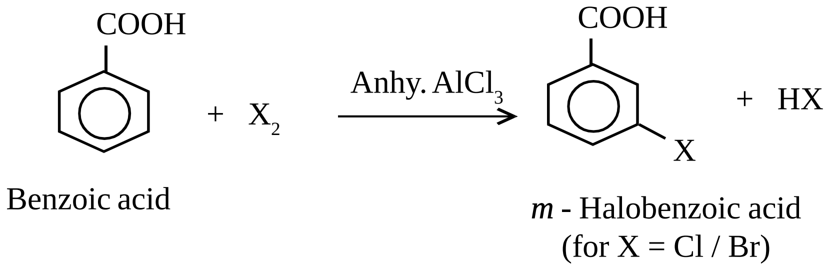
Benzoic acid on heating with conc. H_2SO_4 forms meta sulphobenzoic acid.

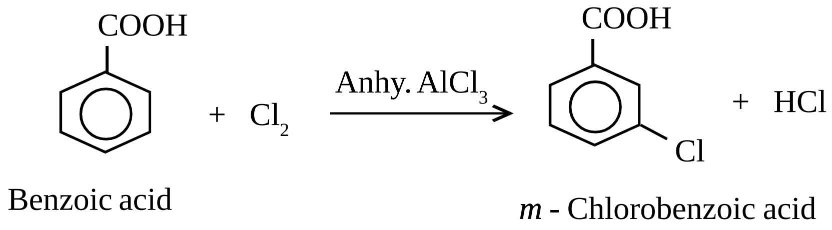


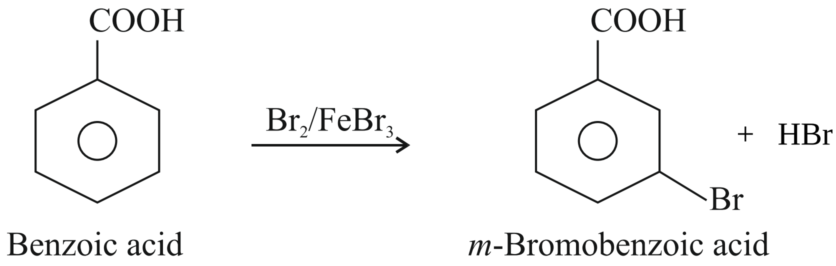
Benzoic acid m-sulphobenzoic acid

(c) Halogenation :

Benzoic acid reacts with a molecule of halogen in ther presence of $FeCl_3$ or Anhy. $AlCl_3$ to form m-halobenzoic acid.







(f) Unique characteristic reactions of Formic acid:

Reducing nature - Formic acid acts as a strong reducing agent since it gets readily oxidised. It reduces ammoniacal solution of silver nitrate (Tollens' regent), Fehling's solution and mercuric chloride to metallic silver, red cuprous oxide and mercurous chloride respectively. Acidified potassium permanganate solution is also decolourised by formic acid. This is due to reducing nature of formic acid, which distinguishes it from other carboxylic acid.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{[O]} CO_2 + H_2O$$

$$HCOOH + \underset{\text{(From Tollens' reagent)}}{Ag_2O} \longrightarrow 2Ag + CO_2 + H_2O$$

$$HCOOH + \underset{\text{(From Fehling's solution)}}{2CuO} \longrightarrow \underset{\text{Cuprous oxide (red)}}{Cu_2O} + CO_2 + H_2O$$

$$HCOOH + 2HgCl_2 \longrightarrow \underset{\text{Mercurous chloride}}{2HgCl} + CO_2 + 2HCl$$

Reaction of formic acid with acidified $KMnO_4$ solution is represented as :

$$\begin{array}{lll} [MnO_4^- + 8H^+ + 5e & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ [HCOOH & \longrightarrow & CO_2 + 2H^+ + 2e] \times 5 \\ \hline 2MnO^-_4 + 6H^+ + 5HCOOH & \longrightarrow & 2Mn^{2+} + 8H_2O + 5CO_2 \end{array}$$

19.6 TESTS :

1. Carboxylic acids react with aqueous sodium bicarbonate to liberate CO_2 with effervescence, which turns lime water milky.
2. Carboxylic acids react with alcohol in presence of a little conc. H_2SO_4 to form ester having fruity smell.

19.7 USES OF CARBOXYLIC ACIDS :

(a) Methanoic acid is used :

(i) as an antiseptic

(ii) in medicine for teatment of gout

(iii) in coagulating rubber latex

(iv) in leather industry

(v) in textile indusry for dyeing and finishing

(vi) in the preservation of fuits

(vii) as a rducing agent

(b) Ethanoic acid used :

(i) as a coagulent for latex in rubber industry

(ii) as vinegar in cooling and in the preparation pickles

(iii) as a laboratory reagent

(iv) in curing meat and fish

(v) in the manufacture of plastics (polyvinyl acetate), rayon (cellulose acetate) and silk.

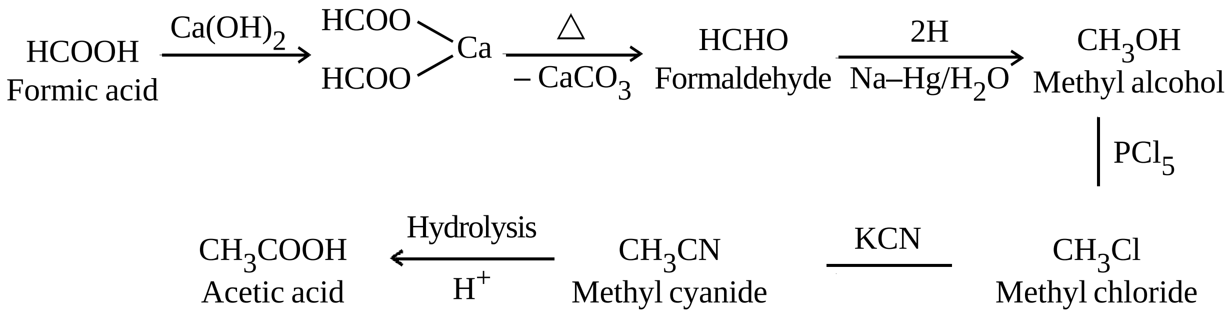
(c) Benzoic acid is used :

- (i) in medicine as urinary antiseptic.
- (ii) for making aniline blue in dye industry.
- (iii) as a preservative. Sodium benzoate is the most useful for this purpose specially for preserving food products like tomato sauce, fruit jams and juices.
- (iv) in ferfumes in the form of its esters.

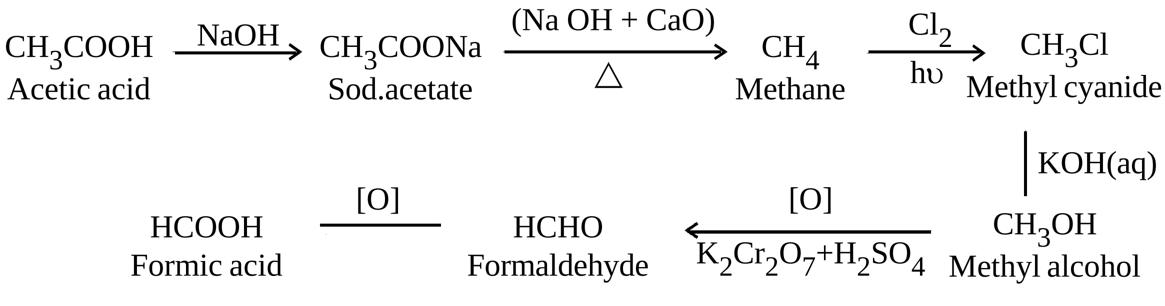
(d) Higher fatty acids are mainly used for the manufacture of soaps and detergents.

SOME IMPORTANT CONVERSIONS

1. Formic acid to Acetic acid:



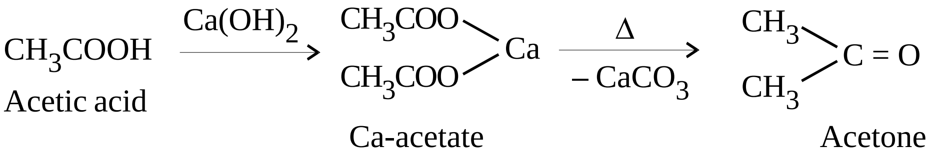
2. Acetic acid to Formic acid :



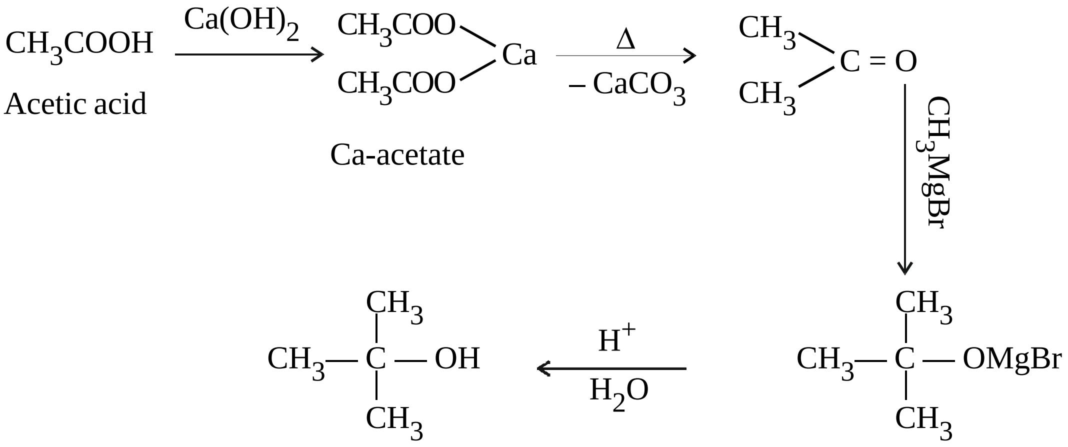
3. Propanoic acid to Propanol :

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} + 4H \xrightarrow{LiAlH_4} \underset{\text{Propanol.}}{CH_3CH_2CH_2OH} + H_2O$$

4. Acetic acid to Acetone :



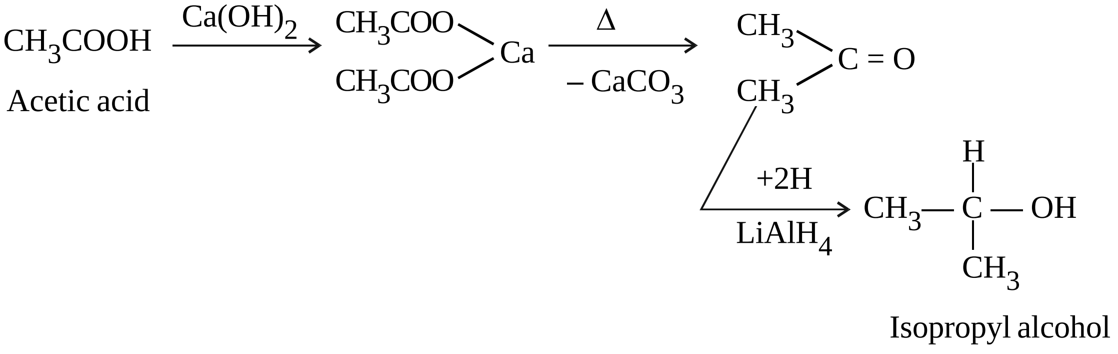
5. Acetic acid to tertiary butyl alcohol.



6. Acetic acid to Acetic anhydride :

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[P_2O_5]{\Delta} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \quad + H_2O$$

7. Acetic acid to Isopropyl alcohol :



8. Acetic acid to Acetaldehyde

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{PCl_5} \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[Pd - BaSO_4, S]{+2H} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

9. Acetic acid to Ethylene

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[+4H]{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2\,OH} \xrightarrow[\substack{conc.H_2SO_4\\ at160^0C}]{\Delta} \underset{\text{Ethylene}}{CH_2= CH_2}$$

10. Acetic acid to Acetylene.

$$\begin{tikzcd}
\underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "LiAlH_4"] & \underset{\text{Ethyl alcohol}}{CH_3CH_2\,OH} \arrow[r, "\Delta", "\substack{conc.H_2SO_4\\ at443K}"'] & \underset{\text{Ethylene}}{CH_2= CH_2} \arrow[d, "Br_2"] \\
& \underset{\text{Acetylene}}{CH \equiv CH} & \underset{\text{Ethylene dibromide}}{\begin{matrix}CH_2\,Br\\ |\\ CH_2\,Br\end{matrix}} \arrow[l, "\substack{KOH(alc)\\ \Delta}"']
\end{tikzcd}$$

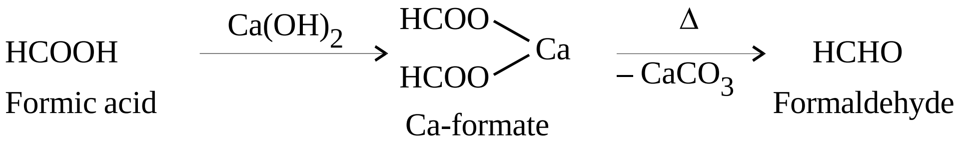
11. Acetic acid to Ethane.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow{Electrolysis} \underset{\text{Ethane}}{CH_3 - CH_3}$$

12. Acetic acid to Methane.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow{Sodalime\ \Delta} \underset{\text{Methane}}{CH_4}$$

13. Formic acid to Formaldehyde.



$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{Ca(OH)_2} \underset{\text{Ca-formate}}{\left.\begin{matrix}HCOO\\ HCOO\end{matrix}\right> Ca} \xrightarrow[-\,CaCO_3]{\Delta} \underset{\text{Formaldehyde}}{HCHO}$$

14. Acetic acid to Acetamide.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2}$$

15. Acetic acid to Diethyl ether.

$$CH_3COOH \xrightarrow[+4H]{LiAlH_4} CH_3CH_2OH \xrightarrow[\text{at 413K}]{conc.H_2SO_4} C_2H_5\text{–}O\text{–}C_2H_5$$

Acetic acid Excess Diethyl ether

16. Propanoic acid to Ethyl bromide.

$$CH_3CH_2COOH \xrightarrow{NaOH} CH_3CH_2COONa \xrightarrow[\text{Sodalime}]{\Delta} CH_3\text{–}CH_3 \xrightarrow[h\nu]{Br_2} CH_3CH_2Br$$

Propanoicacid Sod. propanoate Ethane Ethyl bromide

17. Acetic acid to Methyl amine.

$$CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3\,CO\,NH_2 \xrightarrow{Br_2+KOH} CH_3NH_2$$

Acetic acid Ammonium acetate Acetamide Methyl amine

18. Acetic acid to Methyl alcohol

$$\begin{tikzcd}
CH_3COOH \arrow[r, "NH_3"] & CH_3COONH_4 \arrow[r, "\Delta", "-H_2O"'] & CH_3\,CO\,NH_2 \arrow[d, "Br_2 / KOH"] \\
CH_3OH & & CH_3NH_2 \arrow[ll, "NaNO_2+HCl"']
\end{tikzcd}$$

Acetic acid Ammonium acetate Acetamide

Methyl alcohol Methyl amine

19. Acetic acid to Butane.

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{P + I_2} CH_3CH_2I \xrightarrow[\text{Ether (dry)}]{Na} CH_3CH_2CH_2CH_3$$

Acetic acid Ethyl alcohol Butane

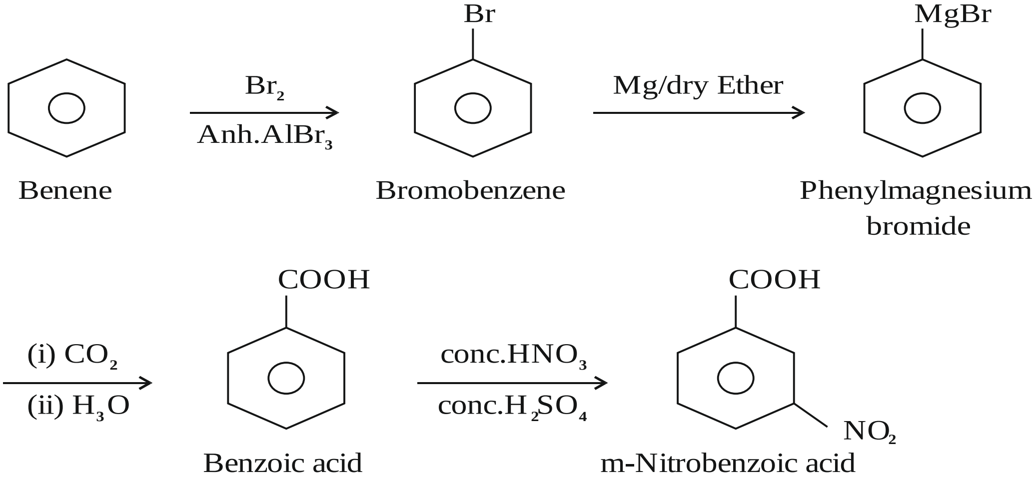
20. Propionic acid to n – Butyl amine

$$\begin{tikzcd}
CH_3CH_2COOH \arrow[r, "LiAlH_4"] & CH_3\,CH_2\,CH_2OH \arrow[r, "P/I_2"] & CH_3\,CH_2\,CH_2\,I \arrow[d, "KCN(alc)"] \\
CH_3\,CH_2\,CH_2\,CH_2\,NH_2 & & CH_3CH_2CH_2CN \arrow[ll, "Zn\text{–}Hg/HCl"', "\text{reduction}"]
\end{tikzcd}$$

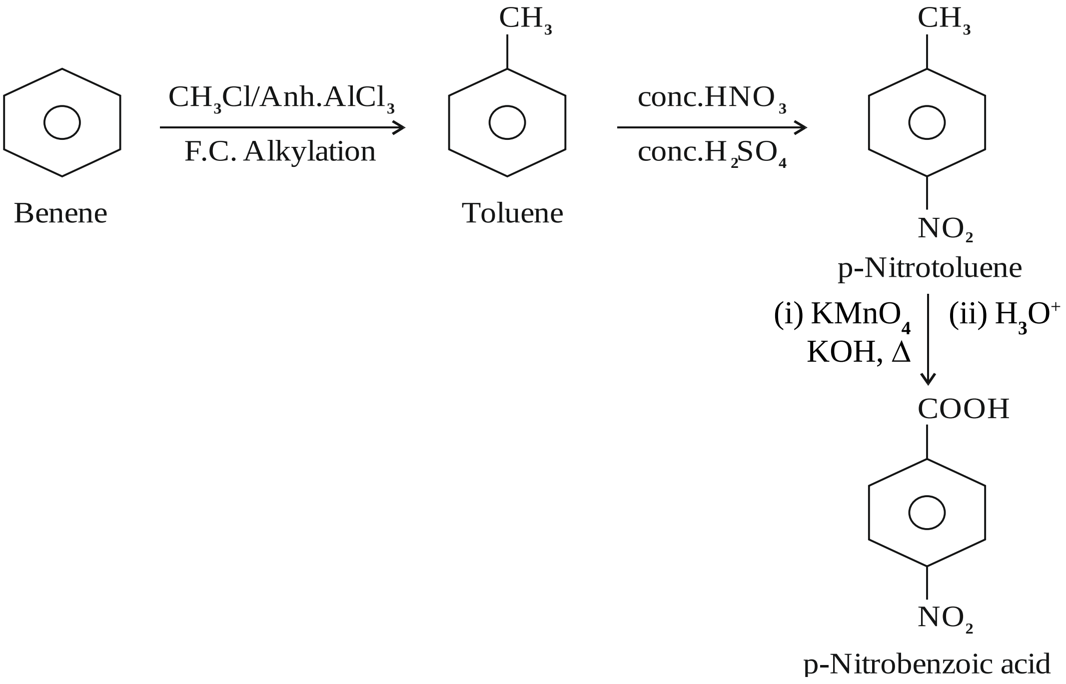
Propionic acid n – propyl alcohol n – propyl iodide

n-Butylamine n-Propyl cyanide

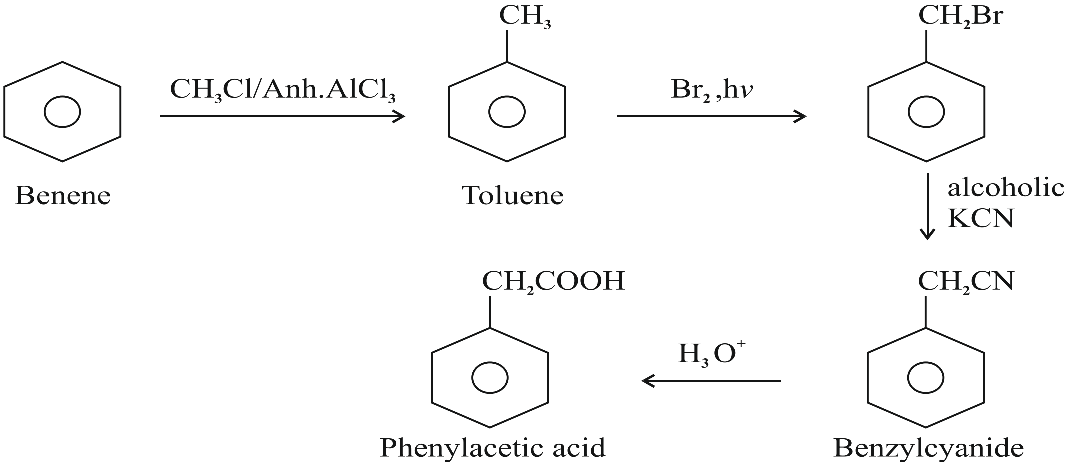
21. Benzene to m-Nitrobenzoic acid.



22. Benzene to p-Nitrobenzoic acid.



23. Benzene to phenylacetic acid



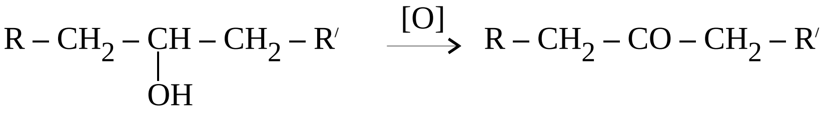
CHAPTER (19) AT A GLANCE

MONOCARBOXYLIC ACIDS

General formula : R – COOH.

1. ***Oxidation of alcohols, aldehydes and Ketones*** **(by $K_2Cr_2O_7$ and conc. H_2SO_4)**

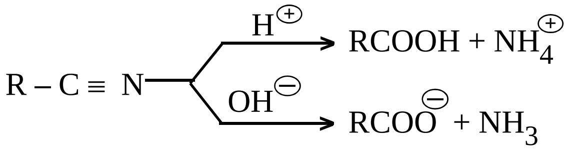
$$R-CH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$$



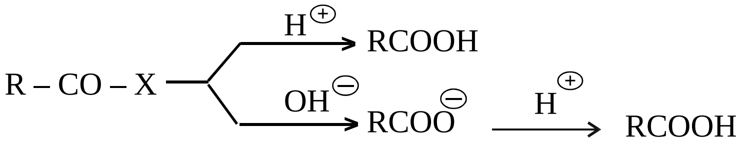
$$R-CH_2-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-R' \xrightarrow{[O]} R-CH_2-CO-CH_2-R'$$

$$\xrightarrow{[O]} \begin{matrix} R-CH_2-COOH + R'COOH \\ \text{or} \\ R-COOH + R'CH_2COOH \end{matrix}$$

2. ***Hydrolysis of alkyl cyanides*** **(by acid or alkali) :**

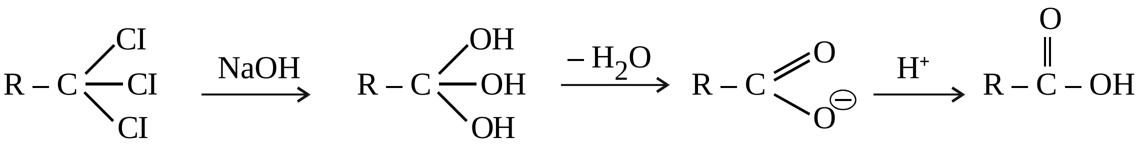


3. ***Hydrolysis of acid chlorides, acid amides, esters and acid anhydrides*** **(by acid or alkali):**

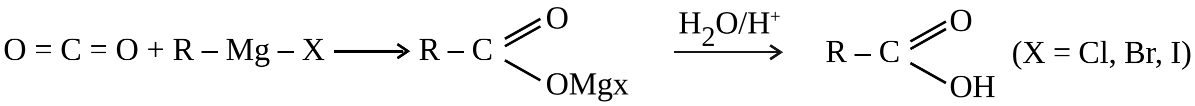


(X = Cl,NH_2, OR′, O.OC.R)

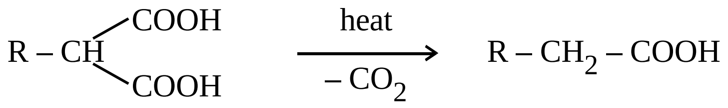
4. ***Hydrolysis of trichloroalkanes*** **(by alkali) :**



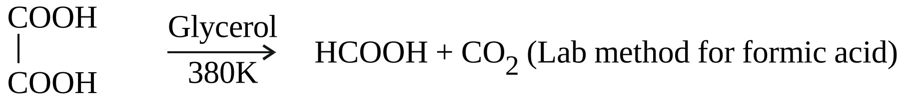
5. ***Carbonation of Grignard reagent :***



6. ***Decarboxylation of dicarboxylic acids :***



$$R-CH(COOH)_2 \xrightarrow[-CO_2]{heat} R-CH_2-COOH$$



$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \xrightarrow[380K]{Glycerol} HCOOH + CO_2 \text{ (Lab method for formic acid)}$$

7. ***Heating sodium alkoxide and carbon monoxide :***

$$R-ONa + CO \xrightarrow[\text{high press.}]{heat} R-COONa \xrightarrow{dil.H_2SO_4} R-COOH + Na_2SO_4$$

$$\text{When } R = H,\ HONa + CO \xrightarrow[\text{High press.}]{\text{High temp.}} HCOONa \xrightarrow{H^{\oplus}} HCOOH + Na_2SO_4$$

REACTIONS:

1. ***Reaction due to H atom of – COOH Group :***

(i) Salt formation (with metals like Na, K, Mg, Zn etc. and with alkali)

$R-COOH + M^{/} \longrightarrow RCOOM^{I} + \frac{1}{2}H_2$ (M^{I} = monovalent metal)

$R-COOH + M^{//} \longrightarrow (RCOO)_2M^{II} + H_2$ (M^{II} = divalent metal)

$2R-COOH + Na_2CO_3 \longrightarrow 2RCOONa + CO_2 + H_2O$

$R-COOH + NaHCO_3 \longrightarrow 2RCOONa + CO_2 + H_2O$

$R-COOH + NaOH \longrightarrow RCOONa + H_2O$

2. ***Reaction due to* –OH *part of* –COOH *group:***

(i) With NH_3 : $R-COOH + NH_3 \longrightarrow \underset{\text{Salt}}{R-COONH_4}$

$R-COONH_4 \xrightarrow{\Delta} \underset{\text{(acid amide)}}{R-CO-NH_2} + H_2O$

(ii) Esterification : $\underset{\text{(acid)}}{R-CO}\boxed{OH + H}\underset{\text{(alcohol)}}{O-R^{/}} \xrightarrow{Conc.H_2SO_4} \underset{\text{(ester)}}{R-COOR^{/}} + H_2O$

(ii) With PCl_3, PCl_5 or $SOCl_2$: $3R-COOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$R-COOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$R-COOH + SOCl_2 \longrightarrow R-COCl + SO_2 + HCl$

(iii) Dehydration : $2RCOOH \xrightarrow[\Delta]{P_2O_5} RCO - O - CO - R + H_2O$

3. *Reaction due to –COOH group:*

(i) Formation of alkanes :

$$R - COOH \xrightarrow[500K]{\text{Red P / HI}} R - CH_3 + I_2 + H_2O$$

$$R - COONa \xrightarrow{\text{NaOH + CaO}} R - H + Na_2CO_3$$

$$\begin{array}{lll} 2RCOONa & \xrightarrow{\text{Electrolysis}} & R - R \quad + 2CO_2 \text{ (Kolbe's reaction).} \\ \quad + 2H_2O & & \text{(at the anode)} \quad + 2H_2 + NaOH \end{array}$$

(ii) Action of heat on the salts of acid :

$$\begin{array}{lll} (RCOO)_2\,Ca & \xrightarrow{\Delta} & \underset{\text{(Ketone)}}{R - CO - R} \quad + \; CaCO_3 \end{array}$$

$$\begin{array}{lll} (RCOO)_2\,Ca + (HCOO)_2Ca & \xrightarrow{\Delta} & \underset{\text{(Aldehyde)}}{RCHO} \quad + \; 2CaCO_3 \end{array}$$

$$\begin{array}{lll} (HCOO)_2Ca & \xrightarrow{\Delta} & \underset{\text{(formaldehyde)}}{HCHO} \quad + \; CaCO_3 \end{array}$$

$$\begin{array}{lll} RCOONH_4 & \xrightarrow{\Delta} & \underset{\text{(amide)}}{RCONH_2} + \; H_2O \end{array}$$

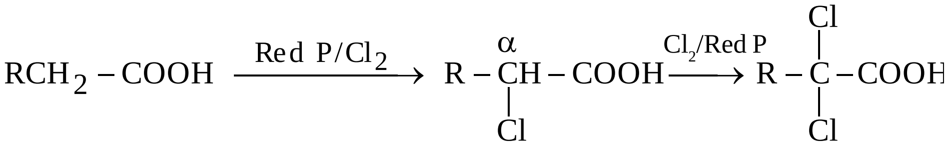
$$\begin{array}{lll} RCOONH_4 & \xrightarrow[P_4O_{10}]{\text{heat}} & \underset{\text{(alkyl cyanide)}}{R - C \equiv N} + \; 2H_2O \end{array}$$

$$RCOOAg + Br_2 \longrightarrow R - Br + CO_2 + AgBr \text{ (Hunsdiecker reaction)}$$

$$RCOOAg + R' - X \longrightarrow \underset{\text{(ester)}}{RCOOR'} + AgX$$

4. *Reaction due to alkyl group :*

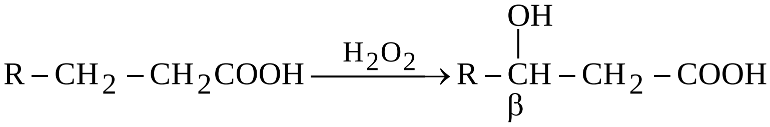
(i) Reaction with halogens : Hell – Volhard – Zelinsky reaction



$$RCH_2-COOH \xrightarrow{Red\ P/Cl_2} R-\overset{\alpha}{CH}(Cl)-COOH \xrightarrow{Cl_2/Red\ P} R-C(Cl)_2-COOH$$

(α–chloroacid) (α, α–Dichloroacid)

(ii) Reaction with H_2O_2 :



$$R-CH_2-CH_2COOH \xrightarrow{H_2O_2} R-\underset{\beta}{CH}(OH)-CH_2-COOH$$

(β–hydroxy acid)

(iii) Reaction with SeO_2 :

$$R-CH_2-COOH \xrightarrow{SeO_2} R-CO-COOH$$

(Keto acid)

5. ***Special reactions of Formic Acid :***

Reducing properties:

HCOOH + Tollens' reagent ⟶ Silver mirror (Ag)

HCOOH + Fehling's solution ⟶ Red precipitate (Cu_2O)

HCOOH + $KMnO_4$ solution ⟶ Decolourisation (Mn^{2+})

HCOOH + $HgCl_2$ solution ⟶ White precipitate (HgCl)

QUESTIONS

A. Very short answer type [1 mark each]

1. Methyl cyanide on hydrolysis yields ——
2. What happens when acetic acid is treated with sodium carbonate solution.
3. How will you prepare acetamide from acetic acid ?
4. Give any two uses of formic acid.
5. C_6H_5COOH is formed by carbonation of ——
6. Write the structural formula of 3 –Hydroxy Butanoic acid.
7. Write the IUPAC name of the following compound $CH_2(Br) - CH_2 - COOH$.
8. Write the IUPAC name of the following compounds :
   (i) $CH_3 - CH_2 - COOC_2H_5$
   (ii) $HOOC - CH_2 - CH_2 - CH_2 - COOH$
9. Write one reaction to distinguish between formic acid and acetic acid. Give equation.
10. Benzoyl chloride is formed by the action of PCl_5 on ——— .

B. Short answer type [2 marks each]

1. What is the reaction of formic acid with Tollen’s reagent and also with sodium ?
2. Explain why formic acid has two different C – O bond lengths i.e. 1.23A° and 1.36A°, where in sodium formate two C – O bond are same having bond length 1.27A°
3. Give two tests to distinguish between formic acid and acetic acid.
4. How can you convert toluene into m-nitrobenzoic acid ?
5. How formic acid can be converted to acetic acid ?
6. What happens when acetic acid is treated with NH_4OH and the product is then heated ?
7. Why m-nitorbenzoic acid is a stronger acid than benzoic acid?
8. Adentify A and B

$$C_6H_5COOH \xrightarrow[\text{conc. } H_2SO_4]{\text{conc. } HNO_3} A \xrightarrow[\Delta]{NaOH/CaO} B$$

9. What happens when acetamide is boiled with NaOH solution ?
10. Adentify A and B

$$C_6H_5COOH \xrightarrow{SOCl_2} A \xrightarrow[Pd/BaSO_4,\ S]{H_2} B$$

11. Distinguish between acetic acid and ethanol

12. Explain why the bond length of C – O in carboxylic acid is slightly larger than that in aldehydes and ketones.

13. What happens when sodium propionate is heated with sodalime.

14. What happens when acetic acid reacts with ethyl alcohol in presence of conc. H_2SO_4 ?

15. How acetic acid is prepared from methyl cyanide ?

16. What happens when sodium acetate is heated with sodalime ?

17. What happens when formic acid reacts with acidified $KMnO_4$ solution ?

18. Explain : acetic acid is stronger acid than ethanol.

19. What is the reaction of acetic acid with lime water ?

20. How can you get acetone form acetic acid ?

21. What happens when formic acid reacts with meruric chloride?

22. Arrange the following in the increasing order of acidic strength.

(i) $ClCH_2COOH$ (ii) $ClCH_2CH_2COOH$

(iii) FCH_2COOH (iv) CH_3COOH [Ans: (iv) < (ii) < (i) < (iii)]

23. How can you distinguish acetic acid from acetone ?

24. How would you convert acetic acid to methylamine ?

25. Explain the reaction of formic acid with Fehling's solution.

26. Complete the following equation by writing the structures of A,B and C.

$$CH_3COOH \xrightarrow{Cl_2/P} A \xrightarrow{NaCN} B \xrightarrow[H^+]{H_2O} C$$

27. How can a carboxylic acid be converted to an aldehyde in two steps?

C. Short answer type (3 marks each)

1. Convert methyl iodide to acetic acid.

2. What happens when CH_3COONa is electrolysed ? Explain with mechanism.

3. Explain: Benzoic acid is more acidic than aliphatic acids.

4. Identify A, B and C from the following, $C_2H_5OH \xrightarrow{PCl_5}$

   $(A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^+} (C)$

5. Acetic acid is weaker than formic acid, but chloroacetic acid is stronger than formic acid. Explain.

6. How will you distinguish between benzoic acid and phenol ?

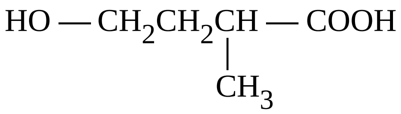
7. How do you prepare 2 - hydroxy propionic acid from acetaldehyde ?

8. Complete the equation

   $$CH_3COOH \xrightarrow{?} ClCH_2COOH \xrightarrow[\text{of } NH_3]{\text{Excess}} ?$$

9. Give the IUPAC name of (i) $CH_3COCH_2COOH.$

   (ii) $CH_3CH = CHCOOH.$

   (iii) 

   $HO — CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}} — COOH$

10. What are the following reagents ? Give one use of each reagent.

    (a) Tollens' reagent (b) Schiff's base (c) Fehling's solution.

11. What is esterification? Explain with mechanism taking the example of benzoic acid.

12. CH_3COOH gives HVZ reaction, where as HCOOH does not. Explain.

D. Long answer type (7 marks each)

1. Give any two methods of preparation of monocarboxylic acids. How formic acid reacts with Tollens' reagent ? How can you obtain acetamide from acetic acid ?

2. Explain with equation how monocarboxylic acid is obtained from alkyl cyanide. How does acetic acid react with the following ?

   (a) C_2H_5OH (b) PCl_5 (c) Sodamide

3. How do you prepare the followings from acetic acid ?

   (a) Acetaldehyde (b) Methyl amine

   (c) Methyl cyanide (d) Acetone

4. Describe any two general methods of preparation of monocarboxylic acid. How does formic acid react with.

   (a) Tollens' reagent (b) alcohol (c) Sodium

5. Discuss any two methods for preparing benzoic acid. How benzoic acid is converted to benzoyl chloride?

6. How is acetic acid prepared ? Give any two methods. Give its reaction with Cl_2 in the presence of Red P, P_2O_5 and ethyl alcohol in presence of sulphuric acid.

7. Give any one method of preparation of acetic acid. Write its reaction with

   (a) chlorine (b) alkali (c) phosphorus pentachloride.

8. (a) Synthesize benzoic acid from toluene

   (b) How does it react with (i) conc. HNO_3 and conc.H_2SO_4

   (ii) Cl_2 in the presence of anhydrous $AlCl_3$

9. Give any two general methods of preparation of monocarboxylic acids. What is the reaction of formic acid with.

   (a) ammonia (b) Tollens' reagent ?

10. Compare the acid characters of formic acid and acetic acid.

11. How acetic acid is prepared by using Grignard's reagent ? Give one method to distinguish acetic acid from formic acid. Mention two uses of acetic acid.

12. Write notes on — (5marks each)

    (i) Halogenation of benzoic acid

    (ii) HVZ reaction

13. Explain why carboxylic acids behave as acids ? Discuss bfiefly the effect of electron - donating and electron withdrawing substitueents on the acidity of aliphatic carboxylic acids.

MULTIPLE CHOICE TYPE

E. Select the correct answer :

1. The oils from which soaps are prepared belong to a class of compound known as :

   (a) Amine (b) Acid

   (c) Hydrocarbon (d) Ester

2. Formic acid and acetic acid may be distinguished by reaction with

   (a) Sodium (b) Dilute acidified $KMnO_4$

   (c) 2, 4 dinitrophenyl hydrazine (d) Sodium ethoxide

3. The end product in the sequence of reaction.

$$R - X \xrightarrow{KCN} A \xrightarrow{NaOH} B \text{ is :}$$

(a)	an alkane	(b)	A carboxylic acid
(c)	sodium salt of carboxylic acid	(d)	Saponification

4. Which of the following reduces $HgCl_2$ to Hg_2Cl_2 ?

(a)	Formic acid	(b)	Ammonia
(c)	Acetic acid	(d)	CCl_4

5. Acetic acid can be halogenated in presence of red P and halogen, but formic acid cannot be halogenated in the same way due to

(a) Presence of α – hydrogen atom in acetic acid

(b) Presence of – COOH group in formic acid

(C) Presence of carbonyl group in acetic acid

(d) None of the above

6. Among acetic acid, phenol and n-hexanol, which of the compounds reacts with $NaHCO_3$ solution to give sodium salt and carbon dioxide ?

(a)	Acetic acid	(b)	n - Hexanol
(c)	Acetic acid and phenol	(d)	Phenol

7. Vinegar contains

(a)	10 to 20% acetic acid	(b)	10% acetic acid
(c)	6 to 10% acetic acid	(d)	100% acetic acid

8. Which acid is strongest ?

(a)	CCl_3 COOH	(b)	$Cl_2CHCOOH$
(c)	$ClCH_2COOH$	(d)	CH_3COOH

9. The acid which does not contain – COOH group is

(a)	Ethanoic acid	(b)	Picric acid
(c)	Lactic acid	(d)	Palmitic acid

10. Which of the following cannot reduce Fehling's solution ?

(a)	Formic acid	(b)	Acetic acid
(c)	Formaldehyde	(d)	Acetaldehyde

11. When benzoic acid is reacted with $LiAlH_4$, it forms

(a)	Benzene	(b)	Benzaldehyde
(c)	Toluene	(d)	Benzylalcohol

12. Electrolysis of sodium salt of maleic acid to ethyne is known as

(a) Wurtz's reaction (b) Clemmensen's reduction

(c) Kolbe's reaction (d) Sabatier Senderen's reaction.

13. Which of the following reactions is expected to readily give a hydrocarbon product in good yield.

(a) $RCOOK \xrightarrow[\text{oxidation}]{\text{electrolysis}}$ (b) $RCOOAg \xrightarrow{I_2}$

(c) $CH_3CH_3 \xrightarrow[h\upsilon]{Cl_2}$ (d) $(CH_3)_3\,C\,Cl \xrightarrow{C_2H_5OH}$

14. Monocarboxylic acids show functional isomerism with

(a) esters (b) alcohols

(c) ethers (d) aldehydes

15. The boiling point of acetic acid is higher than expected from its molecular weight, because of

(a) solubility in water (b) non-polar character

(c) strong oxidising character (d) association through hydrogen bonding

16. Acids are obtained as a result of reaction between a Grignard reagent and

(a) Oxygen (b) CO_2

(c) CH_3COCl (d) CH_3CHO

17. Which acid is weaker than benzoic acid?

(a) *p*-Methyl benzoic acid (b) *p*-chlorobenzoic acid

(d) *p*-Nitrobenzoic acid (d) *o*-Chlorobenzoic acid

18. Carboxylic acids are more soluble in

(a) Ether (b) C_6H_6

(c) Na_2CO_3 solution (d) $CHCl_3$

19. Stinges of bees and wasps contain

(a) formalin (b) formaldehyde

(c) acetic acid (d) formic acid

20. Formic acid is obtained by the hydrolysis of

(a) HCN (b) CH_3CN

(c) $(COONa)_2$ (d) $CO + CO_2$

21. What is the main reason for the fact that carboxylic acids can undergo ionisation?

(a) Absence of α-hydrogen (b) Resonance stabilisation of the carboxylate ion

(c) High reactivity of α-hydrogen (d) Hydrogen bonding.

22. $RCOOH \longrightarrow RCH_2OH$. This mode of reduction of an acid to alcohol can be affected by

(a) Zn/HCl
(b) Na/Alcohol
(c) Aluminium isopropoxide and isopropyl alcohol.
(d) $LiAlH_4$

23. Calcium acetate on heating yields

(a) CaO, CO_2 and H_2O (b) $CaCO_3$ and H_2O
(c) Acetaldehyde and $CaCO_3$ (d) $CaCO_3$ and acetone

24. n-Butyl benzene on oxidation will give

(a) Benzyl alchohol (b) Butanoic acid
(c) Benzoic acid (d) Benzaldehyde

25. Benzoic acid may be converted into ethyl benzoate by reaction with

(a) Ethyl chloride (b) DryHCl – C_2H_5OH
(c) Ethyl alcohol (d) Sodium ethoxide

26. $C_6H_5MgBr \xrightarrow[\text{(ii) } H_3\overset{+}{O}]{\text{(i) } CO_2} P$

In the above equation, Product 'P' is

(a) Benzaldehyde (b) Benzoic acid
(c) Phenol (d) Benzophenone

27. Which of the following does not give benzoic acid on hydrolysis ?

(a) Phenyl cyanide (b) Benzoyl chloride
(c) Benzyl chloride (d) Methyl benzoate

28. Which of the followings is the strongest acid ?

(a) *o*-Nitrobenzoic acid (b) *p*-Nitrobenzoic acid
(c) *p*-Chlorobenzoic acid (d) Benzoic acid

29. Phenol $\xrightarrow[\text{dust}]{\text{Zn}} X \xrightarrow[\text{Anhyd.AlCl}_3]{CH_3Cl} Y \xrightarrow[KMnO_4]{\text{Alk}} Z$, the product 'Z' is

(a) Benzaldehyde (b) Benzoic acid
(c) Benzene (d) Toluene

30. Which has the highest pK_a value ?

(a) Benzoic acid (b) *p*-Nitrobenzoic acid
(c) *m*-Nitrobenzoic acid (d) *o*-Nitrobenzoic acid

31. Which of the following compounds will have the smallest pK_a value ?

    (a) Benzoic acid (b) Formic acid

    (c) Acetic acid (d) Phenylacetic acid

32. Among the following compounds, most acidic is :

    (a) *p*-Nitrophenol (b) *p*-Hydroxybenzoic acid

    (c) *o*-Hydroxybenzoic acid (d) *p*-Toluic acid

ANSWERS

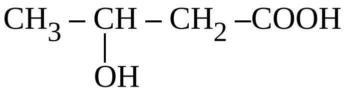
A. 1. Acetic acid,

2. $$2CH_3COOH + Na_2CO_3 \longrightarrow \underset{\text{sodium acetate}}{2CH_3COONa} + CO_2 + H_2O$$

3. $$CH_3COOH + NH_3 \longrightarrow \underset{\text{Amm.acetate}}{CH_3COONH_4} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

4. Formic acid is used in leather industry in tanning for removing lime, from the hides. It is also used for preparing certain medicines and antiseptics.

5. Phenyl magnesiumbromide

6. 

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - COOH$$

7. 3 Bromo propanoic acid.

8. (i) Ethylpropanoate (ii) Pentanedioic acid

9. Formic acid reduces Tollen's reagent or Fehling solution.

10. Benzoic acid

E. 1. (d) 2. (b) 3. (c) 4. (a) 5. (a) 6. (a) 7. (c) 8. (a) 9. (b) 10. (b)
11.(b) 12.(c) 13.(a) 14.(a) 15.(d) 16.(b) 17. (a) 18. (c) 19. (d) 20.(a)
21.(b) 22.(d) 23.(d) 24.(c) 25.(b) 26.(b) 27.(c) 28.(a) 29. (b) 30.(a)
31. (b) 32.(c)

* * *

UNIT - XIII

ORGANIC COMPOUNDS CONTAINING NITROGEN

CHAPTER - 20

AMINES

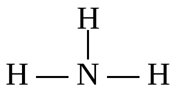
20.1 INTRODUCTION :

The amines are considered as alkyl / aryl derivatives of ammonia in which one or more hydrogen atoms in an ammonia molecule have been replaced by alkyl and / or aryl groups.

20.2 TYPES OF AMINES :

20.2.1 ALIPHATIC AMINES :

Aliphatic amines are the derivatives of ammonia in which one or more hydrogen atoms in ammonia molecule are replaced by alkyl groups. These are classified as primary, secondary and tertiary amines depending on whether one, two or three hydrogen atoms of ammonia molecule are replaced by alkyl groups.

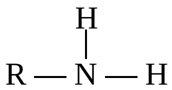


$H-\overset{\overset{H}{|}}{N}-H$

or

NH_3

Ammonia

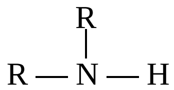


$R-\overset{\overset{H}{|}}{N}-H$

or

RNH_2

Primary amine

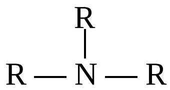


$R-\overset{\overset{R}{|}}{N}-H$

or

R_2NH

Secondary amine



$R-\overset{\overset{R}{|}}{N}-R$

or

R_3N

Tertiary amine

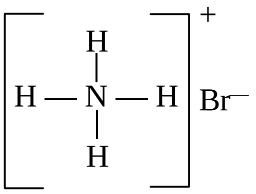
Primary, Secondary and Tertiary amines :

(i) **Primary or 1^0 amines :** The primary amines have the general formula, RNH_2 and are characterised by $-NH_2$ group linked to an alkyl group. The $-NH_2$ group in primary amine is called the *amino* group.

(ii) **Secondary or 2^0 amines :** The secondary amines have the general formula, R_2NH and are characterised by NH group linked to two same or different alkyl groups. The $>NH$ group in secondary amine is called the *imino* group.

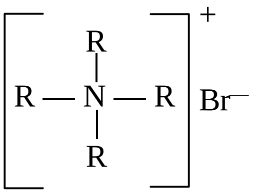
(iii) **Tertiary or 3^0 amines :** The tertiary amines have the general formula, R_3N and are characterised by $\geqslant N$ group linked to three same or different alkyl groups.

Quaternary ammonium salts : If all the four hydrogen atoms of an ammonium salt are replaced by same or different alkyl groups, the compound is called *quaternary ammonium salt* or tetra- alkyl ammonium salt.



$$\left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array}\right]^{+} Br^{-}$$

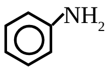
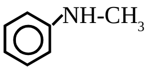
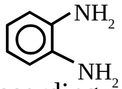
NH_4Br
Ammonium bromide



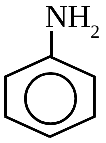
$$\left[\begin{array}{c} R \\ | \\ R-N-R \\ | \\ R \end{array}\right]^{+} Br^{-}$$

R_4NBr
Tetra-alkyl ammonium bromide

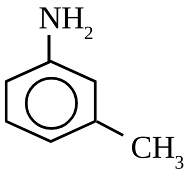
20.2.2 ARYL AMINES :

Arylamines are those having the amino group (one or more) directly attached to an aromatic nucleus. For example : aniline  methylaniline  O-phenylenediamine  etc. Like aliphatic amines, arylamines may be primary (1^0), secondary (2^0) or tertiary (3^0) according as one, two or all the hydrogen atoms of ammonia are replaced by phenyl or aryl radicals. In case of secondary and tertiary amino compounds, all the hydrogen atoms may not be replaced by aryl groups. There may be both alkyl and aryl groups. Such amines are of mixed aliphatic – aromatic type secondary and tertiary amines. A few examples of both pure and mixed amines are given below.

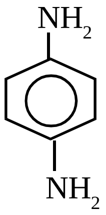
Primary :



Aniline

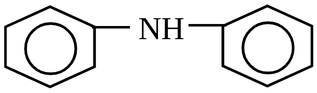


m- toluidine

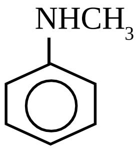


p-phenylenediamine

Secondary :

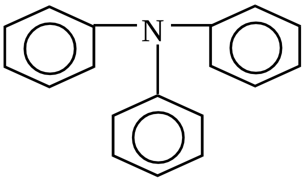


Diphenylamine

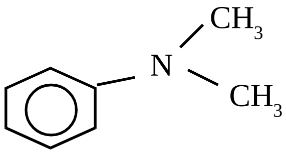


N- Methylaniline
(mixed)

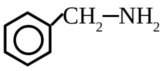
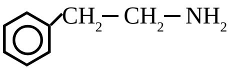
Tertiary :

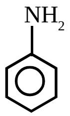


Triphenylamine



N, N -Dimethylaniline
(mixed)

Aromatic compounds with amino groups present in the side chain are called arylalkyl amines. For example, benzylamine  , β - phenylethylamine  etc. These are aryl substituted aliphatic amines and behave very much like aliphatic amines.

Aminobenzene or Benzenamine  or $C_6H_5 - NH_2$

Aniline [$C_6H_5NH_2$] is the simplest primary arylamine.

20.3 NOMENCLATURE :

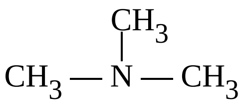
1. **Common system :** The common names of aliphatic amines are derived by listing the alkyl groups on the nitrogen in order of increasing size ending with amine. If same type of alkyl group occurs twice or thrice on the nitrogen atom, the prefix di– or tri– is placed before the name of the alkyl group.

CH_3NH_2

Methylamine

CH_3NHCH_3

Dimethylamine


$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{N}} - CH_3$$

Trimethylamine

$CH_3NHCH_2CH_3$

Methyl ethylamine

2. **IUPAC system :** In IUPAC system primary amines are called alkanamines; secondary amines, alkyl alkanamines and tertiary amines, dialkyl alkanamines. The longest alkyl group is considered as the parent chain.

CH_3NH_2

Methanamine

$CH_3CH_2NH_2$

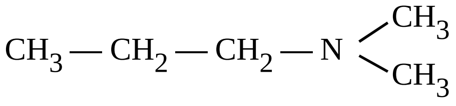
Ethanamine

$CH_3CH_2CH_2NH_2$

Propanamine

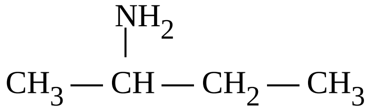
$CH_3CH_2NH_2CH_3$

N – Methyl ethanamine


$$CH_3 - CH_2 - CH_2 - N \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

N, N – dimethyl propanamine

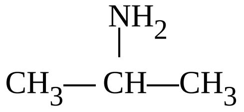
In the higher and more complex compounds the amino group is treated as a substituent and is assigned the locant keeping in view the lower number rules and the order of priority of different functional groups. Names of a few amines are given below.


$$CH_3 - \overset{\displaystyle NH_2}{\overset{|}{CH}} - CH_2 - CH_3$$

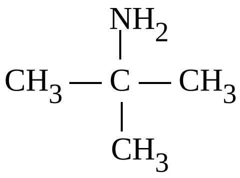
2-Butanamine

$CH_3CH_2CH_2CH_2CH_2NH_2$

1-Pentanamine

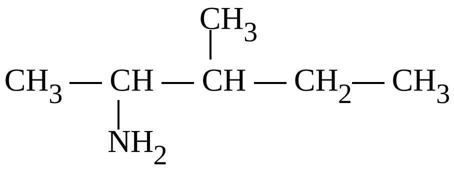

$$CH_3 - \overset{\displaystyle NH_2}{\overset{|}{CH}} - CH_3$$

2-Propanamine



$$CH_3-\overset{NH_2}{\underset{CH_3}{C}}-CH_3$$

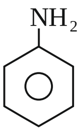
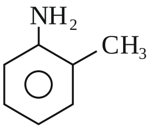
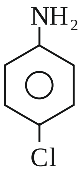
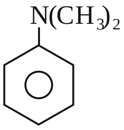
2 – Methyl – 2 –propanamine



$$CH_3-\underset{NH_2}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$$

3–Methyl –2– pentanamine

3. Nomenclature of some common aryl amines are given below :

Structure	**Common name**	**IUPAC name**
	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Methylanine
	p-Cloroaniline	4-Chlorobenzenamine or 4-Chloroaniline
	N, N-Dimethylaniline	N, N – Dimethyl - benzenamine

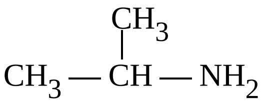
20.4 ISOMERISM :

Amines exhibit (i) Chain isomerism (ii) Position isomerism (iii) Functional isomerism (iv) Metamerism.

(i) Chain isomerism :

$CH_3-CH_2-CH_2-NH_2$

n-Propylamine (common name)



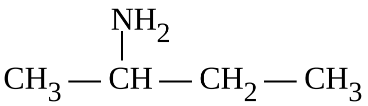
$$CH_3-\overset{CH_3}{CH}-NH_2$$

Isopropylamine (common name)

(ii) Position isomerism :

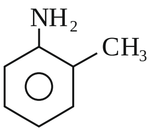
$CH_3-CH_2-CH_2-CH_2-NH_2$

n-Butylamine

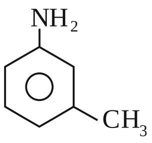


$$CH_3-\overset{NH_2}{CH}-CH_2-CH_3$$

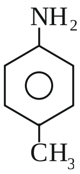
sec-Butylamine



1-Methylaniline



2-Methylaniline



3-Methylaniline

(iii) Functional isomerism :

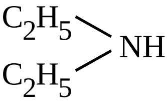
$CH_3 - CH_2 - NH_2$
Ethylamine

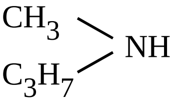
$CH_3 - NH - CH_3$
Dimethylamine

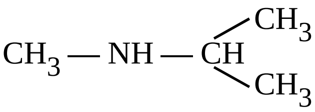
$C_6H_5CH_2NH_2$
Benzylamine

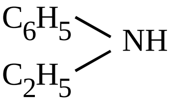
$C_6H_5 - NH - CH_3$
N-Methylaniline

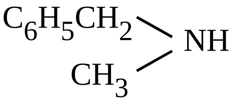
(iv) Metamerism :


Diethylamine


Methyl propylamine


Methyl isopropylamine


N-Ethylaniline


N-Methylbenzylamine

20.5 GENERAL METHODS OF PREPARATION :

1. Ammonolysis of Alkyl halides (Hofmann's method)

Primary amines may be prepared by heating an alkyl halide with excess of alcoholic solution of ammonia in a sealed tube.

$$R - \boxed{X \quad + \quad H} - NH_2 \longrightarrow RNH_2 + HX$$

Alkyl halide Ammonia 1^0 amine

$$CH_3 - \boxed{I + H} - NH_2 \longrightarrow CH_3NH_2 + HI$$

Methyl iodide Methylamine

The primary amine reacts with another molecule of alkyl halide to form secondary amine.

$$R - \boxed{X + H}\ HN\ R \longrightarrow R_2NH + HX$$

2^0 amine

The secondary amine can combine with another molecule of alkyl halide of form a tertiary amine which in turn can combine with another molecule of alkyl halide to form quaternary ammonium salt.

$$R\boxed{X + H}\ N\ R_2 \longrightarrow R_3N + HX$$

3^0 amine

$$R\ X + R_3\ N \longrightarrow R_4NX$$

Tetra - alkyl ammonium halide

Commercially, the amines are separated by fractional distillation.

Simple aryl halides i.e. when the halogen atom (X) is directly attached to the aromatic ring are ordinarily inert towards ammonia. This is because, in aryl halide the C – X bond is stronger than C – X bond in alkyl or benzyl halides. However, aryl halides react with ammonia in presence of catalyst (copper salts) at high temperature and under high pressure to form the corresponding amino compounds.

$$\text{Ar} - \text{X} + \text{NH}_3 \xrightarrow[\Delta,\ \text{pressure}]{\text{Cu}_2\text{O}} \text{Ar} - \text{NH}_2 + \text{HX}$$

Aryl halide 1°-Amine

$$\text{C}_6\text{H}_5 - \text{X} + \text{NH}_3 \xrightarrow[\Delta,\ \text{pressure}]{\text{Cu}_2\text{O}} \text{C}_6\text{H}_5\text{NH}_2 + \text{HX}$$

Halobenzene Aniline

Like aliphatic primary amines, aniline react with alkyl halides (RX) giving successively secondary, tertiary amines and quaternary ammonium salts.

$$\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow{\text{RX}} \underset{2^\circ\ \text{Amine}}{\text{C}_6\text{H}_5\text{NHR}} \xrightarrow{\text{RX}} \underset{3^\circ\ \text{Amine}}{\text{C}_6\text{H}_5\text{Nr}_2} \xrightarrow{\text{RX}} \underset{\text{Quaternary ammonium salt}}{\text{C}_6\text{H}_5\overset{+}{\text{N}}\text{R}_3\text{X}^-}$$

2. **Ammonolysis of alcohols and phenol :** When vapours of an alcohol and ammonia are passed over a dehydrating catalyst such as thoria or alumina at 300^{0}C, a mixture of primary, secondary and tertiary amines is formed.

$$\text{R} - \boxed{\text{OH + H}} - \text{NH}_2 \xrightarrow[300^0\text{C}]{\text{ThO}_2} \text{RNH}_2 + \text{H}_2\text{O}$$

$$\text{R} - \boxed{\text{OH + H}} - \text{H NR} \longrightarrow \text{R}_2\text{NH} + \text{H}_2\text{O}$$

$$\text{R} - \boxed{\text{OH + H}} - \text{NR}_2 \longrightarrow \text{R}_3\text{N} + \text{H}_2\text{O}$$

Phenols react with ammonia in the presence of zinc chloride at about 300°C to form the corresponding amines.

$$\text{Ar} - \text{OH} + \text{HNH}_2 \xrightarrow[300^\circ\text{C}]{\text{ZnCl}_2} \text{Ar} - \text{NH}_2 + \text{H}_2\text{O}$$

$$\text{C}_6\text{H}_5 - \text{OH} + \text{NH}_3 \xrightarrow[300^\circ\text{C}]{\text{ZnCl}_2} \text{C}_6\text{H}_5 - \text{NH}_2 + \text{H}_2\text{O}$$

Phenol Aniline

3. **Reduction of nitroalkanes and nitroarenes :** When a nitro group is reduced it is easily converted to amino group. The reduction can be brought about by tin and hydrochloric acid or iron and hydrochloric acid or hydrogen in presence of nickel or platinum or lithium aluminium hydride.

$$R\,NO_2 + 6H \xrightarrow[\text{or Fe + HCl}]{\text{Sn + HCl}} R\,NH_2 + 2H_2O$$

Nitroalkane

$$CH_3NO_2 + 6H \longrightarrow CH_3NH_2 + 2H_2O$$

Nitromethane Methylamine

$$C_6H_5NO_2 + 6H \longrightarrow C_6H_5NH_2 + 2H_2O$$

Nitrobenzene Aniline

Catalytic reduction :

Nitrobenzene can also be catalytically reduced by hydrogen under pressure in presence of Platinum or Raney nickel.

$$C_6H_5NO_2 + 3H_2 \xrightarrow[\text{Pt or Pd}]{\text{Raney Ni or}} C_6H_5NH_2 + 2H_2O$$

Nitrobenzene Aniline

4. **Hofmann bromamide reaction :** The action of bromine on acid amides in an alkaline (NaOH or KOH) solution produces an amine containing one carbon atom less than the number present in the amide. This reaction was developed by **Hofmann** and used in degradation of carbon chain.

$$RCONH_2 + Br_2 + 4KOH \rightarrow R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

$$CH_3CONH_2 + Br_2 + 4KOH \rightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Acetamide Methylamine

$$C_6H_5CONH_2 + Br_2 + 4KOH \rightarrow C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Benzamide Aniline

5. **Reduction of alkyl and aryl cyanides :**

When alkyl cyanides are reduced by sodium and alcohol **(Mendius reaction)** or lithium aluminium hydride, 1^0amines are formed

$$RCN + 4H \xrightarrow[\text{or } LiAlH_4]{\text{Na+ Alcohol}} RCH_2NH_2$$

$$CH_3CN + 4H \longrightarrow CH_3CH_2NH_2$$

$$C_6H_5CN + 4H \longrightarrow C_6H_5CH_2NH_2$$

6. **From Grignard reagent :** Alkyl magnesium halides react with chloramine to form primary amines.

$$\underset{\text{Grignard reagent}}{RMgX} + ClNH_2 \longrightarrow RNH_2 + Mg\begin{matrix}X\\Cl\end{matrix}$$

7. **From isocyanates :** Acyl azides on heating produce isocyanates. When alkyl isocyanates are boiled with alkali, they undergo hydrolysis to form primary amines. This is known as **Curtius reaction.**

$$RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$$

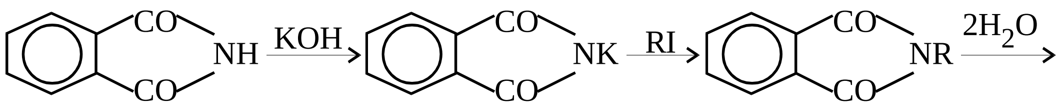
$$\underset{\text{Acyl azide}}{RCON_3} \xrightarrow{\text{heat}} \underset{\text{Alkyl isocyanate}}{R — N = C = O}$$

$$R — N = C = O \xrightarrow{H_2O} RNH_2 + CO_2$$

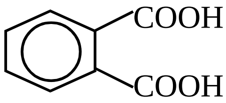
Carboxylic acids react with hydrazoic acid to form primary amines. This is called **Schmidt reaction.**

$$RCOOH + HN_3 \xrightarrow[\text{heat}]{H_2SO_4} RNH_2 + N_2 + CO_2$$

8. **Gabriel's phthalimide synthesis :** Phthalimide reacts with alcoholic potash to form potassium phthalimide which reacts with alkyl halide to give N - alkyl phthalimide. This on hydrolysis with 20% HCl gives primary amine



Phthalimide Potassium phthalimide N — alkyl phthalimide



+ RNH_2

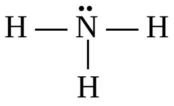
Phthalic acid 1^0Amine

Phthalic acid can be utilised for preparing phthalimide.

Aromatic primary amines cannot be prepared by this method because aryl halides will not react with potasium phtholimide to form N – aryl phthalimide.

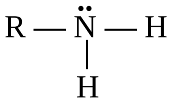
20.6 GENERAL PROPERTIES :

Basicity of aliphatic amines : Amines are derivatives of ammonia and hence like ammonia these are basic in character. The basicity of amines and ammonia is due to the presence of unshared electron pair on nitrogen atom which accepts a proton. The readiness with which the lone pair of electrons is available for coordination with a proton determines the relative basicity of amines.



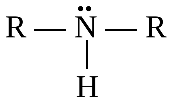
$H-\underset{\underset{H}{|}}{\ddot{N}}-H$

Ammonia



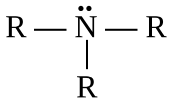
$R-\underset{\underset{H}{|}}{\ddot{N}}-H$

Primary amine



$R-\underset{\underset{H}{|}}{\ddot{N}}-R$

Secondary amine



$R-\underset{\underset{R}{|}}{\ddot{N}}-R$

Tertiary amine

Alkyl groups are electron releasing groups. As a result the nitrogen atoms become electron rich. The lone pair of electrons is more readily available than ammonia. Thus amines are stronger bases than ammonia. Accordingly the basicity should increase with number of alkyl groups. However, the basicity follows the order, [in case of methylamine (1^0), dimithelamins (2^0) and trimethyl amine (3^0)]

Secondary > Primary > Tertiary > Ammonia

The reason for this is the steric factor. In tertiary amines three alkyl groups prevent the proton for coordination with lone pair. Hence tertiary amines are less basic than even primary amine. Ethyl amine is more basic than methyl amine since the +I effect of ethyl group is more than that of methyl group. Since chlorine is electron withdrawing group, chloramine is less basic than ammonia.

$C_2H_5NH_2 > CH_3NH_2$

$NH_3 > ClNH_2$

Basic Character of aromatic amines : Aniline is weakly basic and forms crystalline salts with acids. It also forms double salt with $PtCl_4$ and $AuCl_3$

$$C_6H_5-NH_2 + HCl \longrightarrow [C_6H_5-\overset{+}{N}H_3]\ Cl^-$$

Aniline hydrochloride

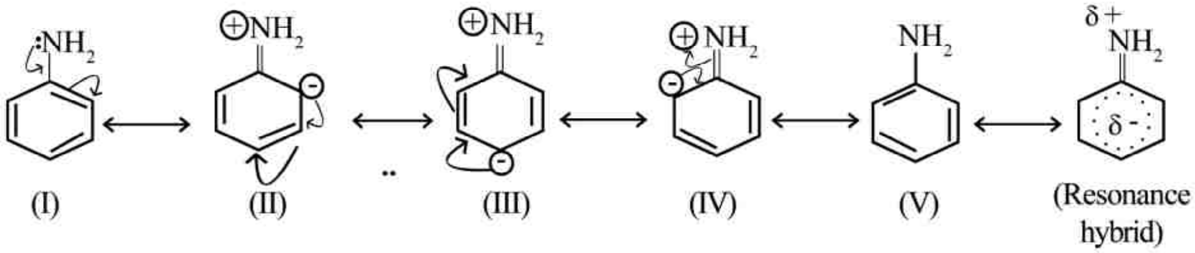
$$C_6H_5\ NH_2 + H_2SO_4 \longrightarrow [C_6H_5-NH_3]\ HSO_4$$

Aniline hydrogensulfate

$$2\ C_6H_5\ NH_2 + 2HCl + PtCl_4 \longrightarrow [C_6H_5\ NH_3Cl]_2\ PtCl_4$$

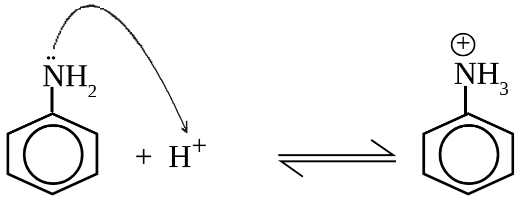
Aniline chloroplatinate

Basicity of a compound is its ability to accept a proton (H^+). We have seen that the amines behave as bases due to the capacity of the lone pair of electron on nitrogen to form a coordinate bond with the proton. Thus aliphatic amines are basic and more basic than ammonia, because the alkyl group pushes the electron towards nitrogen (+I effect). Hence, electron density on nitrogen increases. Aniline is a resonance hybrid of the following canonical structures:



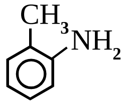
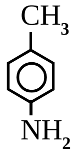
Due to the resonance interaction between the π – electron of the benzene ring and the lone pair of electron on nitrogen atom of the amino group, the lone pair of electron on the nitrogen atom responsible for the basicity of aniline is less available to be donated to a proton. Further, a small amount of positive charge on nitrogen atom tends to repel proton. Hence, aniline is a weak base.

Aniline may accept a proton to form a small amount of anilinium ion.



(Anilinium ion)

But anilinium ion less stable since there is no resonance in this ion. Therefore, the equilibrium shifts to the other side ie. towards aniline which is more stable. The low basicity of aniline is, therefore, due to the fact that aniline is stabilized by resonance to a greater extent than anilinium ion.

Electron releasing substituents, like – CH_3 increase the basicity of aniline whereas electron withdrawing substituents, like Cl, Br, I, NO_2 decrease the basicity. This is due to the fact that electron release stabilizes the anilinium ion relative to aniline by dispersing the positive charge of the anilinium ion. Thus, monomethyl and dimethylanilines are stronger bases than aniline, Again, o-toluidine  and p –toluidine  would be more basic than aniline. It is observed that o-toluidine has a K_b= 2.5 x 10^{-10} and p-toluidine, K_b = 12 x 10^{-10} in comparison to the K_b of aniline (4.2 x 10^{-10}). The anomalous behaviour of o-substituted anilines is, however, possibly due to **ortho effect**. Thus o-substituted anilines tend to have K_b lower than that of aniline irrespective of the nature (electron – releasing or electron withdrawing) of the substituent. The base –weakening effect of electron –withdrawing substituents is most marked when present in ortho position of the amino group.

Physical Properties :

(1) **State :** The lower members of amines are gases. Those of three to eleven carbon atoms (except trimethyl amine) are liquids at ordinary temperature. Higher members are solids.

(2) **Odour :** Amines of lower molecular mass possess odour similar to that of ammonia. As the molecular mass increases these have characteristic unpleasant odour of a decaying fish. In general it can be stated that aliphatic amines possess fishy or fish -like odour.

(3) **Density :** These are lighter than water.

(4) **Solubility :** The lower members (less then six carbon atoms) of the family are highly soluble in water as all amines including tertiary amines are capable of forming hydrogen bonds with water.

(5) **Boiling point :** The boiling points are higher than those of the corresponding alkanes. This is due to the polar nature and intermolecular hydrogen bonding in amines. The boiling points of amines are lower compared to alcohols and carboxylic acids of comparable molecular mass. It is due to weaker hydrogen bonding as oxygen is more electronegative than nitrogen.

(6) **Physical properties of Aniline :** Freshly distilled aniline is a colourless liquid with unpleasant odour, b.p. 184^0C. On exposure to light and air, it undergoes oxidation and turns brown. It is heavier than water and is slightly soluble in it, but it is highly soluble in alcohol, ether and benzene. Aniline is a polar molecule and its dipole moment is 1.48D.

Chemical Properties :

1. **Reaction with water :** Amines combine with water to form alkyl ammonium hydroxides which ionise to give protonated amines and hydroxide ion.

$$\underset{\text{Amine}}{RNH_2} + H_2O \longrightarrow \underset{\text{Alkyl ammonium hydroxide}}{RNH_3OH} \rightleftharpoons \underset{\text{Protonated amine}}{RNH_3^+} + OH^-$$

2. **Reaction with acids :** Amines react with strong acids to form ammonium salts. Methyl amine combines with hydrochloric acid to form methylammonium chloride.

$$CH_3NH_2 + HCl \longrightarrow \underset{\text{Methylammonium chloride}}{CH_3\overset{+}{N}H_3\,Cl^-}$$

$$RNH_2 + HCl \longrightarrow RNH_3Cl$$
1° Amine → Alkylammonium chloride

$$2C_2H_5NH_2 + H_2SO_4 \longrightarrow (C_2H_5NH_3)_2SO_4$$

$$C_6H_5NH_2 + HCl \longrightarrow [C_6H_5-\overset{+}{N}H_3]\,Cl^- \text{ (Crystalline salt)}$$
Aniline → Aniline hydrocloride

$$R_2NH + HCl \longrightarrow R_2NH_2Cl$$
2^0Amine → Dialkyl ammonium chloride

$$R_3N + HCl \longrightarrow R_3NHCl$$
3^0Amine → Trialkyl ammonium chloride.

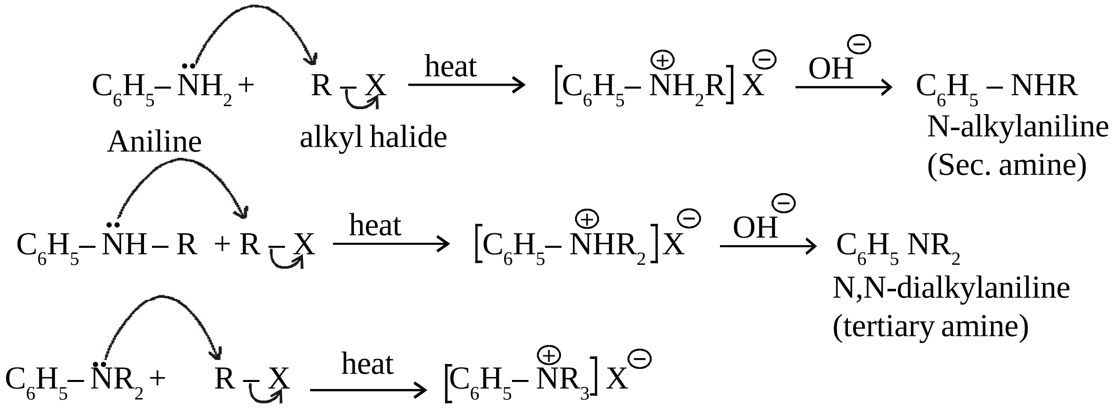
3. **Reaction with alkyl halides :** Primary amines take up three molecules of alkyl halide to form secondary and tertiary amines and quaternary ammonium salts.

$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI$$
Methyl amine → Dimethyl amine

$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI$$
Trimethyl amine

$$(CH_3)_3N + CH_3I \longrightarrow (CH_3)_4NI$$
Tetramethyl ammonium iodide.

Like aliphatic primary amines, aniline can react with alkyl halides giving successively secondary, tertiary amine and quaternary ammonium salts. These are all typical nucleophilic substitution reactions.

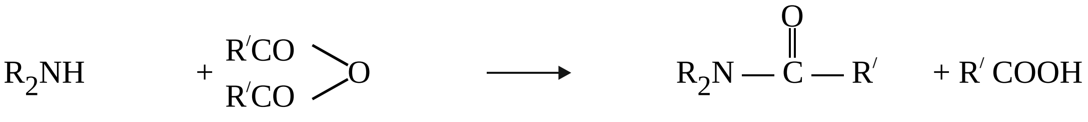


This process of introducing alkyl group in the molecule is called **alkylation. N-arylation** is usually more difficult and purely aromatic quaternary ammonium salt of the type $[(C_6H_5)_4\overset{\oplus}{N})]\,\overset{\ominus}{X}$ is **unknown**.

4. **Reaction with acid chloride and acid anhydride (Acylation) :** Primary and secondary amines react with acid chlorides and anhydrides to form alkyl derivatives of amides (substituted amides).

$$RNH-\boxed{H+\ Cl}-\overset{O}{\overset{\|}{C}}-R' \longrightarrow R-NH-\overset{O}{\overset{\|}{C}}-R'$$

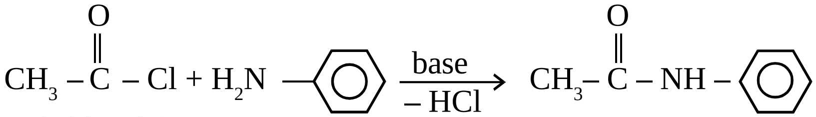
1^0 Amine N – Alkylamide



$$R_2NH + \begin{matrix}R'CO\\ R'CO\end{matrix}\!\!>O \longrightarrow R_2N-\overset{O}{\overset{\|}{C}}-R' + R'COOH$$

2^0 Amine Acid anhydride N, N – dialkylamide

Aniline reacts with acetyl chloride in presence of a base like pyridine or sodium hydroxide to neutalise the acid formed. The product is a substituted acid amide.



(Acetyl chloride) (aniline) (Acetanilide or N-phenylethanamide)

Substituted acid amides like acetanilide can also be considered as acyl derivatives of amines. Thus, acetanilide is acetyl derivative of aniline. It is to be noted that only 1^0 and 2^0 amines containing hydrogen atom attached to nitrogen can undergo **acylation reaction**.

Acylation is a process of introducing $R-\overset{O}{\overset{\|}{C}}-$group into the molecule. Introduction of CH_3–CO – group is called **acetylation.** Similarly, introduction of benzoyl group ($C_6H_5-\overset{O}{\overset{\|}{C}}-$) is called **benzoylation.** Benzoylation of aniline is carried out by treating aniline with benzoyl chloride in presence of NaOH.

$$C_6H_5-NH_2 + Cl-CO-C_6H_5 \xrightarrow{NaOH} C_6H_5-CONHC_6H_5$$

(Aniline) (Benzoyl chlonde) (Benzanilide)

In this reaction, H atom of $-NH_2$ group is substituted by benzoyl group. (C_6H_5-CO-). This reaction is known as **Schotten- Baumann reaction.**

5. **Reaction with nitrous acid : (Distinction):** Amines are distinguished by this reaction. Nitrous acid is formed by the reaction by sodium nitrite with dilute mineral acids.

   (a) Primary amines react with nitrous acid to form primary alcohol with the liberation of nitrogen.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + HONO \longrightarrow \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + N_2 + H_2O$$

Important : Methylamine does not give methyl alcohol with $NaNO_2$ & dil. HCl. Instead it gives methyl nitrite and dimethyl ether.

$$CH_3NH_2 + 2HONO \longrightarrow CH_3 - O - N = O + N_2 + H_2O$$

$$2CH_3NH_2 + 2HONO \longrightarrow CH_3 - O - CH_3 + 2N_2 + 3H_2O$$

(b) Secondary amines react with nitrous acid to form nitrosoamine (yellow oil).

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} + HONO \longrightarrow \underset{\text{Nitrosodimethylamine}}{(CH_3)_2N - N = O} + H_2O$$

(c) Tertiary amines dissolve in nitrous acid to form addition product which decomposes to form nitrosoamine and alcohol.

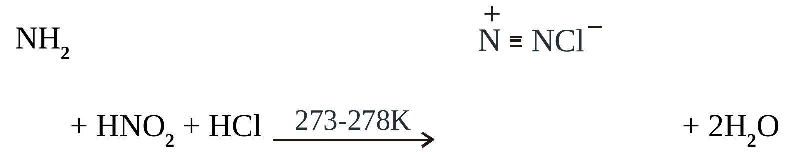
$$(CH_3)_3N \xrightarrow{HNO_2} (CH_3)_3\,NHNO_2 \xrightarrow{heat} \underset{\text{Nitrosodimethylamine}}{(CH_3)_2NNO} + CH_3OH$$

Aryl primary, secondary and tertiary amines react differently with nitrous acid. Since nitrous acid is unstable, it is prepared in the reaction medium by the action of dilute hydrochloric acid on sodium nitrite at low temperature.

(a) Primary amines :

Aromatic primary amines react with nitrous acid at 273 – 278 K (0 – 5^{0}C) to form arenediazonium salts. Thus,

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



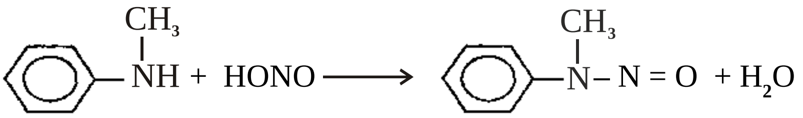
$$\overset{NH_2}{} + HNO_2 + HCl \xrightarrow{273\text{-}278K} \overset{\overset{+}{N} \equiv NCl^-}{} + 2H_2O$$

Benzenediazonium chloride

This reaction of converting primary aromatic amines into diazonium salts by treatment with a cold (273 - 278K) solution of nitrous acid is called **diazotisation**.

(b) Secondary amines :

Secondary amines (both aromatic and aliphatic) react with nitrous acid to give N-nitrosoamine which being insoluble in dilute mineral acids separate out as **yellow oily** compounds.

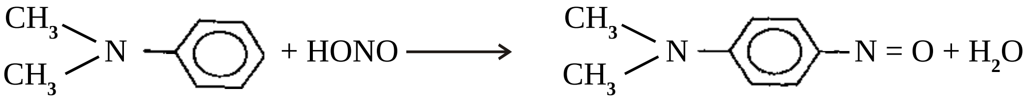


N-Methylaniline N-Nitroso-N-methylaniline
(Yellow oil)

These N-nitrosoamines on warming with a crystal of phenol and a few drops of conc.H_2SO_4 form a green solution which when made alkaline with aqueous NaOH, turns deep blue and then red on dilution. This reaction is called **Liebermann nitroso reaction** and is used as a test for secondary amines.

(c) Tertiary amines :

Aromatic tertiary amines undergo electrophilic substitution with nitrosonium ion at *p*-position of the phenyl ring to form green-coloured *p*-nitrosoamines.



N, N-Dimethylaniline *p*-Nitroso-N, N-dimethylaniline (green)

Thus, the reaction with nitrous acid can be used for the distinction of 1^0, 2^0 and 3^0 amines.

Uses : Aniline is largely used for preparation of dyes and drugs. It is also used in the manufacture of accelerators used in rubber industry. Aniline also finds its use in calico printing.

6. Carbylamine reaction : This reaction is responded only by primary amines. Primary amines on heating with chloroform and alcoholic caustic potash give isocyanides (**carbylamines**) with very unpleasant odour.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{(Carbylamine)}}{\underset{\text{Alkylisocyanide}}{RNC}} + 3KCl + 3H_2O$$

$$CH_3NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3NC + 3KCl + 3H_2O$$

Primary arylamines like aliphatic primary amines undergo **carbylamine reaction.** When heated with chloroform and alcoholic KOH, aniline give obnoxious smelling carbylamine or phenyl isocyanide.

$$\underset{\text{(Aniline)}}{C_6H_5NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{(Phenyl isocyanide)}}{C_6H_5NC} + 3KCl + 3H_2O$$

In general,

$$\underset{\text{(Arylamine)}}{Ar\,NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{or carbylamine}}{\underset{\text{Aryl isocyanide}}{Ar\,NC}} + 3KCl + 3H_2O$$

7. **Reaction with benzene sulphonyl chloride (Distinction):** Primary amines react with benzene sulphonyl chloride to form alkyl benzene sulphonamides, soluble in caustic alkali. Secondary amines form dialkyl benzene suphonamides insoluble in caustic alkali. Tertiary amines do not react.

$$RNH-\boxed{H + Cl}-SO_2\,C_6H_5 \longrightarrow RNHSO_2C_6H_5 + HCl$$

$$R_2N-\boxed{H + Cl}-SO_2\,C_6H_5 \longrightarrow R_2NSO_2C_6H_5 + HCl$$

8. **Reaction with Grignard reagent :** Primary amines react with Grignard reagent to form hydrocarbons.

$$RNH_2 + R'MgX \longrightarrow R'H + RNHMgX$$

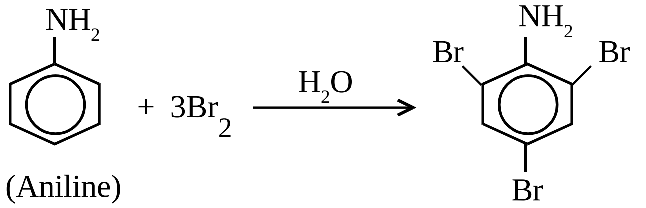
9. **Formation of Schiff's bases :** Primary amines react with aldehydes to form imine or *Schiff's bases*. This is catalysed by acids.

$$RN\boxed{H_2 + O}HCR' \xrightarrow{H^+} R - N = CH - R' + H_2O$$

Schiff's base

10. **Electrophilic Substitution reaction of Aryl amines :** We have seen that due to resonance, the *ortho* – and *para* – positions with respect to – NH_2 group in aniline become electron rich. Therefore, electrophilic substitution in aniline becomes easier, and the substituents enter the *ortho* – or / and *para*-positions in the ring with respect to – NH_2 group.

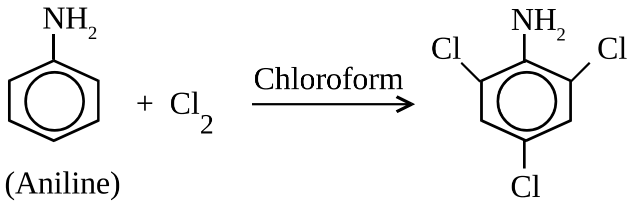
(a) **Halogenation :** The presence of – NH_2 group in aniline activates the nucleus so much that all the H – atoms of *o* – and *p* – positions are readily replaced by bromine or chlorine atoms. Thus, aniline reacts with bromine – water to form 2, 4, 6 – tribromoaniline. Bromine enters *para* and both the *ortho* positions.



(Aniline)

(2, 4, 6 tribromoaniline)

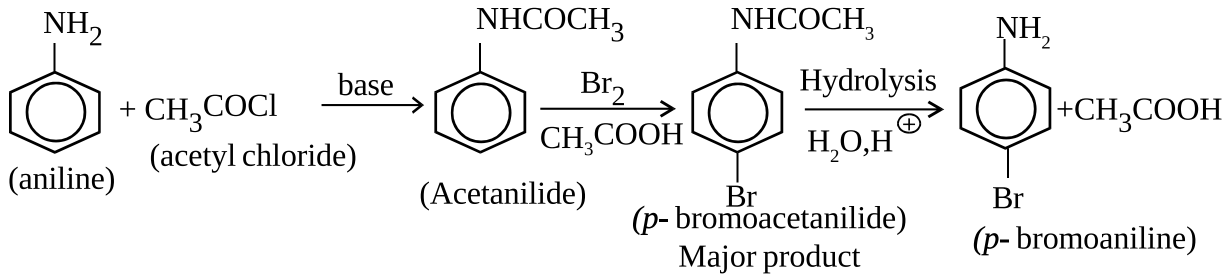
Chlorine, however, reacts with aniline in presence of water – free solvent like chloroform to form 2 , 4, 6 – trichloroaniline.



(Aniline)

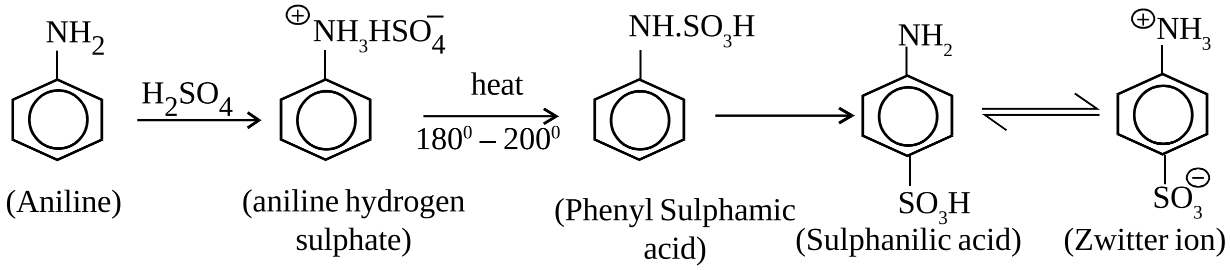
(2, 4, 6 trichloroaniline)

For the preparation of a monobromo compound, aniline is first acetylated before bromination. Finally, the acetyl group is removed through hydrolysis.



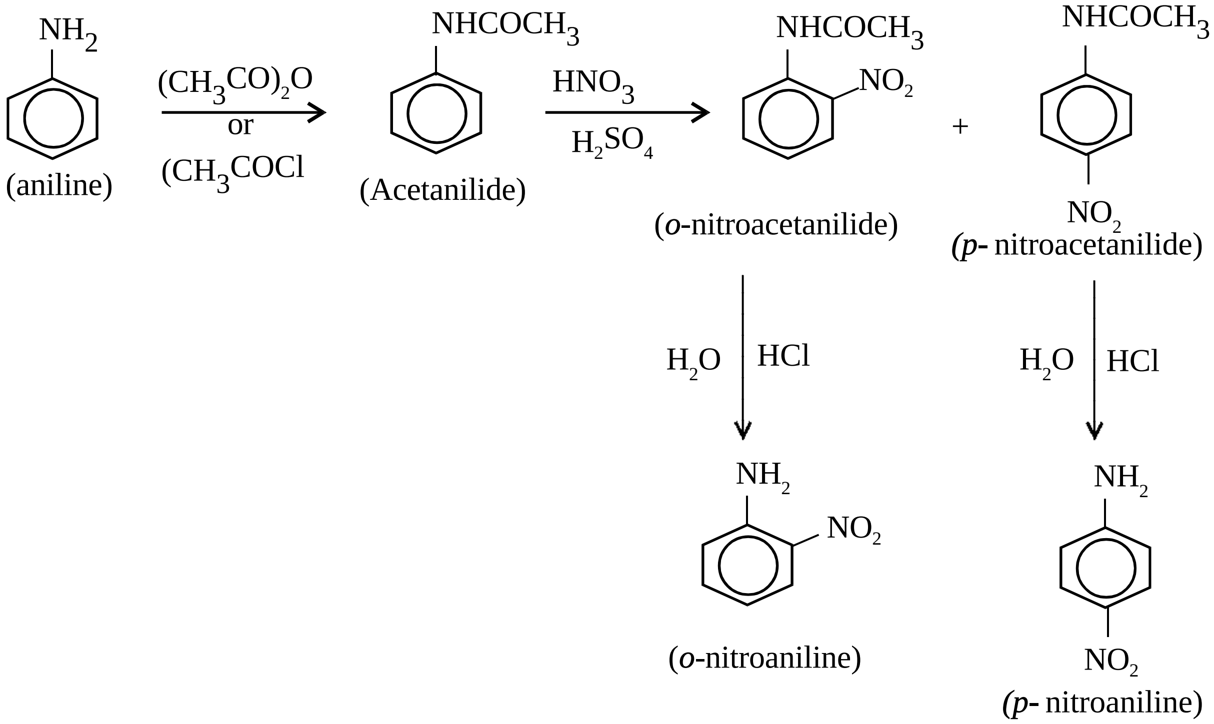
The reactivity of the nucleus is decreased by acetylating – NH_2 group, since activating influence of – $NHCOCH_3$ group is much less than that of – NH_2 group. In that case, only mono substituted product is formed.

(b) **Sulphonation :** When aniline is heated with excess of conc. H_2SO_4 or fuming sulphuric acid at about $180^0 – 200^0$C for 3 – 4 hours, *p* – amino benzene sulphonic acid or sulphanilic acid is formed as the main product. Aniline hydrogen sulphate, formed loses a molecule of water to form phenyl sulphamic acid which rearranges to sulphanilic acid.



Sulphanilic acid contains one acidic group (SO_3H) and one basic group ($-NH_2$). The H ion of – SO_3H group combines with – NH_2 group forming $-\overset{\oplus}{N}H_3$. This is a special type of salt in which an acid group and a basic group of the same molecule neutralize each other. Thus, sulphanilic acid molecule contains both $\overset{+}{N}H_3$ and SO_3^- ions. So, it is a dipolar ion or **Zwitterion.** Sulphanilic acid does not show basic character. The acidic property predominates in the molecule.

(c) **Nitration :** Aniline can not be nitrated directly by the nitrating mixture (conc. H_2SO_4 + Conc. HNO_3), because the amino group is oxidized to form various tarry products. To prevent this oxidation, - NH_2 group is first protected by acetylating the group with acetyl chloride or acetic anhydride and acetanilide formed is then nitrated. – $NHCOCH_3$ group is *o*–, *p*– directing. So, *o*–nitro and *p*–nitroacetanilides are formed. The two isomers are separated and hydrolysed separately with dilute acid, when *o*–nitroaniline and *p*–nitroaniline are formed.



20.7 TESTS :

(1) The aqueous solution of water soluble amines turn red litmus blue. All three classes of amines (1°, 2°. 3°) being basic dissolve in mineral acids like HCl, H_2SO_4 etc. to form salt.

(2) On addition of a concentrated aqueous solution of sodium nitrite to a solution of amine in dil HCl, primary amines give alcohols with rapid effervescence of nitrogen, secondary amines form water-insoluble yellow oil and tertiary amines form nitrite addition salts.

Aromatic primary amines, however, react with HNO_2 at O – 5°C to from arenediazonium salts which couple with an alkaline solution of β-naphthol to form orange or red coloured azo dyes. (distinction form primary alkyl amines).

(3) **Carbylamine test (For primary amines) :** When a primary amine (aliphaticor aromatic) is heated with chloroform and alcoholic KOH, an alkyl isocyanide is formed which has a foul smell.

(4) **Liebermann nitroso reaction (For secondary amines) :**

$$R_2NH + (NaNO_2 + HCl) \longrightarrow R_2N - N = O + H_2O$$

(Nitrosoamine)

Insoluble yellow oil

Nitrosoamines on warming with phenol and conc. H_2SO_4 give a brown or red colour and when the mixture is poured into alkaline solution, a blue or violet colour is observed. This is known as **Liebermann's nitroso reaction** and often used to detect a secondary amino group.

20.8 SEPARATION OF PRIMARY, SECONDARY AND TERTIARY AMINES :

Hinsberg's method — The mixture of amines is treated with Hinsberg's reagent (Benzene sulphonyl chloride). Primary and secondary amines react and tertiary amines do not react.

$$R - NH_2 + C_6H_5SO_2Cl \xrightarrow{-HCl} R.NH.SO_2C_6H_5$$

1^0 amine N– alkyl benzene sulphonamide

$$R_2NH + C_6H_5SO_2Cl \xrightarrow{-HCl} R_2N.SO_2C_6H_5$$

2^0 amine N, N– dialkyl benzene sulphonamide

To the above mixture some NaOH solution and ether are added. Sulphonamide from primary amine forms its sodium salt.

$$RNHSO_2 .C_2H_5 + NaOH \longrightarrow R.N(Na)SO_2C_6H_5$$

Sodium salt (in aqueous layer)

Sulphonamide from secondary and unreacted tertiary amine dissolves in ether and forms the upper layer. The two layers are separated.

(1) The aqueous layer is acidified with dilute hydrochloric acid and then hydrolysed with conc. HCl. It is then distilled over NaOH when primary amine passes over.

$$R.N(Na)SO_2.C_6H_5 + HCl \longrightarrow R.NH\,SO_2C_6H_5 + NaCl$$

$$R.NHSO_2.C_6H_5 + HCl + H_2O \longrightarrow R.NH_2HCl + C_6H_5SO_2OH$$

$$R.NH_2HCl + NaOH \longrightarrow R.NH_2 + NaCl + H_2O$$

Primary amine

(2) Ether layer is subjected to fractional distillation when tertiary amine distils over. The remaining sulphomamide of secondary amine is treated with conc. HCl

$$R_2NSO_2C_6H_5 + HCl + H_2O \longrightarrow C_6H_5SO_2OH + R_2NH.HCl$$

Dialkylamine hydrochloride is then distilled over NaOH when secondary amine is produced.

$$R_2NH.HCl + NaOH \longrightarrow R_2NH + NaCl + H_2O$$

20.9 USES :

1. Methyl and ethylamines are used in leather industries for dehairing of hides .
2. Methylamine is used as a refrigerant.
3. Methylamine and ethylamine are used in preparing dyes and medicines.
4. Amines are used in organic synthesis as condensing agents and catalysts.

5. Aromatic amines such as aniline are widely used in the manufacture of dyes and drugs. Used as additives (antioxidants) and vulcanization accelerators in rubber industry. It is used for the preparation of phenyl isocyanate needed for the manufacture of polyurethane plastics. It is also used for the preparation of arenediazonium salts which in turn is used in the synthesis of wide variety of aromatic compound.

20.10 CONVERSIONS :

1. Methyl amine to ethyl amine

$$CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{P + I_2} CH_3I$$

$$\xrightarrow{KCN} CH_3CN \xrightarrow[4H]{Reduction} CH_3CH_2NH_2$$

2. Ethyl amine to Methyl amine :

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow[K_2Cr_2O_7]{Acidified}$$

$$\xrightarrow{[O]} CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{heat} CH_3CONH_2 \xrightarrow{Br_2+KOH} CH_3NH_2$$

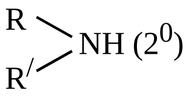
20.11 DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES :

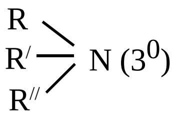
Reaction	Primary	Secondary	Tertiary
1. Action of nitrous acid	Alcohol and N_2 are formed $RNH_2 + HONO \longrightarrow ROH + N_2 + H_2O$ (Aromatic primary amines undergo diazotisation) at 0 to 5°	Nitrosoamine is formed. $R_2NH + HNO_2 \longrightarrow R_2N{-}N{=}O + H_2O$	No reaction (Only salt is formed.)
2. Action of CH_3I	Three molecules CH_3I react to form quaternary salt	Two molecules of CH_3I react to form quaternary salt	One molecule of CH_3I reacts to form quaternary salt.
3. Action of CH_3COCl	Forms N– alkyl amide	Forms N,N– dialkyl amide	No reaction.
4. Carbylamine reaction	Forms isocyanide having a foul smell	No reaction	No reaction.
5. Action of Hinsberg's reagent($C_6H_5SO_2Cl$)	Forms N-alkyl benzene sulphonamide soluble in aqueous NaOH	Forms N,N– dialkyl benzene sulphonamide insoluble in aqueous NaOH	No reaction.

20.12 CYANIDES AND ISOCYNIDES :

These classes of organic compounds are not dealt separately. Their methods of preparation and chemical reactions have been discussed at relevant places in the text.

CHAPTER (20) AT A GLANCE

General formula: $R–NH_2(1^0)$, 
$\begin{matrix}R \\ R^/\end{matrix}\rangle NH\ (2^0)$


$\begin{matrix}R \\ R^/ \\ R^{//}\end{matrix}\rangle N\ (3^0)$ (R, R$^/$, R$^{//}$ may be same or different alkyl groups)

Methods of Preparation :

1. *Hofmann's method:*

$$NH_3 + RX \xrightarrow[100^0C]{alc.soln.} \underset{(1^0amine)}{RNH_2} + HX$$

$$R\,NH_2 + RX \longrightarrow \underset{(2^0amine)}{R_2NH} + HX$$

$$R_2NH + RX \longrightarrow \underset{(3^0amine)}{R_3N} + HX$$

$$R_3N + RX \longrightarrow R_4\overset{\oplus}{N}\overset{\ominus}{X}$$

Quaternary ammonium salt

2. *Ammonolysis of Alcohols:*

$$R — \boxed{OH\ \ +\ H}\ NH_2 \xrightarrow[300^0C]{ThO_2\ orAl_2O_3} \underset{(1^0amine)}{R–NH_2} + H_2O$$

$$R — \boxed{OH\ \ +\ H}\ NHR \longrightarrow \underset{(2^0amine)}{R_2NH} + H_2O$$

$$R — \boxed{OH\ \ +\ H}\ NR_2 \longrightarrow \underset{(3^0amine)}{R_3N} + H_2O$$

3. *Reduction of nitroalkanes :*

$$R – NO_2 + 6H \xrightarrow{Sn/conc.HCl} \underset{(1^0amine)}{R–NH_2} + 2H_2O$$

4. *Hofmann bromamide reaction:*

$$RCONH_2 + Br_2 + 4KOH \longrightarrow \underset{(1^0amine)}{RNH_2} + 2KBr + K_2CO_3 + 2H_2O$$

5. *Reduction of alkyl cyanides : Mendius reaction*

$$\underset{}{R-CN} \quad + \quad 4H \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} \underset{(1^0\text{amine})}{R-CH_2-NH_2}$$

6. *From Grignard reagent :*

$$RMgX \quad + \quad ClNH_2 \longrightarrow \underset{(1^0\text{amine})}{R-NH_2} \quad + \quad Mg(X)Cl.$$

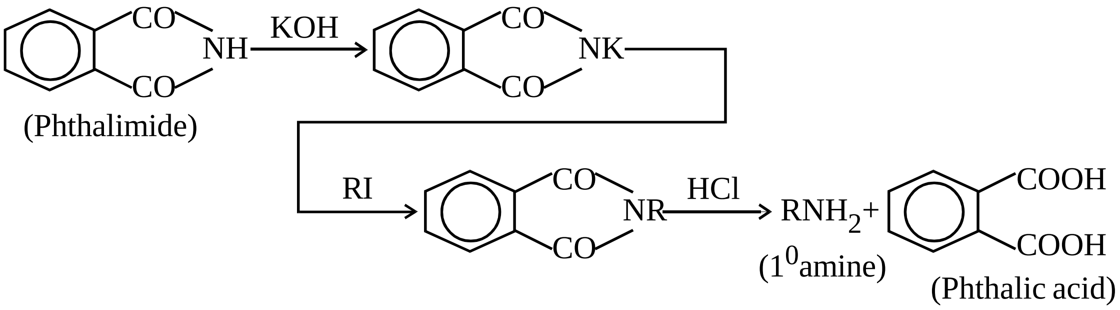
7. *From Acids and Acid derivatives :*

Curtius reaction : $RCOCl + NaN_3 \longrightarrow RCON_3 + NaCl$

$$\underset{(\text{Acid azide})}{RCON_3} \xrightarrow{\text{heat}} \underset{(\text{alkyl isocyanate})}{RNCO} \xrightarrow[\text{boil}]{NaOH} \underset{(1^0\text{amine})}{R\text{–}NH_2}$$

Schmidt reaction : $\underset{(\text{Acid})}{RCOOH} + \underset{(\text{Hydrazoic acid})}{HN_3} \longrightarrow \underset{(1^0\text{amine})}{RNH_2} + N_2 + CO_2$

8. *Gabriel's Phthalimide synthesis :*



General Properties :

1. ***Basicity :*** Amines are more baisc than ammonia due to the alkyl group(s) attached to nitrogen. Aromatic amines are less basic than aliphatic amines.

2. ***Boiling points :*** Amines have higher boiling points than the corresponding alkanes due to intermolecular hydrogen bonding.

3. ***Chmical reactions :***

(i) *Basic nature :*

$$RNH_2 + H_2O \longrightarrow R\overset{\oplus}{N}H_3\ OH^{\ominus}$$

$$\left.\begin{array}{l} RNH_2 + HX \longrightarrow R\overset{\oplus}{N}H_3\ X^{\ominus} \\ R_2NH + HX \longrightarrow R_2\overset{\oplus}{N}H_2\ X^{\ominus} \\ R_3N + HX \longrightarrow R_3\overset{\oplus}{N}H\overset{\ominus}{X} \end{array}\right\} \text{Free bases (amines) can be obtained from the salts by adding dilute base solution.}$$

(ii) *Alkylation :*

$$\underset{(1^0\text{amine})}{RNH_2}\ \underset{(-HX)}{\xrightarrow[\text{Pressure}]{\text{RX(heat)}}}\ \underset{(2^0\text{amine})}{R_2NH}\ \xrightarrow[-HX]{RX}\ \underset{(3^0\text{amine})}{R_3N}\ \xrightarrow{RX}\ \underset{\text{Quarternary salt}}{R_4NX}$$

(iii) *Acylation :* By acid chloride and acid anhydride.

$$RNH_2 + R'COCl \longrightarrow \underset{\text{(N–Alkyl amide)}}{RNHCOR'} + HCl$$

$$R_2NH + R'COCl \longrightarrow \underset{\text{(N, N–Dialkylamide)}}{R_2NCOR'} + HCl$$

$$R_3N \xrightarrow{\text{No – NH group}} \text{No acylation.}$$

Acid anlydrides react in a similar way as above.

(iv) *With* HNO_2 ($NaNO_2$ and cold dilute mineral acid)

$$\underset{(1^0\text{amine})}{R-NH_2} + HONO \longrightarrow \underset{\text{(alcohol)}}{R-OH} + N_2 + H_2O$$

$$\underset{(2^0\text{amine})}{R_2NH} + HONO \longrightarrow R_2N-N=O + H_2O$$

(Nitrosoamine)

(Insoluble yellow oil)

$$R_2N{-}N{=}O + \text{phenol} + \text{conc.}H_2SO_4 \xrightarrow{\text{heat}} \text{Brown or red colour} \xrightarrow{\text{NaOH}} \text{Blue or Violet colour}$$

(Liebermann's nitroso reaction)

$$R_3N + HNO_2 \longrightarrow R_3\overset{\oplus}{N}HNO_2^{\ominus}$$

Aryl primary amines, however, react with HNO_2 to form arenediazonium salts.

(v) *Carbylamine reaction :* For 1^0 amines only.

$$\underset{}{R{-}NH_2} + CHCl_3 + \underset{\text{(alcoholic)}}{3KOH} \xrightarrow{\text{heat}} \underset{\substack{\text{(Carbylamine)}\\ \text{unpleasant odour}}}{RNC} + 3KCl + 3H_2O$$

R_2NH and R_3N do not respond to this reaction.

(vi) *With benzene sulphonyl chloride :*

$$\underset{(1^0\text{amine})}{R{-}NH_2} + C_6H_5SO_2Cl \xrightarrow{\text{KOH}} \underset{\text{(benzene sulphonamide)}}{C_6H_5SO_2NHR} \xrightarrow[\text{KOH}]{\text{Excess}} \text{soluble}$$

$$\underset{(2^0\text{amine})}{R_2NH} + C_6H_5SO_2Cl \xrightarrow{\text{KOH}} C_6H_5SO_2NR_2 \xrightarrow{\text{KOH}} \text{Insoluble}$$

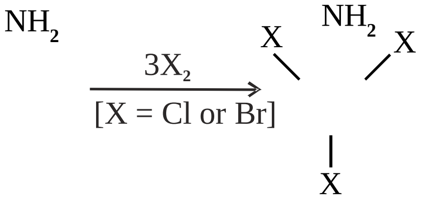
No reaction with 3^0amine

(vii) *With aldehydes :* Formation of Schiffs base.

$$\underset{\text{(1 amine)}}{R - NH_2} + R' - CHO \xrightarrow{H^{\oplus}} \underset{\text{(Schiff's base)}}{R - N = CH - R' + H_2O}$$

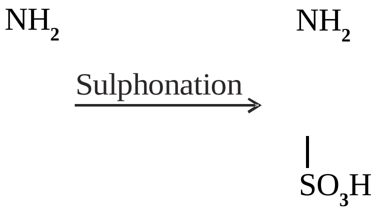
(viii) Aryl amines undergo electrophlic substitution reactions.

(a)

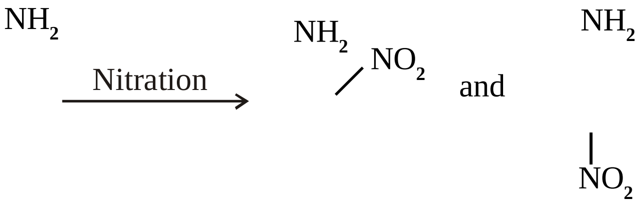


2,4,6 - trihaloaniline

(b)



(c)



(d) $C_6H_5NH_2 \xrightarrow{\text{Diazotisation}} [C_6H_5{-}N \equiv N]^+X^-$

(e) $1^0, 2^0, 3^0$ Amines $\xrightarrow{HNO_2}$ React differently

4. Distinction between 1^0, 2^0 and 3^0 amines :

(i) *By the action of nitrous acid :*

1^0 amine $\longrightarrow$ alcohol + N_2 gas. (except methylamine)

2^0 amine $\longrightarrow$ nitrosoamine $\longrightarrow$ responds to Liebermann nitroso reaction.

3^0 amine $\longrightarrow$ salt formation (dissolves in HNO_2 solution).

Aryl primary amines form arenediazonium salts which couple with alkaline solution of β- naphthol to red or orange colour azo dyes.

(ii) *Alkylation :*

1^0 amine takes up 3 moles of CH_3I for quaternisation.

$$RNH_2 + 3RI \longrightarrow R_4\overset{\oplus}{N}\,\overset{\ominus}{I}$$

2^0 amine takes up 2 moles of CH_3I for quaternisation.

$$R_2NH + 2RI \longrightarrow R_4\overset{\oplus}{N}\,\overset{\ominus}{I}$$

3^0 amine takes up 1 moles of CH_3I for quaternisation.

$$R_3N + RI \longrightarrow R_4\overset{\oplus}{N}\,\overset{\ominus}{I}$$

(iii) *Acylation:*

1^0 amine $\xrightarrow{RCOCl}$ N–alkyl acid amide

2^0 amine $\xrightarrow{RCOCl}$ N, N–dialkyl acid amide

3^0 amine $\xrightarrow{RCOCl}$ No reaction.

(iv) *Carbylamine reaction :*

1^0 amine $\xrightarrow[\text{alc.KOH}]{CHCl_3}$ Isocyanide (unpleasant odour)

2^0 amine $\longrightarrow$ No reaction

3^0 amine $\longrightarrow$ No reaction

(v) *Hinsberg's reagent ($C_6H_5SO_2Cl$)*

1^0 amine $\longrightarrow$ N–alkyl benzene sulphonamide. (soluble in alkali)

2^0 amine $\longrightarrow$ N, N–dialkyl benzene sulphonamide. (insoluble in alkali)

3^0 amine $\longrightarrow$ No reaction.

5. Separation :

A mixture of 1^0, 2^0 and 3^0 amines can be conveniently separated by Hinsberg's method.

QUESTIONS

A. Short questions (one mark each)

1. Which of the following is basic ?

(a) $CH_3\,CH_2\,OH$ (b) $CH_3\,COOH$

(c) $CH_3\,NH_2$ (d) $CH_3\,OCH_3$

2. Complete the following reaction and give the names of the products ?

$CH_3CH_2NH_2 + HNO_2 \longrightarrow$ ______ + ____ ?

What happens when an alkyl cyanide is reduced by sodium metal in ethanol ?

3. Why aniline is soluble in aqueous HCl.

4. Write the IUPAC name for $C_6H_5N\,(CH_3)_2$

5. Identify the products in the following

(i) $C_6H_5NO_2 \xrightarrow{\text{Sn/HCl}}$

(ii) $C_6H_5NO_2 \xrightarrow[H_2]{\text{Raney Ni or Pt or Pd}}$

(iii) $C_6H_5NH_2 \xrightarrow{RX} A \xrightarrow{RX} B \xrightarrow{RX}$ C (identify A, B & C)

(iv) $C_6H_5NH_2 \xrightarrow{Br_2\text{ water}}$

(v) $C_6H_5NH_2 \xrightarrow{\text{Sulphonation}}$

(vi) $C_6H_5NH_2 \xrightarrow{\text{Nitration}}$

(vii) $C_6H_5NH_2 \xrightarrow{\text{Diazotsation}}$

(viii) $C_6H_5NHCH_3 \xrightarrow{HNO_2}$

(ix) $C_6H_5N(CH_3)_2 \xrightarrow{HNO_2}$

6. Fill in the Blanks :

(i) Benzyl amine is ______ basic than aniline

(ii) Among the isomeric *o*- *m*- and *p*- anisidine ______ is the weakest base.

(iii) The reaction of aniline with $NaNO_2$ and HCl at 0^0 C to from benzenediazonium chloride is called ______

(iv) Aniline on treatment with bromine water gives ______

(v) Tetra-alkyl ammonium salts are called ______

Answer : 1. (more), 2. (*m*-Anisidine), 3. (diazotisation), 4. (2,4,6 - tribromoaniline), 5. (quaternary ammonium salts)

B. Short questions (Two marks each)

1. How will you prepare ethyl amine from methyl iodide ?
2. Give a method of preparation of primary amine.
3. Why methylamine is more basic than aniline ?
4. What is carbylamine reaction ? Give equation.
5. How will you obtain methanol from methyl amine ?
6. How can you get methylamine from ethylamine?
7. Give the IUPAC name of the following compounds:
   (a) $CH_3CH_2CH_2NH_2$
   (b) $CH_3NHCH_2CH_3$
   (c) $(CH_3)_2CHNH_2$
   (d) $(CH_3)_3\ C.NH_2$
   (e) $(CH_3)_2\ NCH_2CH_2CH_3$
   (f) $CH_3CH_2CH\ (NH_2)\ CH_2CH_3$
8. Give the structural isomers of C_3H_9N and $C_4H_{11}N$ and give their names. Classify each as primary, secondary and tertiary amines.
9. Name the functional groups in the following compounds :- $CH_3CH_2NH_2$ and CH_3CONH_2
10. What happens when nitromethane is reduced ?
11. Give a chemical test and reagents used to distinguish between ethylamine and diethylamine.
12. A compound molecular formula CH_5N on treatment with HNO_2 liberates a colourless and odourless gas. What is the name of the compound and the gas liberated ? Write the equation.
13. How you will distingush $C_2H_5NH_2$ for $C_6H_5NH_2$
14. What is carbylamine test?
15. Why aniline is less basic than ammonia?
16. Why ethyl amine is more basic than ammonia?
17. How will you carry out the conversion of benzene to *p*-nitroaniline ?
18. Direct nitration of aniline is not carried out at all. Explain why ?
19. Give an example of a Zwitterion.

[Ans. $H_3\overset{+}{N}$  SO_3^- Sulphanilic acid]

C. Short questions (Three marks each) :

1. Arrange the following compounds in decreasing order of basicity, Give reason.

   Methyl amine, dimethylamine, aniline, N-methyl aniline

2. How will you prove that amines are basic compounds ?

3. Distinguish between primary and secondary amines Give one test only with equation.

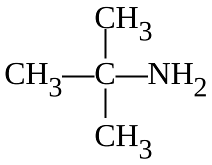
4. Complete the following equation and balance.

$$C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C \xrightarrow{NH_3} D$$

5. How will you prepare ethylamine from

   (a) Methyl cyanide (b) Propanamide

6. Name a tertiary amine in IUPAC system which is isomeric with



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-NH_2$$

and $C_2H_5 - CH_2 - CH_2 - NH_2$

7. Describe a test to distinguish between aniline, N-methylaniline and N-ethyl-N-methylaniline

8. How will you convert the following

   (i) Benzene to aniline and (ii) Aniline to N,N-dimethylaniline ?

9. Write reactions of the final alkylation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

10. Write the chemical reaction of aniline with benzoyl chloride and mention the name of the product.

11. Convert aniline to 1,3,5 – tribromobenzene.

12. Account for the following.

    (i) Aniline is less basic than methylamine

    (ii) *p*-Nitroaniline is less basic than aniline

    (iii) *p*-Toluidine is more basic than aniline.

13. Describe a method for the identification of primary, secondary and tertiary amines.

14. Accomplish the conversion of aniline to *p*-bromoaniline.

15. Write the reactions of aromatic and aliphatic primary amines with nitrous acid.

16. How you will prepare benzenediazonium chloride?

17. How you will obtain 2,4,6-trichloroaniline from aniline ?

18. How will you convert nitrobenzene to (i) acetanilide and (ii) benzamide ?

D. Long questions :

1. Give any two methods for the preparation of a primary amine. How does it react with

   (a) HNO_2 (b) CH_3CHO (c) CH_3COCl

2. Give any two methods for the preparation of a an aromatic primary amine. How does it react with

   (a) CH_3COCl (b) HNO_2

3. Write notes on :

   (a) Hofmann reaction

   (b) Hofmann bromamide reaction

   (c) Hinsberg's method for distriction of 1^0, 2^0 & 3^0 amines ?

4. What are amines ? Explain three types of aliphalic amines giving one example from each. Write with equations how amines react with

   (a) alkyl halide and (b) acid chloride

5. Give any two methods of preparation of primary amine. How does it react with $CHCl_3$ presence of alcoholic KOH?

6. What are different types of amines ? Give two methods for the preparation of primary amine. How does it react with methyl iodide? $C_2H_5NH_2$ is more basic than CH_3NH_2; Explain.

7. What are different types of amines ? How primary amines are prepared from

   (a) nitroparaffins (b) cyanides (c) alkyl halides ?

   What happens when methylamine reacts with methyl iodide ?

8. What are different types of aliphatic amines? How aliphatic primary amines are prepared from (i) acid amides, (ii) alkyl cyanides. What happens when methylamine reacts with nitrous acid?

9. Describe the methods of preparation of aromatic monoamines, taking example of aniline. Discuss the relative basic character of aniline and methyl amine Explain the weak basic character of aniline.

10. Give the general chemical reactions of aryl amines.

11. How is aniline prepared on a laboratory scale ? Summarise its chemical reactions.

12. How is basicity of aniline affected by substituents on the benzene ring ? How do you explain the *ortho* and *para* directive influence of $-NH_2$ group ?

13. Explain the action of nitrous acid on primary, secondary and tertiary amines. How aniline differs from methyl amine in its reaction with nitrous acid ?

14. How does aniline react with the following reagents ?

    (i) Acetic anhydride, (ii) benzoylchloride (iii) Sodium nitrite / HCl.

15. How will you distinguish between aniline and benzylamine ?

    How N, N-dimethylaniline is prepared ? How will you distinguish it from aniline ?

E. Multiple Choice Questions :

1. Most basic among the following is $C_6H_5NH_2$, $(C_2H_5)_2$ NH $(C_2H_5)_3$ N, $C_2H_5NH_2$

I II III IV

(a) I (b) II (c) III (d) IV

2. Which of the following compounds gives dye test ?

(a) Aniline (b) Methylamine (c) Diphenylamine (d) Ethylamine

3. In the following reaction, X is

$$X \xrightarrow{\text{Bromination}} Y \xrightarrow{NaNO_2/HCl} Z \xrightarrow[C_2H_5OH]{\text{Boiling}} \text{Tribromobenzene}$$

(a) Benzoic acid (b) Salicylic acid (c) Phenol (d) Aniline

4. The correct increasing order of basic strength for aniline (I), *p*-nitroaniline (II), and *p*-toluidine (III) is.....

(a) II < III < I (b) III < I < II (c) III < II < I (d) II < I < III

5. In the nitration of benzene using a mixture of conc. H_2SO_4 and conc. HNO_3, the species which initiate the reaction is.....

(a) NO_2 (b) NO^+ (c) NO_2^+ (d) NO_2^-

6. Reduction of nitrobenzene by which of following reagent gives aniline ?

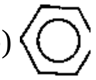
(a) Sn/HCl (b) $LiAlH_4$ (c) Zn/NH_4OH (d) $SnCl_2$

7. $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5X$

In the above reaction 'X' is

(a) Cl (b) NH_2 (c) $NH_3^+Cl^-$ (d) $\overset{\oplus}{N_2}-Cl^-$

8. Which of the following is the weakest Bronsted base ?

(a) NH_2 (b)  N– H (c) CH_3 — NH_2 (d) $CH_2 - NH_2$

9. Which of the following will react with CH_3COCl ?

(a) Trimethylamine (c) Dimethylethylamine

(b) Dimethylamine (d) Trimethylamine

10. Acetamide is treated separately with the following reagents. Which of these would give methylamine?

(a) PCl_5 (c) NaOH + Br_2

(b) Sodalime (d) Hot Conc. H_2SO_4

11. Which of the following shows optical activity?

(a) Butanamine - 1 (c) Isopropylamine

(b) Butanamine - 2 (d) Ethylmethylamine

12. Number of saturated isomeric primary amines possible for the molecular fomula C_3H_5N is

(a) Zero (c) 2

(b) 3 (d) 4

13. Primary amines on reaction with alcoholic KOH yields :

(a) Isocyanide (c) Cyanide

(b) Aldehyde (d) Alcohol

14. The compound on reaction with aqueous HNO_2 at low temperature produces oily nitrosoamine is

(a) Methylamine (c) Diethylamine

(b) Ethylamine (d) Triethylamine

Answer : 1. (b), 2. (a), 3. (d), 4. (d), 5. (c), 6. (a), 7. (c), 8. (a), 9. (b), 10. (c), 11. (b), 12. (a), 13. (a), 14. (c).

* * *

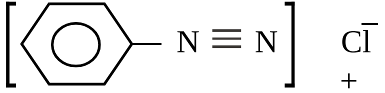
CHAPTER - 21

ARYL DIAZONIUM SALTS

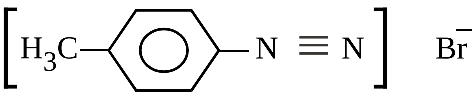
When primary arylamines or their salts react with nitrous acid in ice-cold solution, an important class of compounds called the **diazonium salts** are formed. They are so called, because they contain diazo group $-N\equiv N$ (Di means two, azo from French word **azote**, meaning nitrogen). These salts have the general formula $Ar\overset{+}{N}_2 X^-$ where Ar is an aryl group (e.g. benzene ring) and X^- is any anion like Cl^-, Br^-, HSO_4^- etc. Structurally, they may be represented as

$$[Ar-\overset{\oplus}{N}\equiv N:]\overset{\ominus}{X}$$

and are named by adding diazonium to the parent aromatic compound to which they are related, followed by the name of the anion. For example –



is benzenediazonium chloride,



is p-toluenediazonium bromide etc.,

21.1 PREPARATION OF BENZENEDIAZONIUM CHLORIDE :

Aniline is dissolved in dil. hydrochloric acid and the solution is cooled to 0^0-5^0C. Aqueous solution of sodium nitrite is added to the cooled solution in small portions with stirring. The temperature is maintained at 0^0-5^0C. Addition of sodium nitrite solution is discontinued when a drop of the solution turns starch-iodide paper blue indicating the presence of slight excess of nitrous acid. Benzenediazonium chloride is formed in the solution.

$$NaNO_2 + HCl \xrightarrow{0^0-5^0C} NaCl + HNO_2$$

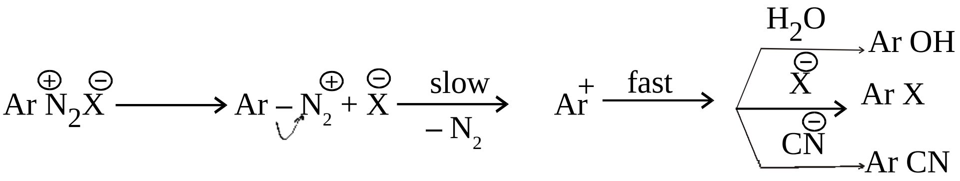
$$\underset{\text{(Aniline)}}{C_6H_5-NH_2} + HNO_2 + HCl \xrightarrow{0^0-5^0C} \underset{\text{(Benzenediazonium chloride)}}{C_6H_5\overset{+}{N}_2\overset{-}{Cl}} + 2H_2O$$

This reaction between a primary arylamine and nitrous acid in presence of a mineral acid to produce aryldiazonium salt is called **diazotisation.** Nitrous acid is unstable and it is always generated **in situ** from $NaNO_2$ and mineral acid like HCl or H_2SO_4. The reaction is carried out at a low temperature (0^0-5^0C), because both nitrous acid and diazonium salt would decompose at higher temperature.

21.2 PROPERTIES :

Physical : Dry aryldiazonium salts are unstable crystalline solids and readily explode when in dry state liberating nitrogen gas. Therefore, they are not isolated and are used in the solution in which they are prepared.

Chemical : Aryldiazonium salts are very reactive and undergo a large numbers of substitution reactions in which the diazo group is replaced by different univalent atoms or groups. These are all unimolecular nucleophilic substitution reactions. (SAr_N1)



i. Replacement by hydrogen : Synthesis of benzene :

When benzene diazonium salt solution is treated with hypophosphorus acid, the diazo group is replaced by hydrogen and benzene is formed.

$$C_6H_5\overset{+}{N_2}\,\overset{-}{Cl} + H_3PO_2 + H_2O \longrightarrow C_6H_6 + H_3PO_3 + HCl + N_2$$

(Benzenediazonium chloride) (Benzene)

The reaction is carred out simply by dissolving the amine in hypophosphorus acid and cold $NaNO_2$ solution is added. The reaction takes place immediately. The net result is removal of NH_2 group from the aromatic ring and hence the process is known as **de-amination**. Nitro group can also be removed after converting it to $– NH_2$ group.

ii. Replacement by halogens : Synthesis of chlorobenzene, bromobenzene and iodobenzene

Sandmeyer's Reaction : When benzenediazonium chloride solution is added to a solution of cuprous chloride dissolved in HCl or cuprous bromide dissolved in HBr, the diazo group is replaced by chlorine or bromine respectively resulting in the formation of chlorobenzene or bromobenzene.

$$C_6H_5\overset{+}{N_2}\,\overset{-}{Cl} \xrightarrow{CuCl,\ HCl} C_6H_5Cl + N_2$$

(Chlorobenzene)

$$C_6H_5\overset{+}{N_2}\,\overset{-}{Cl} \xrightarrow{CuBr,\ HBr} C_6H_5Br + N_2$$

(Bromobenzene)

The reaction is known as **Sandmeyer's reaction**. Gatterman used a modified method in which cuprous halides were replaced by copper powder to prepare chlorobenzene and bromobenzene. The reaction is known as **Gattermann reaction.**

$$C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow[HCl]{Cu\text{-powder}} C_6H_5\text{–}Cl + N_2$$

(Chlorobenzene)

$$C_6H_5\overset{+}{N_2}\overset{-}{Br} \xrightarrow[HBr]{Cu\text{-powder}} C_6H_5\text{–}Br + N_2$$

(Bromobenzene)

The best method for introducing iodine atom in benzene nucleus is to add a saturated solution of potassium iodide to benzene diazonium chloride solution. It is not necessary to add copper salt.

$$C_6H_5\overset{+}{N_2}\overset{-}{Cl} + KI \longrightarrow C_6H_5\text{–}I + N_2 + KCl$$

(Iodobenzene)

iii. Replacement by cyano group:Synthesis of cyanobenzene or benzonitrile or phenyl cyanide

When diozonium salt solution is treated with cuprous cyanide dissolved in aqueous potassium cyanide, the diazo group is replaced by –CN group and aryl cyanide is formed. This is also called **Sandmeyer's reaction.** Benzene diazonium chloride with cuprous cyanide in aqueous KCN yields phenyl cyanide or cyanobenzene.

$$C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{CuCN,\ KCN} C_6H_5 - CN + N_2$$

(Phenyl cyanide or cyanobenzene)

This is a method for introducing – CN group and hence – CH_2 – NH_2 and – COOH groups in the benzene nucleus (how?)

$$\begin{tikzcd}
\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} & \underset{\text{Phenyl cyanide}}{C_6H_5\text{–}CN} \arrow[l, "H_2 / Ni"'] \arrow[r, "H_2O/ H^+"] \arrow[d, "SnCl_2 / \text{Conc. } HCl"] & \underset{\text{Benzoic acid}}{C_6H_5\text{–}COOH} \\
 & \underset{\text{(Benzaldehyde)}}{C_6H_5\text{–}CHO} &
\end{tikzcd}$$

iv. Replacement by hydroxyl group : Synthesis of phenol

When benzenediazonium salt solution is boiled with water containing dil H_2SO_4, it undergoes hydrolysis and diazo group is replaced by – OH group. Phenol is formed.

$$C_6H_5\overset{+}{N_2}Cl + H_2O \xrightarrow[\text{boil}]{[H^+]} C_6H_5 - OH + N_2 + HCl$$

(Phenol)

v. Replacement by fluorine : Synthesis of fluorobenzene

When an aqueous solution of a diazonium salt is treated with fluoroboric acid (HBF_4), diazonium fluoroborate gets precipitated. It is filtered and dried. Unlike other diazonium salts, diazonium fluoroborates are fairly stable. When dry diazonium fluoroborate is heated, it composes to aryl fluoride and boron trifluoride.

$$ArN_2^+Cl^- + HBF_4 \longrightarrow ArN_2^+BF_4^- + HCl$$

Diazonium fluoroborate

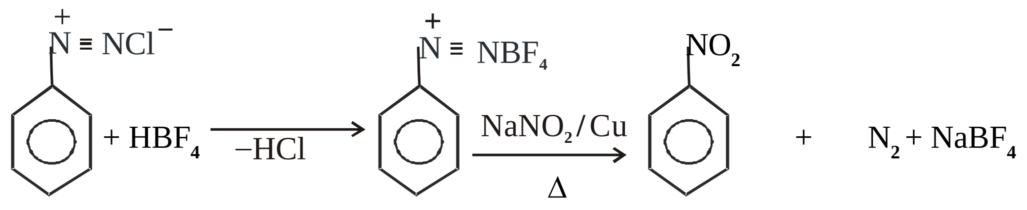
$$Ar-\overset{+}{N}\equiv NBF_4 \xrightarrow{\Delta} Ar-F + N_2 + BF_3$$

Aryl fluoride

This reaction is known as **Balz - Schiemann reaction.**

vi. Replacement by nitro ($-NO_2$) group : Synthesis of nitrobenzene.

Nitro compounds are generally prepared by treating an arenediazonium fluoroborate with an aqueous solution of sodium nitrite in presence of copper powder.



Benzenediazonium chloride

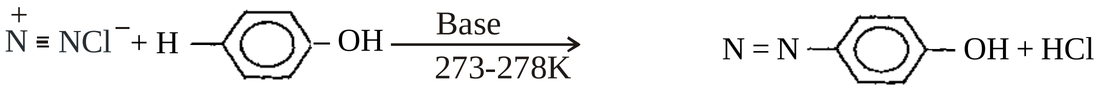
Benzenediazonium fluoroborate

Nitrobenzene

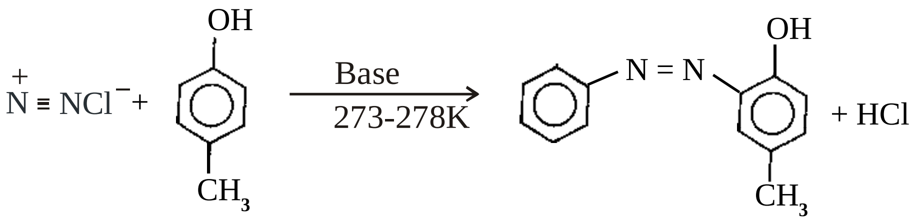
vii. Coupling reactions :

Arene diazonium salts react with electron rich (highly reactive) aromatic compounds such as phenols and amines to form brightly coloured azo compounds, Ar – N = N – Ar. This reaction is known as **Coupling reaction**. Azo compounds are used as dyes.

Coupling takes place almost exclusively at the **para** position if it is unoccupied. If it is not, then coupling takes place at **ortho** position. Coupling with phenols occurs in basic medium (pH 9-10) whereas with amines it occurs in faintly acidic medium (pH 4 – 5) at 273 – 278 K.

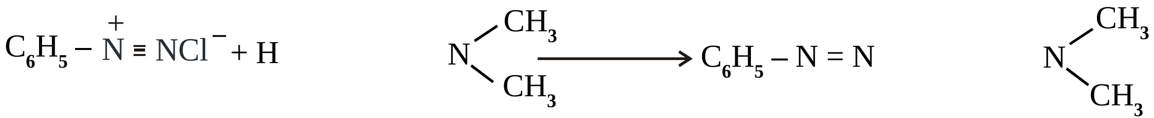


Benzenediazonium chloride Phenol *p*-Hydroxyazobenzene



p-cresol 2-phenylazo-4-methylphenol

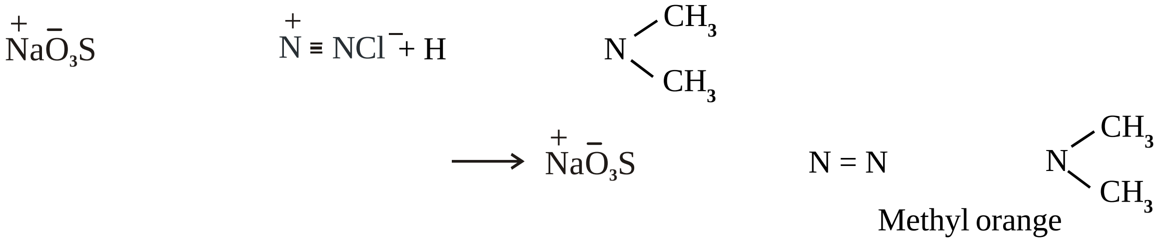
(**Para** position occupied)



(Butter yellow) + HCl

p-N,N-Dimethylazobenzene

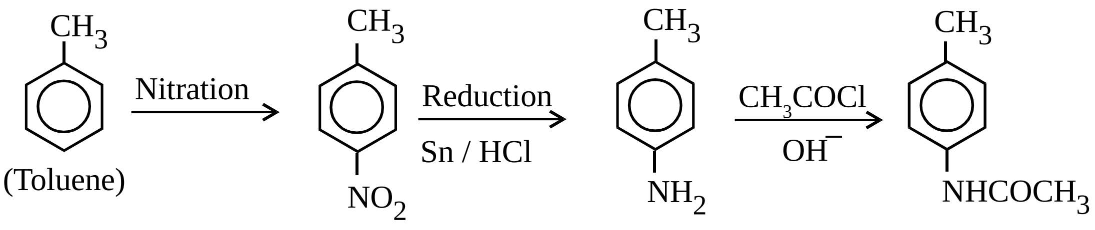
Azo dyes almost always contain one or more than one $SO_3^-Na^+$ groups so that they are soluble in water.



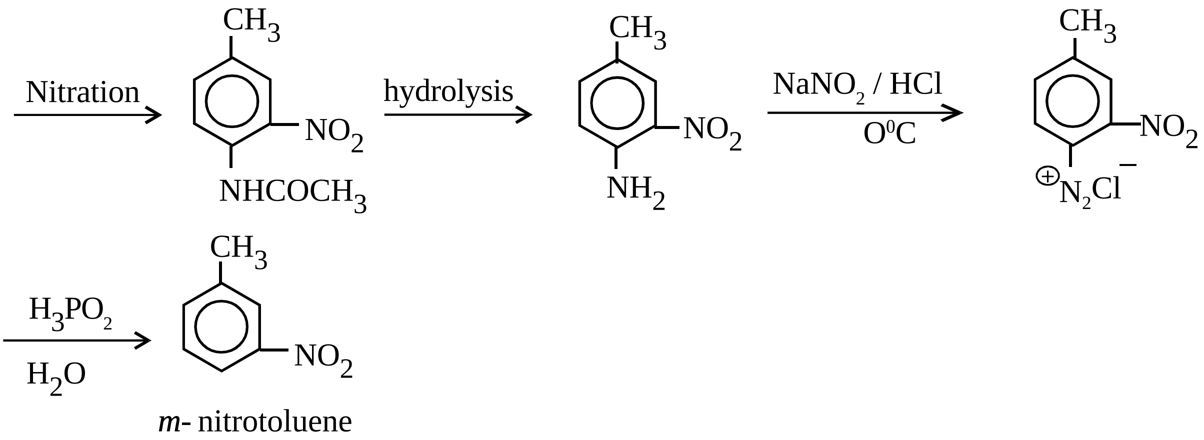
Methyl orange

21.3 SOME IMPORTANT CONVERSIONS :

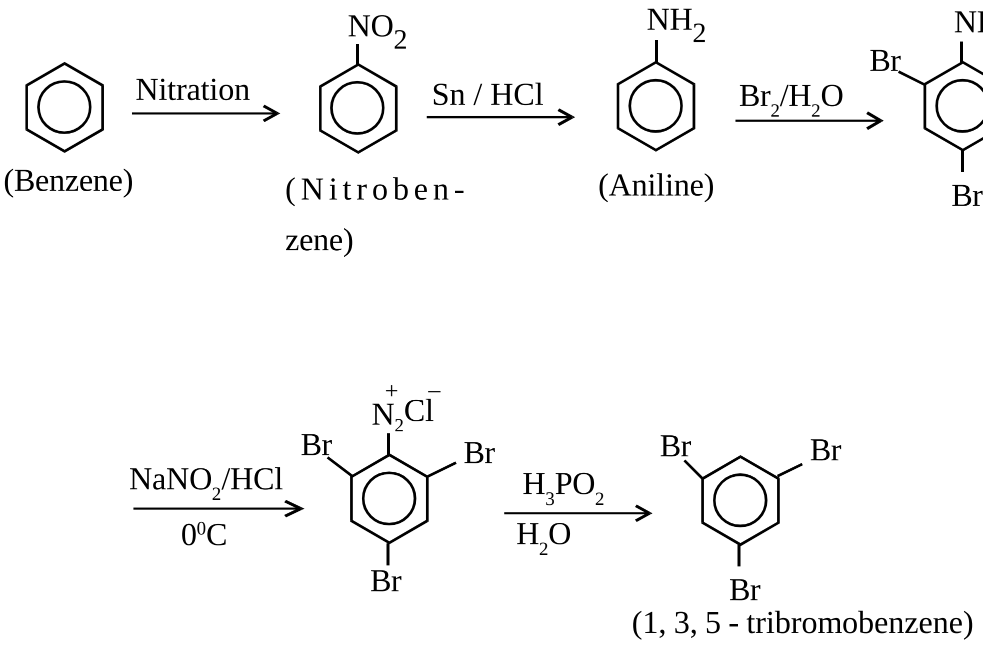
1. Toluene to m- nitrotoluene



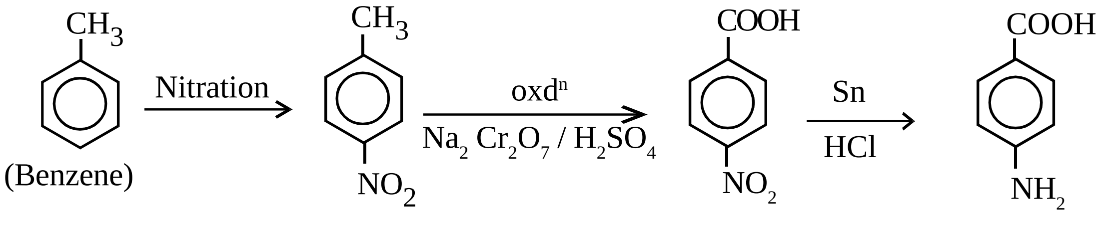
(Toluene)

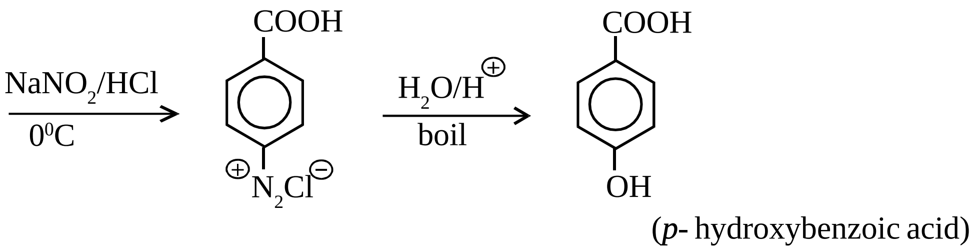


2. Benzene to 1, 3, 5 - tribromobenzene

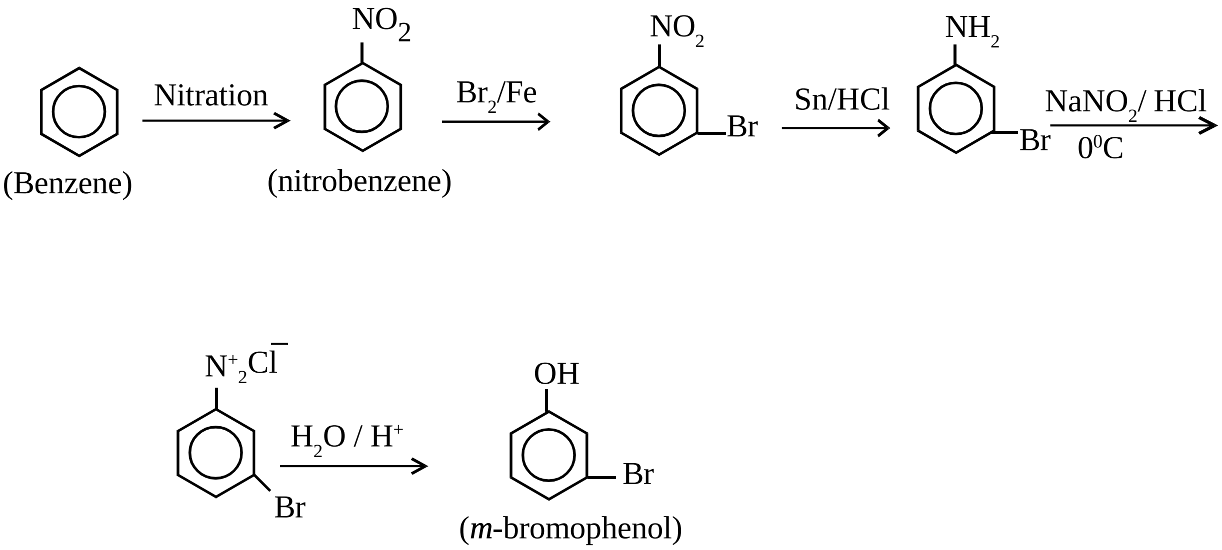


3. Toluene to p-hydroxybenzoic acid

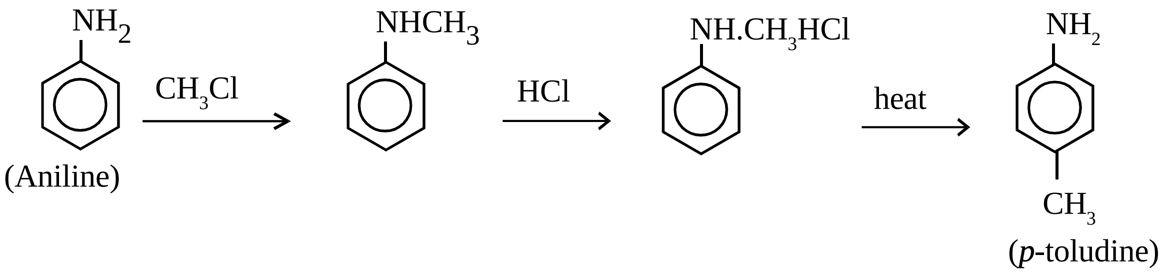




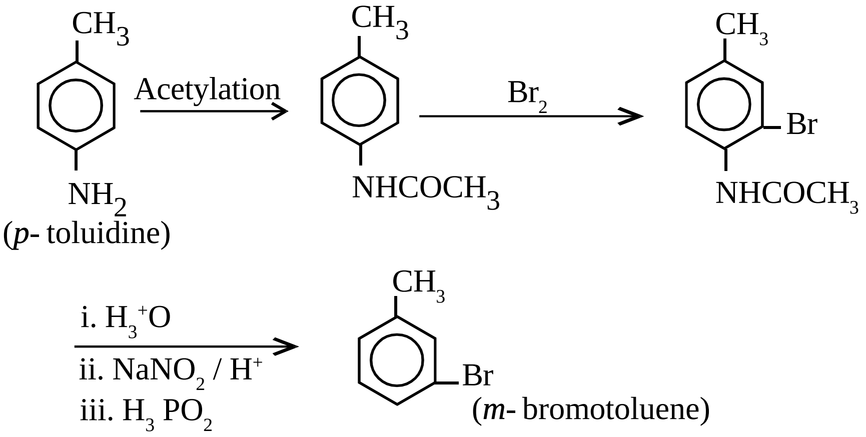
4. Benzene to m-bromophenol



5. Aniline to p-toluidine



6. *p* - Toluidine to m - bromotoluene

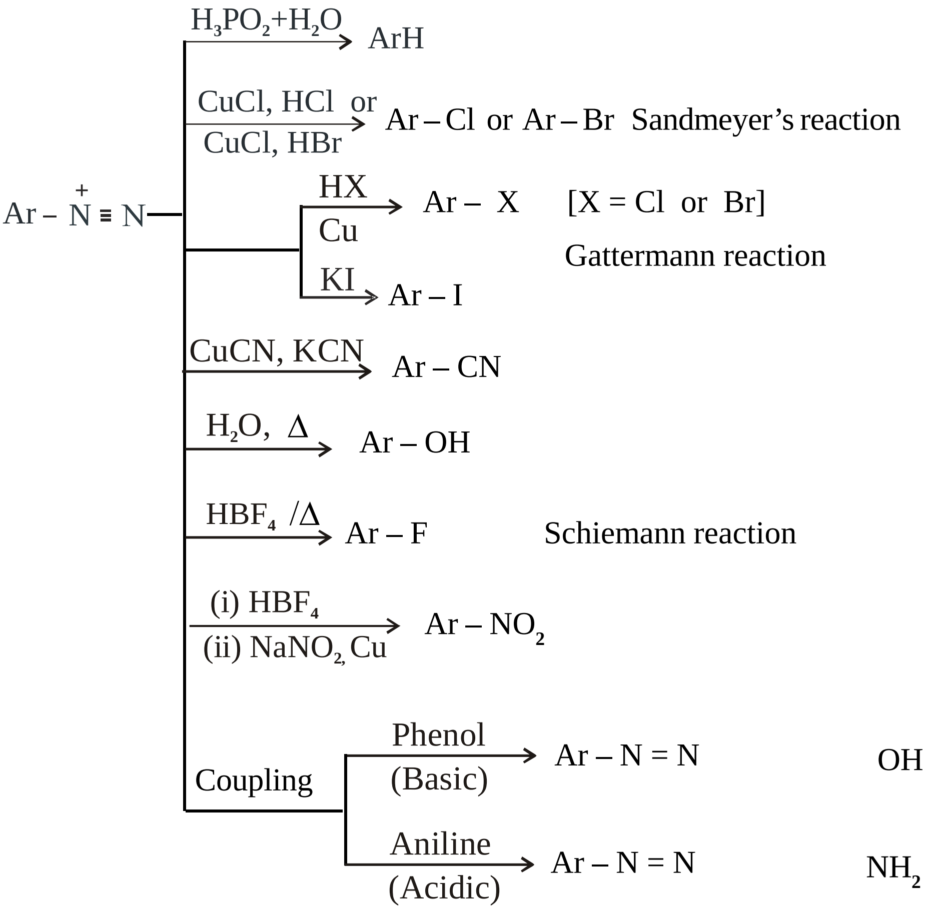


CHAPTER (21) AT A GLANCE

Methods of Preparation

$$C_6H_5\,NH_2 \xrightarrow[273\text{-}278K]{NaNO_2/HCl} C_6H_5-\overset{+}{N}\equiv NCl^-$$

Synthetic applications (Properties)



QUESTIONS

A. Short Answer questions : (1 mark)

1. Write the structure of benzenediazonium chloride.
2. Why benzenediazonium salts are soluble in water ?
3. What should be the nature of medium (neutral/acidic/basic) for diazotisation of arylamines.
4. Give only the equations for the synthesis of the following from benzenediazonium chloride.

   (i) Benzene (ii) Phenol (iii) Chlorobenzene (iv) Fluorobenzene (v) Phenyl cyanide

   (vi) *p*-Hydroxyazobenzene

B. Short Answer Questions (2 marks)

1. Suggest reasons why excess mineral acid is used in diazo reaction.
2. Complete the following equations

   (i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

   (ii) $C_6H_5N_2Cl \xrightarrow[\text{(ii) NaNO}_2\text{/Cu, }\Delta]{\text{(i) HBF}_4}$

   (iii) $C_6H_5N_2Cl + H_2O \xrightarrow{\Delta}$

   (iv) $C_6H_5N_2Cl \xrightarrow[\text{HCl}]{\text{CuCl}}$

   (v) $C_6H_5OH \xrightarrow[OH^-]{Ar\overset{+}{N_2}Cl^-}$

   (vi) $C_6H_5N_2Cl + ArNH_2 \xrightarrow[\text{pH 4-5}]{\text{ice cold}}$

3. Give the chemical equation for the following.

   (i) Diazotisation reaction

   (ii) Coupling reaction

   (iii) Sandmeyer reaction

4. How will you convert ?

   (a) Aniline to nitrobenzene, (b) Aniline to iodobenzene

C. Short Answer Questions (3 marks)

1. Why the diazonium salts of aromatic amines are more stable than those of aliphatic amines ?
2. How you will obtain *p*-hydroxyazobenzene from aniline ?
3. What is coupling reaction ? give two examples.
4. How will you carry out the conversion of aniline to *m*-bromonitrobenzene ?
5. Give the structure of A, B and C in the following reactions.

(i) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\text{-}278K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

D. Long Answer Questions

1. Discuss in detail the preparation of benzenediazonium chloride from aniline. Why it is not separated in solid state and used as soon as produced in solution ? How can you convert benzenediazonium chloride to fluoro and iodobenzene.
2. Describe the synthetic applications of aryl diazonium salts.
3. How will you obtain

   (a) Iodobenzine from nitrobenzine

   (b) m-Dichlorobenzene from benzene
4. How will you synthesise the following ?

   (a) Azobenzene from benzene

   (b) Benzene from azobenzene

   (c) Azobenzene from nitrobenzene

   (d) Nitrobenzene from azobenzene
5. Write notes on :

   (a) Sandmeyer reaction

   (b) Coupling reaction
6. How can benzene diazonium chloride be prepared from nitrobenzene ? Starting from a diazonium salt how can you prepare (a) iodobenzene (b) benzoic acid ?

E. Multiple Choice Questions

1. The diazonium salts are the reaction products of the reaction of nitrous acid with

   (a) primary aliphatic amines
   (b) primary aromatic amines
   (c) secondary aliphatic amines
   (d) secondary aromatic amines
2. Preparation of a diazonium salt from a primary aromatic amine is known as :

   (a) Coupling reaction
   (b) Sandmeyer reaction
   (c) Diazotisation
   (d) Corey-House synthesis
3. Which of the following reagents is used to prepare benzenediazonium chloride from aniline ?

   (a) $NaN0_2$ + HC1
   (b) $LiAlH_4$
   (c) NH_2NH_2 + KOH
   (d) NaOH
4. Which of the following are optimum temperature conditions for making benzonediazonium chloride from aniline ?

   (a) 0°C to 10°C
   (b) 20°C to 25°C
   (c) 30°C to 40°C
   (d) 45°C to 50°C

5. Benzenediazonium chloride reacts with warm water to give

(a) Aniline	(b) Phenol
(c) Benzene	(d) Chlorobenzene

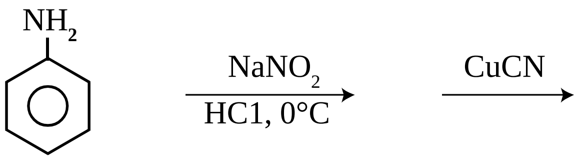
6. Bromobenzenes can be prepared by treating aniline with

(a) Conc. HBr	(b) $Br_2/FeBr_3$
(c) CuBr	(d) Nitrous acid then CuBr

7. Chlorobenzene can be prepared by treatment of aniline with
   (a) Cuprous chloride
   (b) Chlorine in the presence of UV light
   (c) Nitrous acid followed by treatment with CuCl
   (d) Chlorine in the presence of $FeCl_3$.
8. lodobenzene can be prepared by
   (a) treating chlorobenzene with I_2 using $FeCl_3$ catalyst.
   (b) treating phenol with I_2 in NaOH solution.
   (c) treating benzenediazonium chloride with KI
   (d) treating benzene with CH_3I using $A1C1_3$ catalyst.
9. Benzene diazonium chloride reacts with Kl to form :

(a) Benzene diazonium iodide	(b) *m*-Diiodobenzene
(c) lodobenzene	(d) o-, plus *p*-Diiodobenzene

10. What is the major product of the following reaction ?



(a) Benzonitrile	(b) Benzoic acid
(c) Nitrobenzene	(d) Benzene diazonium chloride

11. Benzene diazonium chloride reacts with hypophosphorus acid to form :

(a) Phenol	(b) Benzaldehyde
(c) Aniline	(d) Benzene

12. Benzene diazonium chloride reacts with phenol to form :

(a) *p*-chlorophenol	(b) Chlorobenzene
(c) *p*-Hydroxyazobenzene	(d) DDT

ANSWERS

1. (b) 2. (c) 3. (a) 4. (a) 5. (b) 6. (d) 7. (c) 8. (c) 9. (c) 10. (a) 11. (d) 12. (c)

❑❑❑

UNIT - XIV

CHAPTER - 22

BIOMOLECULES

22.1 INTRODUCTION :

The branch of Chemistry dealing with the structure, composition and the chemical changes which take place in the living system is called **biochemistry**. Living cells, the fundamental unit of life are composed of some complex biologically important organic molecules otherwise termed as **biomolecules**. Important biomolecules constituting the ultimate structure of living cells are carbohydrates, fats, proteins, lipids, nucleic acids etc. In this chapter elementary ideas on such biomolecules are described in brief which are related to the living organism in the following sequence.

Living organisms → Organs → Tissues → Cells → Organelles → Biomolecules.

22.2 CARBOHYDRATES :

Introduction : The glucose, cellulose, starch and glycogen, all belong to the class of organic compounds known as carbohydrates. Carbohydrates are the main source of energy for our body in the form of food. The carbohydrates provide us with three necessities of life, that is food, clothing and shelter.

The term "carbohydrate" was originally given to the compounds with general formula, $C_x(H_2O)_y$ where x and y may be same or different and they were considered to be hydrates of carbon. However, this definition could not hold ground for long due to following reasons:

(i) Compounds like formaldehyde (HCHO), acetic acid (CH_3COOH) etc. have the general formula $C_x(H_2O)_y$, but they do not show the characteristic properties of carbohydrates.

(ii) Some carbohydrates, such as deoxyribose ($C_5H_{10}O_4$) do not have the required ratio of hydrogen to oxygen.

To accommodate wide variety of compounds, the carbohydrates are now-a-days broadly defined as polyhydroxy aldehydes or ketones and their derivatives or as substances that yield one of these compounds on hydrolysis.

A. CLASSIFICATION OF CARBOHYDRATES :

I. CLASSIFICATION ON THE BASIS OF HYDROLYSIS PRODUCTS :

Carbohydrates are classified into following classes depending upon their behaviour towards hydrolysis.

(i) Monosaccharides

(ii) Oligosaccharides

and (iii) Polysaccharides.

(i) Monosaccharides : (Greek: *Mono* = one; *Sakcharon*= sugar):

Monosaccharides are simple sugars and can not be hydrolysed to still simpler compounds. Monosaccharides contain 3 to 7 carbon atoms each. Monosaccharides are generally sweet to taste, soluble in water and crystalline.

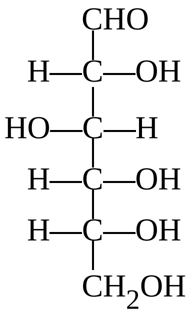
Monosaccharides may be further subdivided into trioses, tetroses, pentoses, hexoses, heptoses etc. depending upon the number of carbon atoms they possess.

Monosaccharides which contain an aldehyde (–CHO) group are called *aldoses*. Since the aldehyde group is monovalent, it is present at one end of the carbon chain. Similarly, monosaccharides which contain a keto group are called *ketoses*. As keto group is divalent, it is present anywhere along the chain. In all, the naturally occurring ketoses, keto group is present at the carbon atom next to the terminal carbon, that is, at C–2.

Some important examples of monosaccharides are :

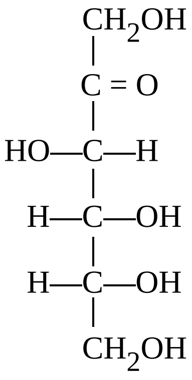
Name	**Formula**	**Aldoses (Aldo Sugars)**	**Ketoses (Keto Sugars)**
Trioses	$C_3H_6O_3$	Glycerose	Dihydroxyacetone
Tetroses	$C_4H_8O_4$	Erythrose	Erythrulose
Pentoses	$C_5H_{10}O_5$	Ribose	Ribulose
Hexoses	$C_6H_{12}O_6$	Glucose	Fructose
Heptoses	$C_7H_{14}O_7$	Glucoheptose	Sodoheptulose

Both these characters, that is, number of carbon atom and the nature of functional group may also be combined into one. For example, glucose is an aldohexose and fructose is a ketohexose



$$\begin{array}{c} \mathrm{CHO} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Glucose (Aldohexose)



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{C=O} \\ | \\ \mathrm{HO{-}C{-}H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Fructose (Ketohexose)

(ii) Oligosaccharides : (Greek : *Oligos* = a few):

There are carbohydrates which on hydrolysis give two to ten molecules of the same or different monosaccharides on hydrolysis.

Depending upon the number of monosaccharide molecules obtained on hydrolysis, they are further classified as di, tri, tetrasaccharides etc.

(a) *Disaccharides* : These carbohydrates on hydrolysis give two molecules of monosaccharides. The general formula of disaccharides is $C_n(H_2O)_{n-1}$

The exmaples of disaccharides are sucrose, lactose, maltose, cellobiose etc.

(b) *Trisaccharides* : These carbohydrates on hydrolysis give three molecules of monosaccharides.

For example, raffinose, $C_{18}H_{32}O_{16}$.

(c) *Tetrasaccharides* : These carbohydrates on hydrolysis give four molecules of monosaccharides. Example : Stachyose, $C_{24}H_{42}O_{21}$.

(iii) Polysaccharides : (*Poly* = many) :

These are carbohydrates which on hydrolysis give a large number of monosaccharide molecules. The most commonly occurring polysaccharides are starch, glycogen, cellulose and gums. Their general formula is $(C_6H_{10}O_5)_n$ where n = 100 to 3000.

II. Sugars and Non-sugars :

Carbohydrates can be classified on the basis of their taste as follows :

(a) Sugars :

All the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet in taste and hence are termed as sugars.

(b) Non-sugars :

Polysaccharides are amorphous in nature, insoluble in water and tasteless and hence are called non-sugars.

III. Reducing and Non-reducing sugars :

On the basis of the reducing character of carbohydrates, they can be classified into two types.

(a) Reducing sugars :

All those carbohydrates which contain free aldehydic or ketonic group, thus reducing Tollen's reagent and Fehling's solution are called **reducing** carbohydrates or sugars. Examples are glucose, fructose, maltose, lactose.

(b) Non-reducing sugars :

Those carbohydrates which are incapable of reducing Tollens' reagent or Fehling's solution are called non-reducing sugars. Examples : sucrose.

B. FUNCTIONS OF CARBOHYDRATES :

Carbohydrates have a number of diverse functions in the living organisms. These are,

(i) *Structural material* : The chief structural material in the cell walls of all plants are cellulose, which is a polysaccharide. We make furnitures from cellulose in the form wood and clothe ourselves with cellulose in the form of cotton fibre. Cellulose is the raw material for industries like textiles, paper etc.

(ii) *Reserve food materials*: Some polysaccharides act as reserve food materials for plants and animals. For example, starch is a major food reserve in plants. In seeds, starch acts as a reserve food material for the tiny plant till it is capable of preparing its own food by the process of photosynthesis. Similarly, in animals glycogen acts as a reserve food material, which is present in liver cells. Glycogen is a source of glucose for the blood.

(iii) *As a biofuel* : Carbohydrates, such as glucose, fructose, starch, glycogen etc. provide energy for the functioning of living organisms and act as a biofuel. In the living systems, polysaccharides such as starch and glycogen present are hydrolysed by enzymes to glucose. Glucose is then transported to the various cells, where it is oxidised to CO_2 and H_2O by a series of enzyme catalysed reactions. The energy thus released during oxidation, provides energy for the functioning of cells.

$$\underset{\text{(glucose)}}{C_6H_{12}O_6} + O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy.}$$

(iv) In nucleic acids : Monosaccharides like ribose and 2-deoxyribose are the essential components of RNA and DNA respectively. Nucleic acids play an essential role in the biosynthesis of proteins.

C. MONOSACCHARIDES

1. GLUCOSE

Glucose, the most common monosaccharide is also known as Dextrose because it occurs in nature as the optically active dextrorotatory isomer. Glucose is found in most of the sweet fruits especially grapes and honey.

(a) Preparation :

(i) From starch :

Glucose is produced commonly by the hydrolysis of starch with dilute hydrochloric acid at high temperature under pressure. atm

$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow[393K,\ 2\ -\ 3\ atm]{HCl} n\,C_6H_{12}O_6$$

Starch Glucose

(ii) From sucrose :

Sucrose i.e. cane sugar on acid hydrolysis produces an equal amounts of glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\Delta]{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose Glucose Fructose

(a) Structure of Glucose :

The structure of glucose can be elucidated basing on its following characteristics

I. Open Chain Structure of Glucose :

(i) **Molecular formula :** Elemental analysis and molecular weight determination have established the molecular formula of glucose to be $C_6H_{12}O_6$

(ii) **Presence of 6-carbon unbranched chain :** The complete reduction of glucose with concentrated hydrogen iodide and red phosphorus gives n-hexane proving that glucose molecule is made of an unbranched i.e. a straight chain of six carbon atoms.

$$C_6H_{12}O_6 \xrightarrow[\Delta]{Conc.\ HI/Red\ P} CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

Gluclose n-Hexane

(iii) Presence of 5-OH groups : Glucose forms a pentacetyl derivative when refluxed with acetic anhydride showing the presence of five hydroxyl groups. Since it is a stable compound, no two - OH groups are attached to the same carbon and hence the five -OH groups are on different carbons.

$$C_6H_{12}O_6 + 5\,(CH_3CO)_2O \xrightarrow{Reflux} C_6H_7O\,(OCOCH_3)_5 + 5\,CH_3COOH$$

Glucose Glucose penta-acetate

(iv) Presence of $>C = O$ Group : Presence of a carbonyl group in glucose is proved by the following observations.

(1) With HCN, it forms an addition product, called glucose cyanohydrin.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + HCN \longrightarrow \underset{\text{Glucose cyanohydrin}}{C_5H_{11}O_5CH\ (OH)\ CN}$$

(2) It forms an oxime with hydroxylamine.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + NH_2OH \xrightarrow{H^+} \underset{\text{Glucoxime}}{C_5H_{11}O_5CH = NOH} + H_2O$$

(v) Presence of – CHO (aldehyde) group : On mild oxidation with bromine water, glucose is converted to gluconic acid which when reduced with excess of HI yields n-hexanoic acid.

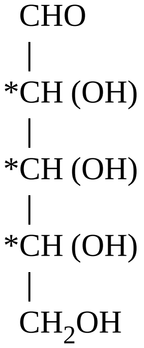
$$\underset{\text{Glucose}}{C_5H_{11}O_5 \cdot CHO} \xrightarrow[Br_{2(aq)}]{(O)} C_5H_{11}O_5 \cdot COOH \xrightarrow{HI} \underset{\text{n-Hexanoic acid}}{CH_3\ (CH_2)_4\ COOH}$$

This shows that glucose contains a straight chain of six carbon atoms with – CHO at one end, which has been oxidised to – COOH

(vi) Presence of a primary alcoholic group (–CH_2OH) : On heating with nitric acid, glucose forms dicarboxylic acid (glucaric acid) with the same number of carbon atoms confirming the presence of a terminal primary alcohol group.

$$\underset{\text{Glucose}}{OHC - (CHOH)_4 - CH_2OH} \xrightarrow{HNO_3} \underset{\text{Glucaric acid}}{HOOC - (CHOH)_4 - COOH}$$

(vii) Open chain structure of glucose : Basing on the above observations the open chain structure of glucose can be represented as :

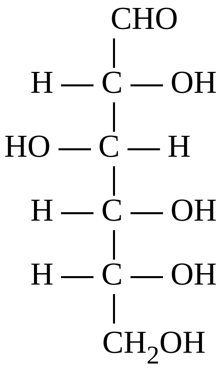


$$\begin{array}{l} CHO \\ | \\ {}^*CH\ (OH) \\ | \\ {}^*CH\ (OH) \\ | \\ {}^*CH\ (OH) \\ | \\ CH_2OH \end{array}$$

The above structure having four chiral carbon atoms correspond to 16 (= 2^4) optically active isomers, out of which one isomer is Glucose.

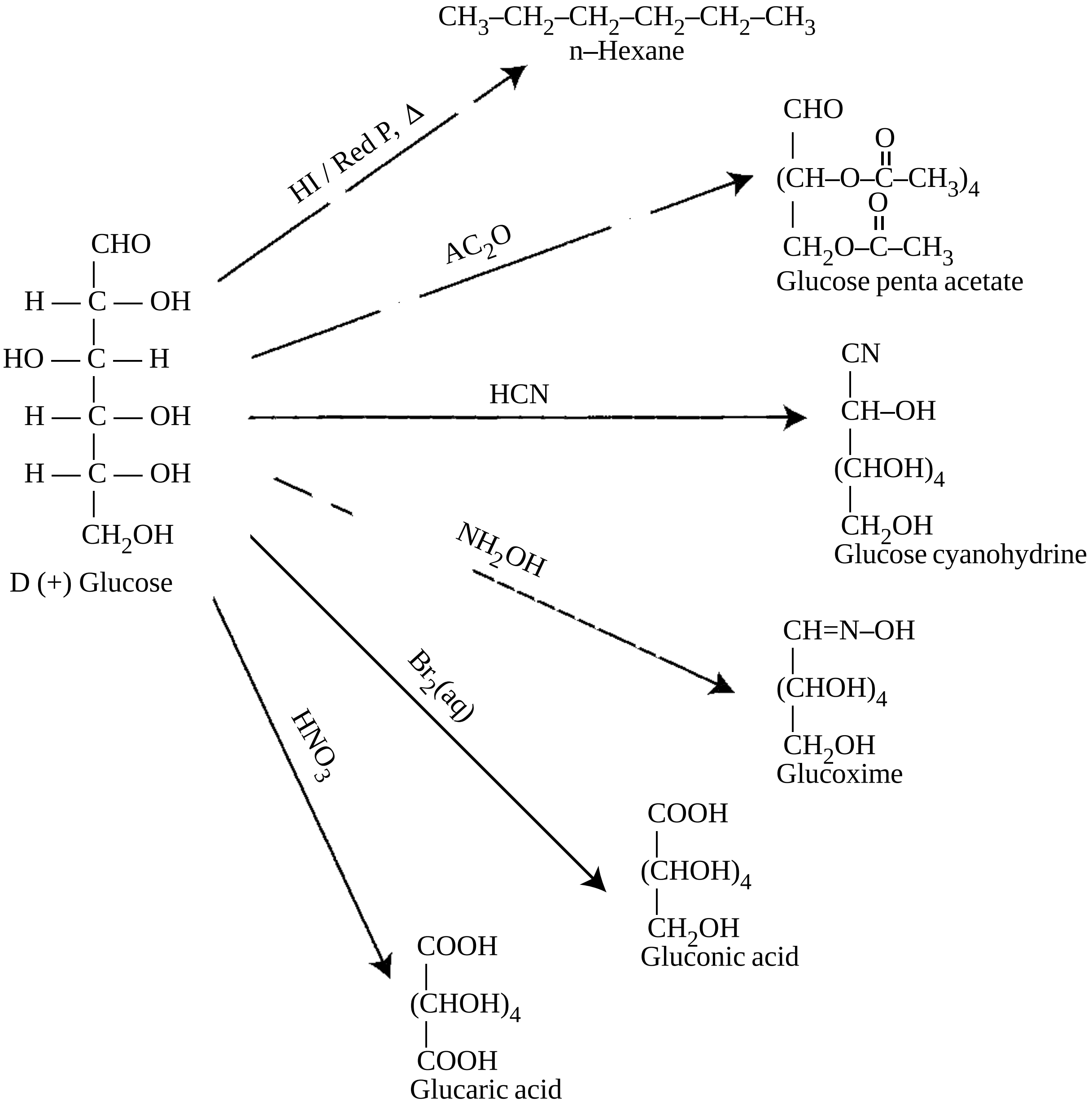
II. Configuration of Glucose :

Basing on its preparation from lower aldose and its properties Fischer put forth the exact arrangement of different –OH groups in space around the chiral centres and the open chain structure of glucose with correct canfiguration can be reprsented as :



D (+) Glucose

Here D stands for configuration, where as (+) represents the dextrorotatory nature of glucose. This open chain structure is able to explain all the above reaction.



III. Evidence against open chain structure :

The open chain structure of glucose explains most of the properties, but unable to explain the followings

(i) It does not react with $NaHSO_3$ and also with ammonia, although it contains a free–CHO group.

(ii) Penta acetyl derivative of glucose is not oxidized by Tollen's reagent or Fehling's solution, indicating the absence of free –CHO group.

(iii) Two stereo isomeric forms (α– and β–) are found to exist with different value of specific rotation. Crystallization from alcohol produces α– Glucose (+110°) whereas from pyridine results with β– Glucose (+19°). This behaviour could not be explained by open structure.

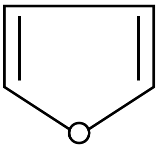
(iv) **Mutarotation :** The phenomenon involving spontaneous change in specific rotation of the aqueous soluton of an optically active compound without any change in other properties is known as muta-rotation.

Muta rotation is observed in glucose. The optical rotation of the aqueous solution of α–Glucose (+110°) and β– Glucose (+19°) change gradually with time till finally a constant value of +53° is reached, which represents the state of equilibrium between α-D-glucose and β-D-glucose.

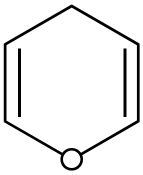
$$\underset{[\alpha]_D = +110^\circ}{\alpha\text{–D (+) Glucose}} \rightleftharpoons \underset{[\alpha]_D = +53^\circ}{\text{Equilibrium mixture}} \rightleftharpoons \underset{[\alpha]_D = +90^\circ}{\beta\text{–D (+) Glucose}}$$

IV. Cyclic structure of D-Glucose :

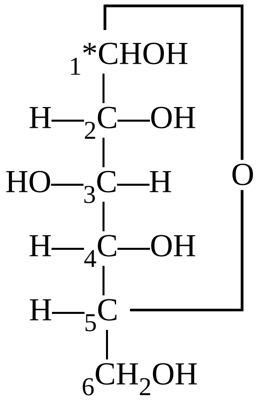
Failure of open chain structure to explain some of the important characeristics of glucose suggests that the –CHO gr is not free, rather it combines with one of the –OH grs to form a cyclic hemiacetal structure. The stable cyclic structure expected is either a six-membered ring (pyranose structure) or a five-membered ring (furanose structure), out of which the pyranose structure for glucose is confirmed explaining the existence of two cyclic forms in equilibrium with open chain structure.



Furan

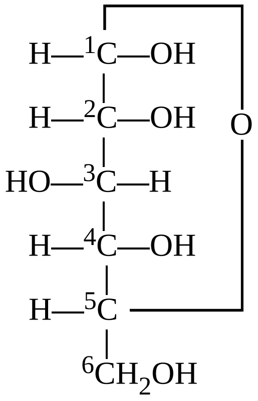


Pyran

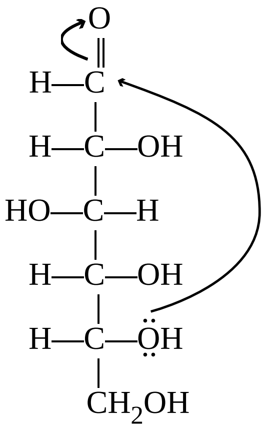


Pyranose structure of glucose

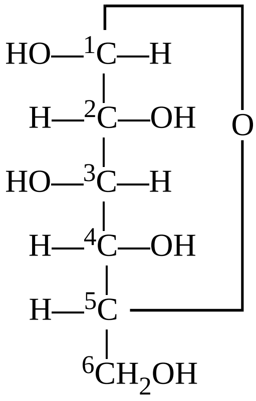
During hemiacetal formation C_1 - aldehydic group combines with C_5 – OH group resulting with a chiral centre at C_1 and thus it has two possible arrangements of H and OH groups around it. Hence D-glucose exists in two stereoisomeric forms i.e. α-D-glucose and β-D-glucose. Such pair of stereoisomers which differ in configuration only around C_1 are called **anomers** and C_1 carbon is called **anomeric carbon**.



α-D- (+) Glucose

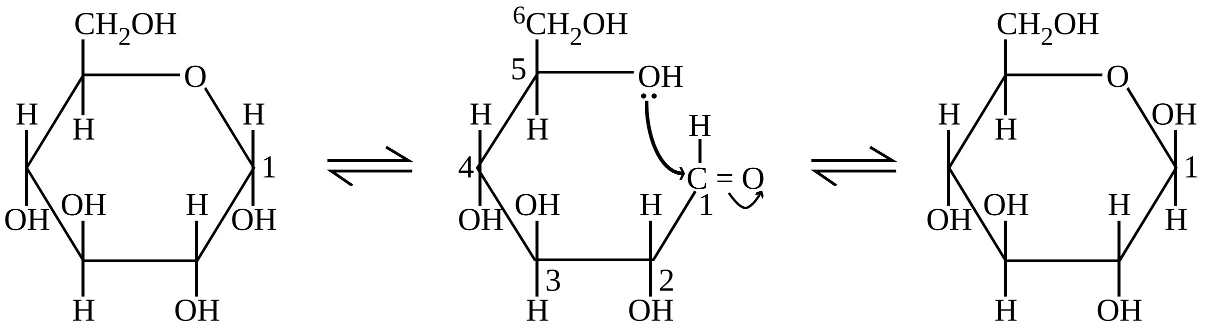


D (+) Glucose
(Open chain form)



β-D- (+) Glucose

The cyclic pyranose structure of glucose can be more correctly represented by Haworth structures as shown below.



α-D- (+) Glucose

D (+) Glucose
(Open chain form)

β-D- (+) Glucose

2. FRUCTOSE

Fructose, the important ketohexose is otherwise termed as **levulose** bcause the naturally occurring form of fructose is laevorotatory. It is found along with glucose in the juices of ripe fruits and in honey. In the combined state it occurs in sucrose.

(a) Preparation

Fructose is obtained from sucrose (cane sugar by warming with dilute sulphuric acid or with enzymes inverstase.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H_2SO_4} \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

(a) Structure of fructose :

I. Open Chain Structure of fructose :

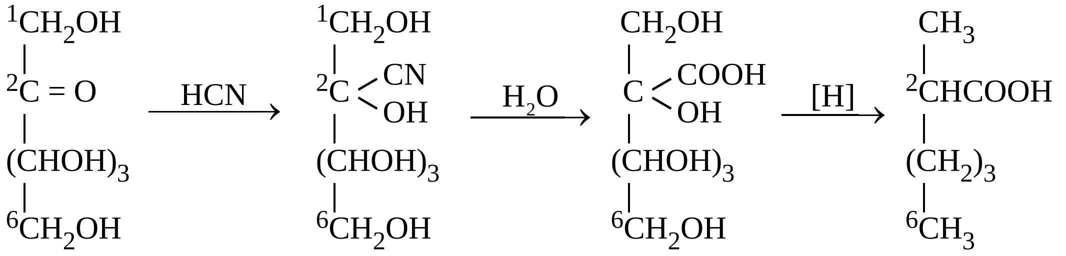
(i) Molecular formula : As per elemental analysis and molecular weight determination, the molecular formula of fructose is $C_6H_{12}O_6$.

(ii) Presence of a straight chain of six carbon atoms : On complete reduction with HI and red P, it forms n-Hexane thus proving the presence of a straight chain of six carbon atoms.

(iii) Presence of 5 –OH groups : It gives pentaacetyl derivative on reaction with acetic anhydride indicating the presence of five hydroxy groups, each being attached to a separate carbon as fructose is a stable compound.

(iv) Presence of carbonyl ($>C = O$) group : On oxidation with nitric acid fructose forms a mixture of trihydroxy glutaric aicd, tartaric acid and glycollic acid, all containing fewer carbon atoms than six. Thus, the carbonyl group is fructose must be ketonic.

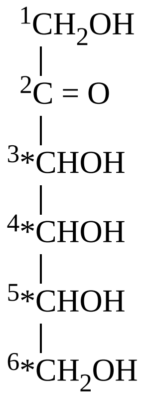
(vi) Carbonyl is on C-2 : Fructose forms cyanohydrin which upon hydrolysis and subsequent reduction with HI and red P yields 2-methylhexanoicacid. Since the COOH has appeared in place of CN, it is bonded to C-2 in the cyanohydrin confirming the position of carbonyl group at position 2 on the six carbon chain.



$$\begin{array}{l} {}^1CH_2OH \\ | \\ {}^2C=O \\ | \\ (CHOH)_3 \\ | \\ {}^6CH_2OH \end{array} \xrightarrow{HCN} \begin{array}{l} {}^1CH_2OH \\ | \\ {}^2C\begin{smallmatrix} CN \\ OH \end{smallmatrix} \\ | \\ (CHOH)_3 \\ | \\ {}^6CH_2OH \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2OH \\ | \\ C\begin{smallmatrix} COOH \\ OH \end{smallmatrix} \\ | \\ (CHOH)_3 \\ | \\ {}^6CH_2OH \end{array} \xrightarrow{[H]} \begin{array}{l} CH_3 \\ | \\ {}^2CHCOOH \\ | \\ (CH_2)_3 \\ | \\ {}^6CH_3 \end{array}$$

Fructose Cyanohydrin 2-Methylhexanoic acid

(vii) Open-chain structure : From the above observations, the open chain structure of fructose can be represented as :

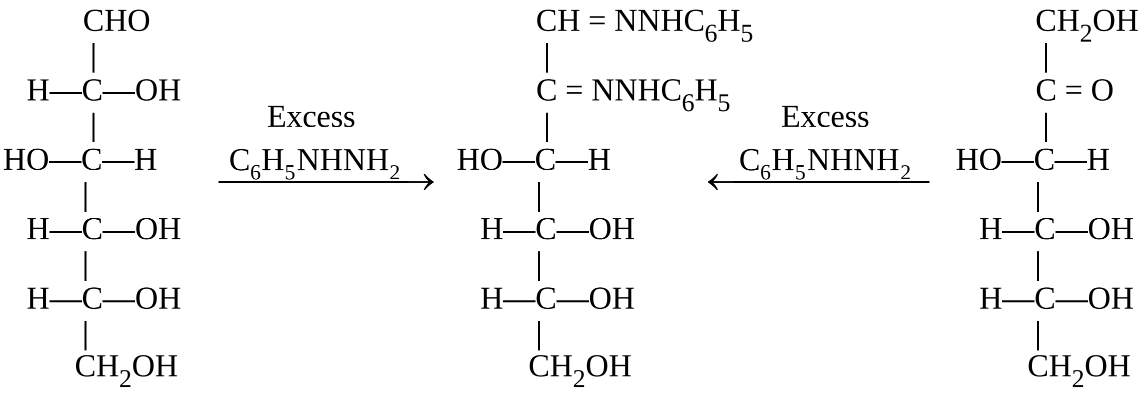


$$\begin{array}{l} {}^1CH_2OH \\ | \\ {}^2C=O \\ | \\ {}^{3*}CHOH \\ | \\ {}^{4*}CHOH \\ | \\ {}^{5*}CHOH \\ | \\ {}^{6*}CH_2OH \end{array}$$

This structure has three chiral centres with 8 ($= 2^3$) optically active forms out of which one is D (–) fructose.

II. Configuration of Fructose :

In the presence of excess phenyl hydrazine fructose forms the osazone which is identical with that obtained from glucose. This shows that the configuration of asymmetic carbon atoms C–3, C–4 and C–5 in D-fructose is the same as in D-glucose. Thus,



D - Glucose

Osazone

D-fructose
Open chain structure
with correct
configuration

III. Evidence against open chain structure :

Open chain structure of fructose fails to explain the following :

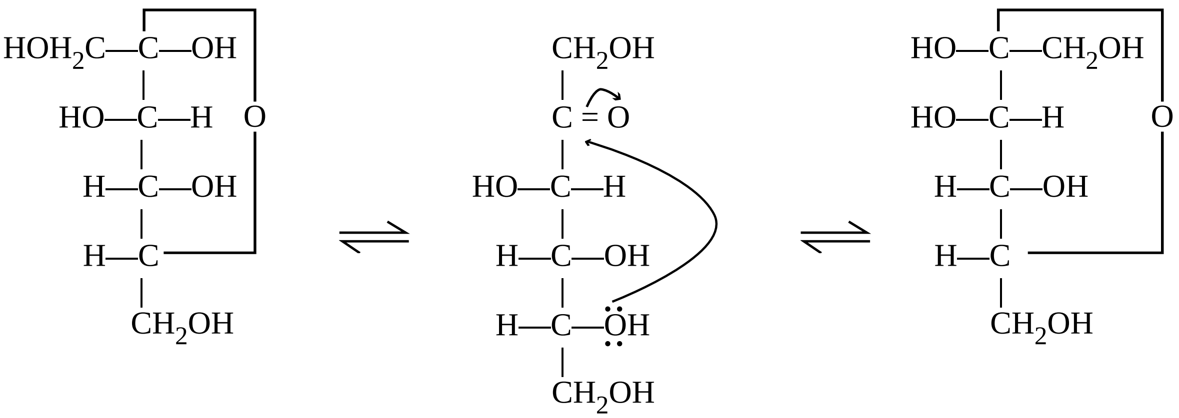
(i) It does not form addition product with $NaHSO_3$, although it contains a ketonic group.

(ii) Since an aqueous solution of fructose shows the properties of mutarotation, it shows the existence of two stereo-isomers of fructose (α and β varieties)

(iii) The α - and β - isomers of fructose are also confirmed as it forms two stereo-isomeric methyl fructosides.

IV. Ring or cyclic structure of fructose :

To explain the objection led against open chain structure, a five membered cyclic structure i.e. furanose structure was proposed for fructose which is confirmed.

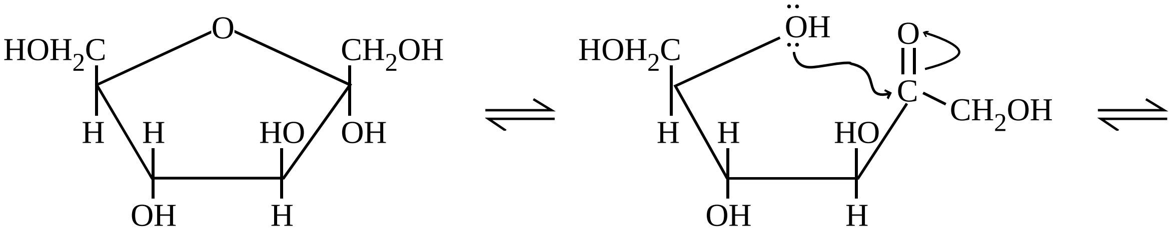


α-D- (–) Fructofuranose

Open chain structure
of D (–) Fructose

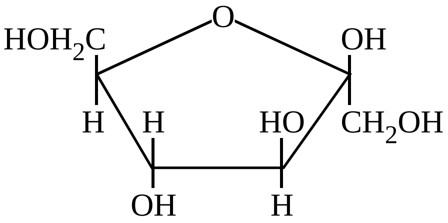
β-D- (–) Fructofuranose

The furanose structures can be better represented by Haworth structures.



α-D- (–) Fructofuranose

Open chain structure
of D (–) Fructose



β-D- (–) Fructofuranose

D. DISACCHARIDES

Disaccharides ($C_{12}H_{22}O_{11}$) are carbohydrates that produce two monosaccharides on acid hydrolysis.

$$\text{Sucrose} \xrightarrow{H_2O/H^+} \text{Glucose + Fructose}$$

$$\text{Maltose} \xrightarrow{H_2O/H^+} \text{2 Glucose}$$

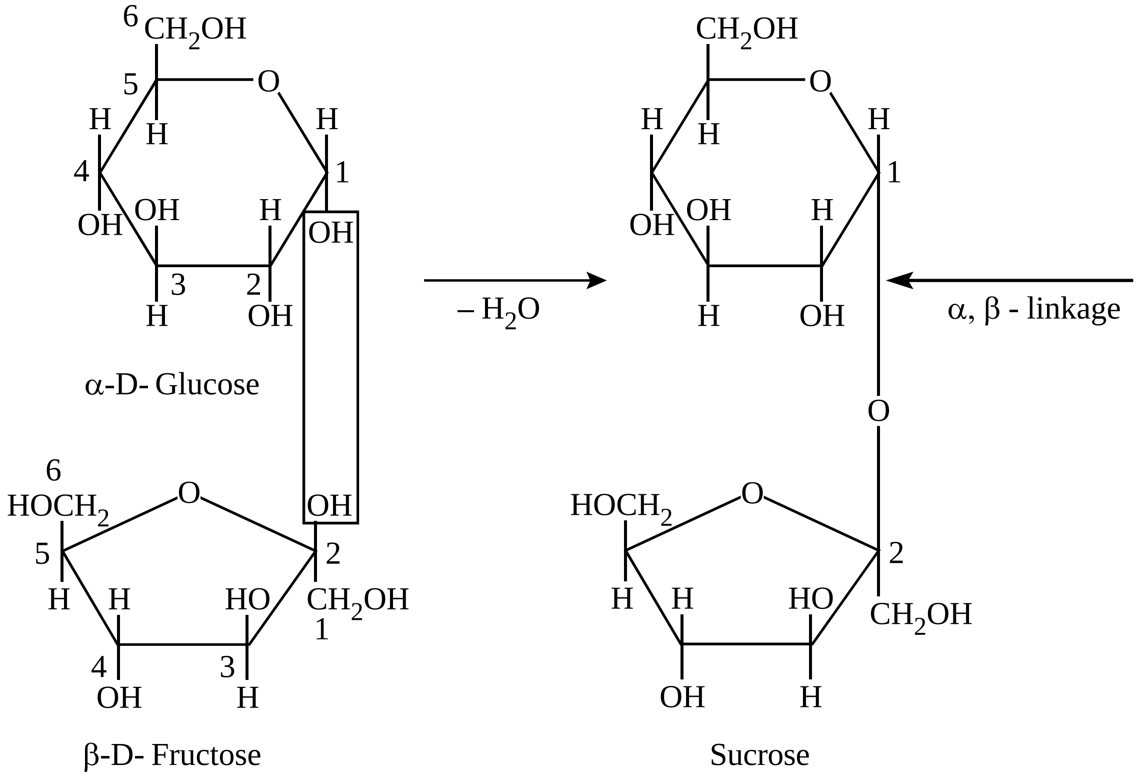
$$\text{Lactose} \xrightarrow{H_2O/H^+} \text{Glucose + Galactose}$$

Disaccharides are composed of two units of monosaccharides joined by a glycosidic linkage with the elimination of a water molecule.

I. SUCROSE :

Sucrose is ordinary table sugar obtained from cane sugar.

(i) Sucrose is composed of α-D-glucose and β-D-fructose unit being joined by α, β - glycosidic linkage between C–1 of the glucose unit and C–2 of the fructose unit.



(ii) The structure of sucrose explains the following characteristics.

(a) Sucrose does not form an osazone with phenyl hydrazine.

(b) It does not reduce Tollens' reagent or Fehling's solution.

(c) It does not exhibit mutarotation.

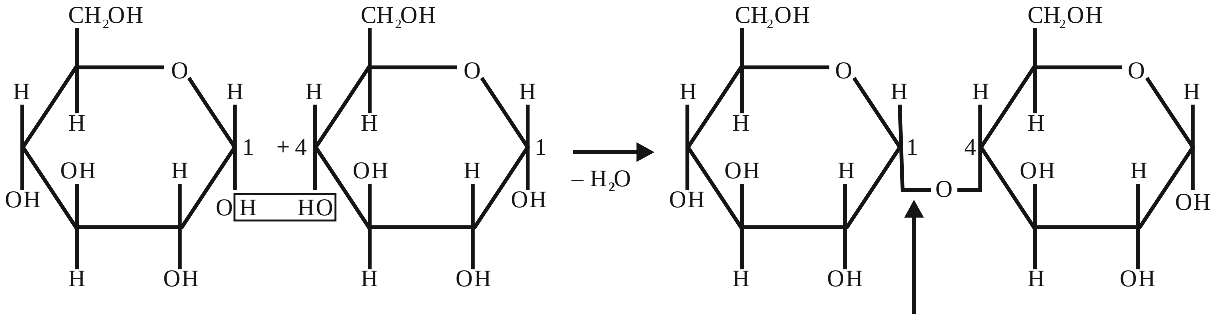
(iii) Sucrose is dextrorotary but after hydrolysis gives dextrorotary glucose (+52.5°) and laevorotatory fructose (– 92.4°) and hence the mixture is laevorotatory. Thus hydrolysis of sucrose is associated with change in the sign of rotation, for which the product is termed as **invert sugar**.

$C_{12}H_{22}O_{11}$	+	H_2O	$\xrightarrow{H^+}$	$C_6H_{12}O_6$	+	$C_6H_{12}O_6$
Sucrose				D (+) Glucose		D (–) Fructose
$[\alpha]_D = 66.5°$				+ 52.5°		– 92.4°

Equimolar mixture $[\alpha]_D = -19.85°$

2. MALTOSE :

Maltose is obtained from starch, being composed of two α-D-Glucose units joined by an α-glycosidic linkage between C–1 of one unit and C–4 of the other unit.



Two α-D-Glucose units

α-Linkage
Maltose

(i) C–1 of the second Glucose unit in the maltose structure is a hemiacetal carbon and hence can exist in α - and β forms.

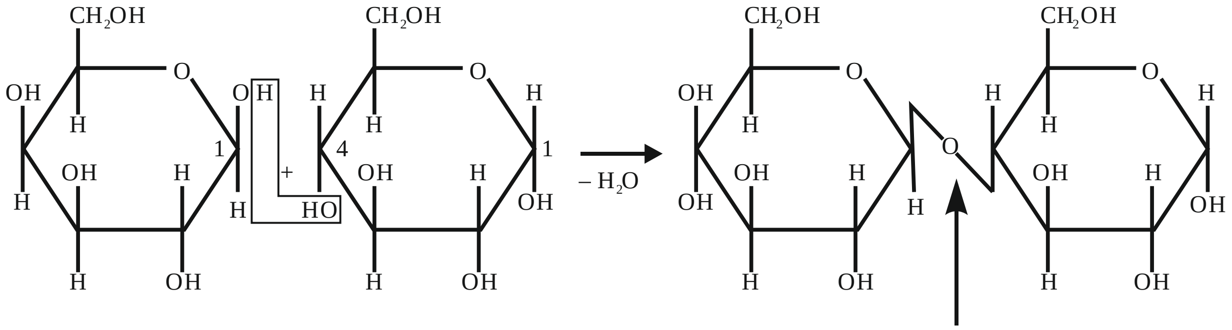
(ii) Since it has a potential aldehyde group, it shows mutarotation.

(iii) It forms osazone.

(iv) It reduces Fehling's solution and Tollen's reagent. Thus maltose in a reducing sugar.

3. LACTOSE :

Lactose is found in the milk of all animals, and hence commonly known as milk sugar. Lactose is composed of β-D-Galactose unit and α-D-Glucose unit joined by β-D-Glycosidic linkage beween C–1 of the galactose and C–4 of the glucose unit.



β-D-Galactose

α-D-Glucose

β-Linkage
Lactose

(i) Because of potential aldehyde group present lactose exists in both α – and β – forms.

(ii) It is a reducing sugar reducing Tollen's reagent and Fehling's solution.

(iii) It shows mutarotation.

E. POLYSACCHARIDES :

Polysaccharides are made of a large number of monosaccharide units joined together by glycosidic linkages. The most common naturally occurring polysaccharides mainly acting as the food storage or structural materials are :

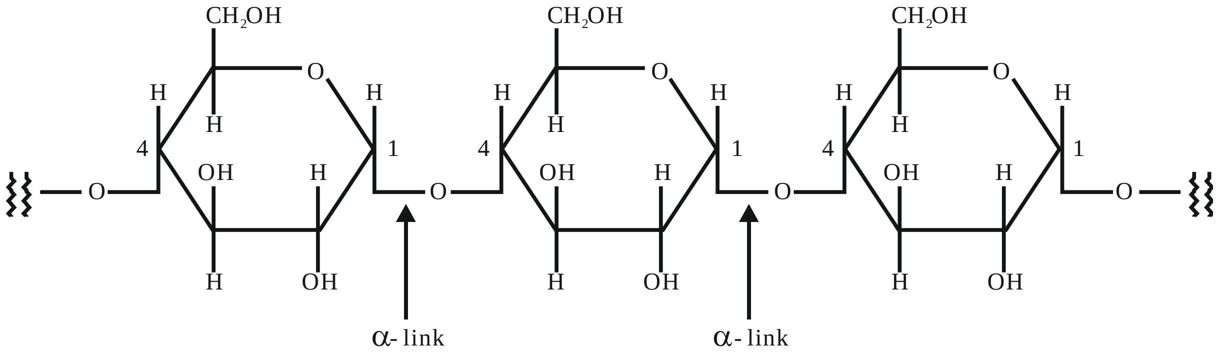
(a) STARCH :

Starch is the main contributor of carbohydrates in our diet. It exists exclusively in plants, stored in seeds, roots and fibres as food reserve. The chief sources of starch are cereals, potatoes, corn and rice.

Structure :

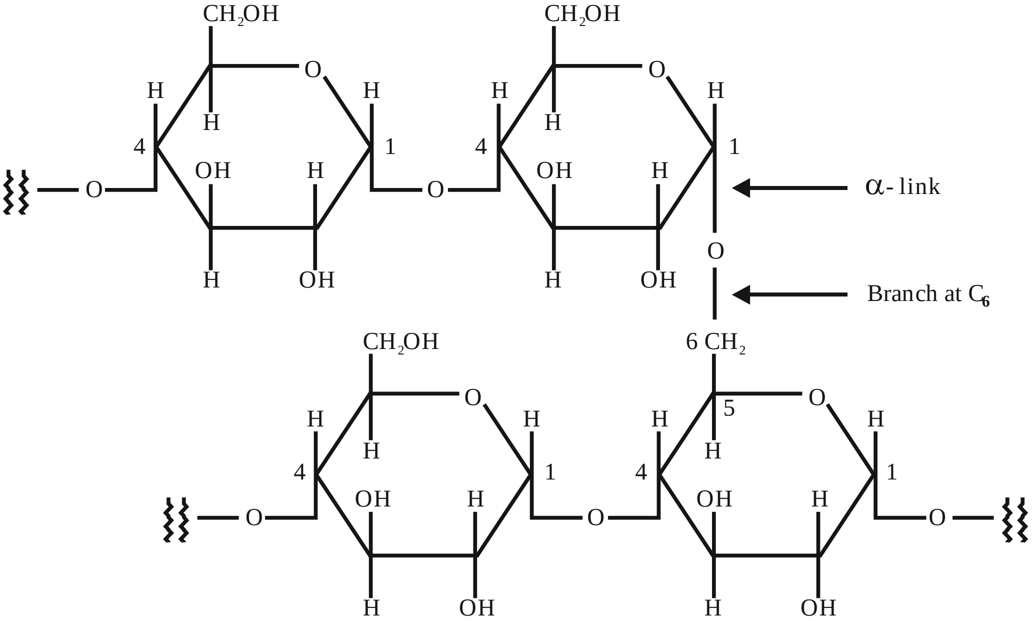
Starch is a polymer of α-glucose and consists of two components.

(i) **Amylose :** The water soluble component of starch is amylose. The amylose molecule is made up of D-glucose units joined by α – glycosidic linkages between C-1 of one glucose unit and C–4 of the next glucose unit.



Amylose

(ii) **Amylopectin :** Amylopectin has a branched chain structure and insoluble in water constituting about 80-85% of starch. It is composed of chains of 25 to 30 D-glucose unit joined by α-glycosidic linkages between C-1 of one glucose unit and C-4 of the next glucose unit. These chains are in turn connected to each other by 1, 6 - linkages.

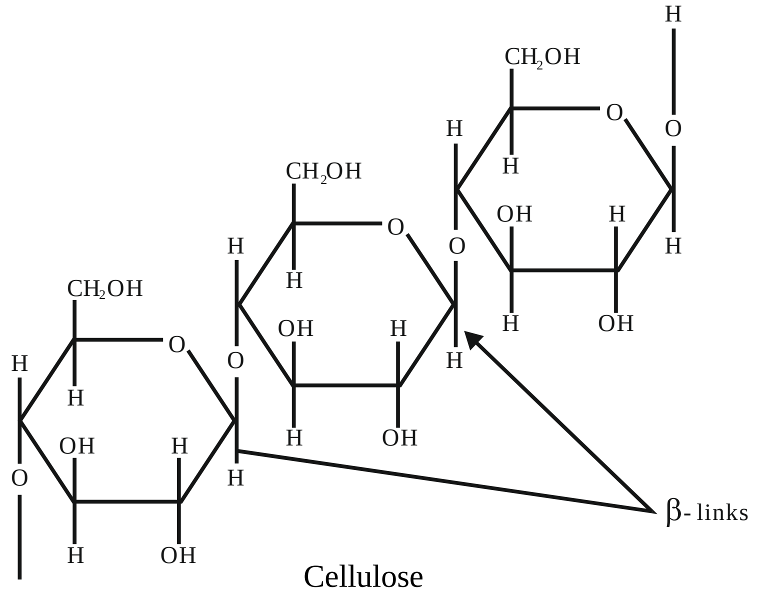


Amylopectin

(b) CELLULOSE :

Cellulose is the main structural material of trees and other plants. Wood is 50% cellulose, while cotton wool is almost pure cellulose. Other sources of cellulose are straw, corncobs, bagasse and other agricultural wastes.

(i) Structure : Cellulose is a straight-chain polysaccharide composed of D-glucose units being joined by β - glycosidic linkages between C–1 of one glucose unit and C–4 of the next glucose unit. The number of D-glucose units in cellulose ranges from 300 – 2500.



Cellulose

(ii) The grazing animals like, cow, deer etc. can digest cellulose of grass and plants as the enzyme cellulase is present in their stomach, whereas the humans can not digest cellulose because of the absence of cellulase.

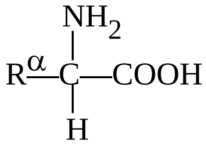
(C) GLYCOGEN :

Glycogen is present in liver and muscles and is known as the reserve carbohydrate of animals or animal starch. When energy i.e. glucose is needed for any work by the body, glycogen is broken down to glucose by enzymes.

The structure of glycogen is similar to that of amylopectin and it has 1,6 as well as 1,4 glycosidic linkages, but it is much more branched than amylopectin.

22.3 AMINO ACIDS :

Proteins are linear polymers of α–amino acids. Therefore amino acids are regarded as “building blocks of proteins.” The general structure of α–amino acid is represented as,



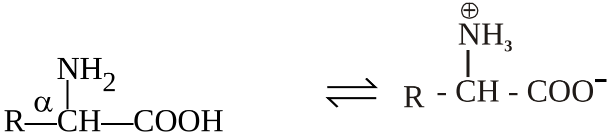
$$R\overset{\alpha}{—}\underset{H}{\overset{NH_2}{C}}—COOH$$

Here amino group is present at α–carbon atom, R may be a hydrogen atom or any alkyl group or an aromatic ring or a heterocyclic ring. Hence each amino acid is a nitrogeneous compound containing both an acidic carboxyl and a basic amino group. Except in glycine, α–carbon atom in all the amino acids is asymmetric in nature.

About 20 commonly occurring α–amino acids are known, which are obtained by the hydrolysis of proteins. These amino acids differ from one another due to the different nature of their side chain group, R. The properties of side chain present in the amino acid determine the properties of proteins they constitute.

A. Structure of amino acids :

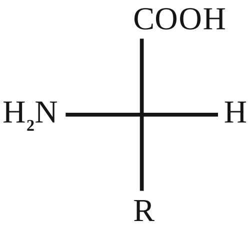
According to the general formula, amino acids contains both an acidic (—COOH) group and a basic ($-NH_2$) group. In fact, these two groups interact resulting in the transfer of a proton from acidic carboxylic acid group to basic amino group, thereby resulting in the formation of an internal salt as shown below.



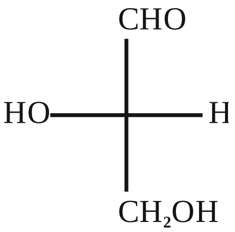
$$R\!-\!\overset{\overset{\displaystyle NH_2}{|}}{\underset{\alpha}{C}H}\!-\!COOH \rightleftharpoons R-\overset{\overset{\displaystyle \overset{\oplus}{N}H_3}{|}}{C}H-COO^{-}$$

The dipolar structure of internal salt is known as *zwitter ion.*

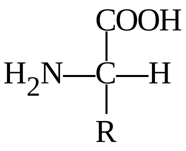
The α– carbon atom of all amino acids (except glycine) is asymmetric. Hence, except glycine all amino acids are optically active. They give two stereoisomers, which are mirror images of each other. However, all the naturally occurring amino acids have L-configuration having–NH_2 group on the left as –OH group in L-glyceraldehyde.



L-aminoacid

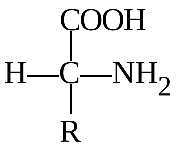


L-glyceraldehyde



L (–) α - Amino acid

Mirror



D (+) α - Amino acid

B. Classification of Amino acids :

Amino acids can be classified mainly in two ways;

(a) Neutral, acidic and basic amino acids.

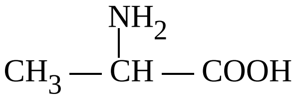
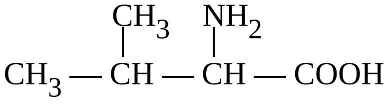
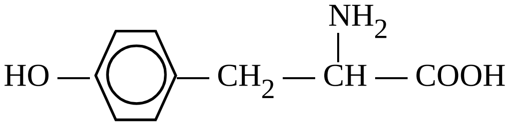
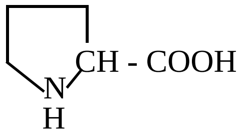
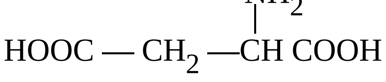
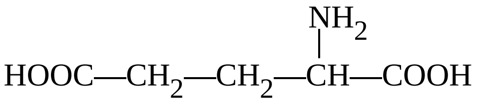
(b) Essential and non-essential amino acids.

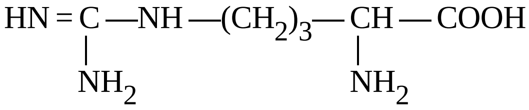
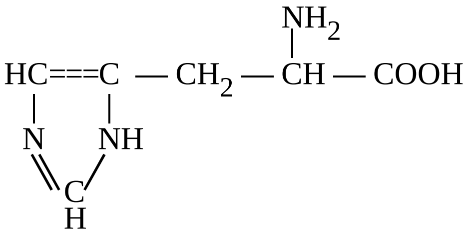
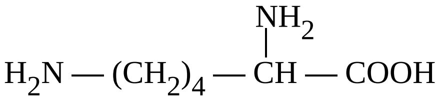
(a) Neutral, acidic and basic amino acids :

Amino acids are classified as neutral, acidic and basic according to the relative number of amino and carboxyl groups in the molecule.

(i) Neutral amino acids contain one amino group and one carboxyl group. (ii) Acidic amino acids contain one amino group and two carboxyl groups. (iii) Basic amino acids contain two amino groups and one carboxyl group. Examples of each type are given in Table 22.1

Table 22.1 Amino acids derived from proteins

Common name	Abbreviated name	Structure
NEUTRAL AMINO ACIDS:		
Glycine	Gly	H_2N-CH_2-COOH
Alanine	Ala	 $CH_3-\overset{\overset{NH_2}{\vert}}{C}H-COOH$
Valine	Val	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}H-\overset{\overset{NH_2}{\vert}}{C}H-COOH$
Tyrosine	Tyr	
Proline	Pro	
ACIDIC AMINO ACIDS :		
Aspartic acid	Asp	 $HOOC-CH_2-\overset{\overset{NH_2}{\vert}}{C}H\ COOH$
Glutamic acid	Glu	 $HOOC-CH_2-CH_2-\overset{\overset{NH_2}{\vert}}{C}H-COOH$

Common name	Abbreviated name	Structure
BASIC AMINO ACIDS :		
Arginine	Arg	 $HN = \underset{NH_2}{C} — NH — (CH_2)_3 — \underset{NH_2}{CH} — COOH$
Histidine	His	
Lysine	Lys	 $H_2N — (CH_2)_4 — \overset{NH_2}{CH} — COOH$

(b) Essential and non-essential amino acids :

Amino acids can also be classified as essential and non-essential amino acids.

(i) Those amino acids that can not be synthesised by the body and must be supplied in the diet are called **essential** amino acids. For example; valine, leucine, isoleucine etc.

(ii) But the amino acids that can be synthesised by the human body are called **non-essential** amino acids. Examples are glycine, alanine, tyrosine etc.

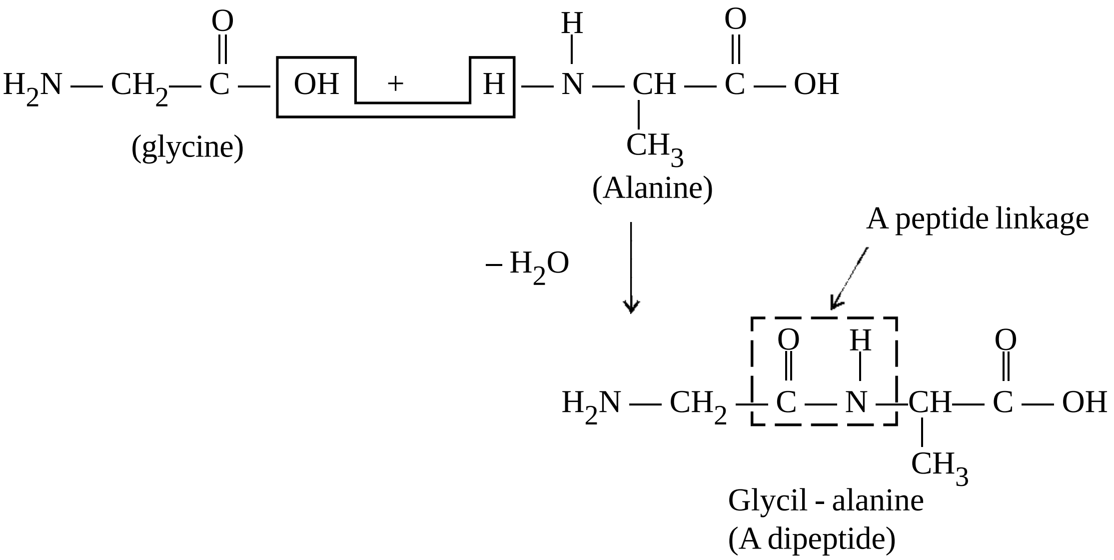
C. PEPTIDES & POLYPEPTIDES

Peptides are the condensation products of two or more α–amino acids. The bond between two adjacent amino acids is a special type of amide bond, known as the **peptide bond** and the chain thus formed, is called a **peptide chain**.

Peptides can be classified as dipeptides, tripeptides and polypeptides depending upon the number of amino acid molecules taking part in the condensation.

When two amino acids condense together, the resulting product is called a *dipeptide*. Similarly, when theree amino acids combine, the product is called a tripeptide. When four or more amino acids combine in this way, the product is called a *polypeptide*. Proteins are polypeptides containing atleast 100 or more amino acids, but there is no clear demarcation between polypeptides and proteins.

As for example, when glycine and alanine condense together, a *dipeptide* results.



22.4 PROTEINS :

Proteins are essential compounds for living cells. The name protein (Greek : *Proteios* = pre-eminent or first) was suggested by Berzelius. According to him, proteins are complex organic nitrogeneous substances found in the cells of the living beings and essential to cell structure and cell function. Thus, proteins are vital chemical substances essential for the growth and maintenance of life. Proteins are present in almost all living cells of plants and animals.

Chemically, *proteins* are linear unbranched polymers of α–amino acids. In a protein molecule, α–amino acids are linked together by peptide bonds formed between amino and carboxylic groups of successive amino acids. Hence, proteins are polypeptides with more than 100 amino acids.

1. CLASSIFICATION OF PROTEINS :

(a) On the basis of structures, the proteins are classified into three main groups namely simple, conjugated and derived proteins.

(i) **Simple proteins** give aminoacids on hydrolysis, carried out by acid, alkali or enzyme. Examples are globulins, collagens, elastins etc.

(ii) **Conjugated proteins** are simple proteins which are bonded with non-proteinous prosthetic groups. Examples are nuclein, nucleohistone, haemoglobin, chlorophyll, cytochrome, albumin, casein, serum proteins etc. Albumin contains glycoprotein as protein and carbohydrates as prosthetic group. Casein has phosphoprotein and phosphoric acid other than nucleic acid. Serum protein has lipoprotein and lipid as prosthetic group.

(iii) **Derived proteins** are obtained from simple proteins by regulated hydrolytic process.

(b) According to solubility, proteins are classified as *fibrous* proteins and *globular* proteins.

(i) **Fibrous proteins** are insoluble in water and possess long threadlike structures. They are found in nails, horn, hair (keratin), wool, silk and feathers.

(ii) **Globular proteins** are soluble in water, acid and alkali. These are highly branched and cross-linked. These proteins perform various functions related to maintenance and regulation of life process. They include all enzymes, many hormones (insulin), albumin in egg, haemoglobin, antibodies responsible for allergies and for defence against foreign organisms.

2. STRUCTURE OF PROTEINS :

The complete structure of a protein is quite complex. Therefore, their structures are usually discussed in four different levels such as primary, secondary, tertiary and quaternary structures of the protein.

(i) **Primary structure :** The primary structure of proteins refers to the sequence in which various amino acids are linked together by peptide linkages. The primary structure of a protein is determined by its successive hydrolysis with acids, alkalies or enzymes. Successive hydrolysis of proteins yield different products having decreasing molecular masses as shown below.

Proteins → Proteoses → Peptones → Polypeptides → Simple Peptides → α – amino acids

In primary structure, the peptide bonds form the backbone and the side chains of amino acids project outside the peptide backbone.

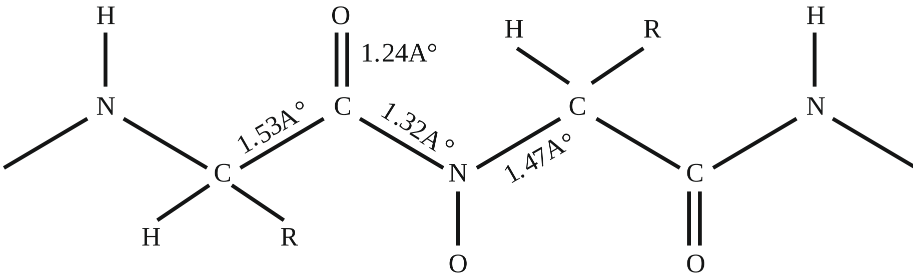


Fig : 22.1 Primary structure of protein

The amino acid sequence of a protein determines its function and is critical to its biological activity. The amino acid sequence in proteins can be determined by taking the following generalisations. They are (a) Proteins are made up of L-amino acids only; (b) Sequence of amino acids along the protein chain is random; and (c) Even a change of just one amino acid can drastically alter the properties of the entire protein molecule. For example a disease called sickle cell anaemia is caused when one α-amino acid is replaced in haemoglobin.

(ii) *Secondary structure :* The secondary structure of proteins refers to the conformation which the polypeptide chains assume as a result of hydrogen bonding between the carboxylic acid and amino groups. Two different secondary structures are possible depending on the size of the side chain (R–)

(a) *α–Helix structure* : When the size of the R– group is very large, intermolecular hydrogen bonding occurs between $>C = O$ group of one amino acid unit with $>N — H$ group of the fourth amino acid unit present in the chain. As a result, the polypeptide chain coils up into a spiral structure, called right handed α– helix structure. α– Helix structure are seen in most of fibrous proteins like α–keratin in hair, nail and myosin in muscles.

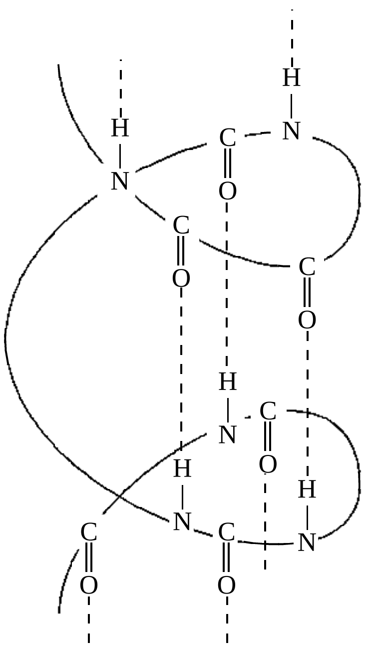


Fig : 22.2 α–Helix structure

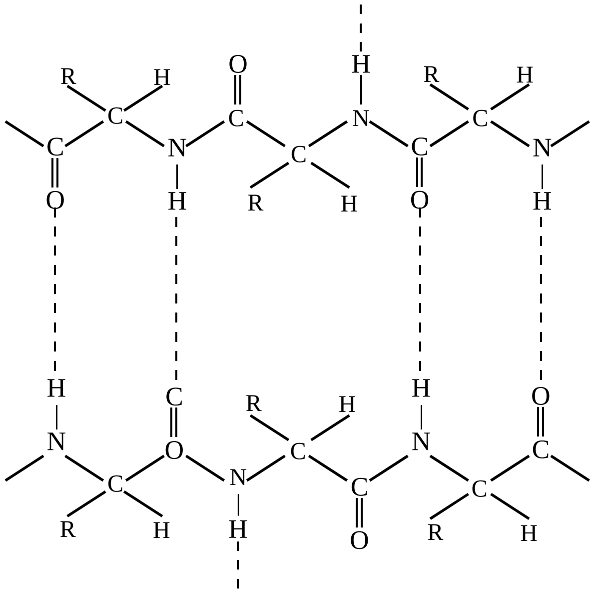


Fig : 22.3 β–Pleated sheet structure

(b) *β–pleated sheet structure:* When the size of R–group is small, the polypeptide chains lie side by side in a zig-zag manner with alternate R– groups on the same side situated at fixed distances. As a result of which intermolecular hydrogen bonding occurs between two neighbouring chains. This results in the formation of a flat sheet structure.

(iii) ***Tertiary structure*** **:** An α– helix may be considered to be a piece of a rope which is free to bend, twist and fold. The tertiary structure of a protein refers to the final three - dimensional shape that results from the twisting, bending and folding of the protein helix with main forces operating are hydrogen bonding, disulphide linkage, and van der Waal's forces of attraction. Tertiary structures of proteins results with fibrous and globular molecular shapes.

(iv) ***Quaternary structure*** **:** Complex proteins are formed by the combination of two or more polypeptide chains. Each chain is a complete protein with a characteristic primary, secondary and tertiary structure. The quaternary structure refers to the way in which these polypeptide chains of a complex protein are associated with each other.

3. BIOLOGICAL ROLES OF PROTEINS :

Proteins are of great importance to biological systems. These are most essential to life and perform various functions. Some of their important roles are given below:

(i) Many proteins act as catalysts, which enhance the rate of chemical reactions to an appriciable extent as required by the living cells and are known as **enzymes.**

(ii) The fibrous proteins act as "components of the tissues" holding together the skeletal elements. For example, **collagen** is a structural unit of connective tissues.

(iii) Protein hormones regulate the growth of plants and animals, besides controlling many other physiological functions.

(iv) Interferon is a cellular protein, which is naturally produced by the body in response to virus infections.

(v) Blood plasma, which is a solution of proteins in water is used for the treatment of shock produced by serious injuries and operations.

4. DENATURATION OF PROTEINS :

The process after which proteins lose their physiological activity and certain other properties is called denaturation which is caused by

(i) action of bacteria

(ii) action of heat

(iii) by shaking with alcohol and

(iv) by treatment with acids.

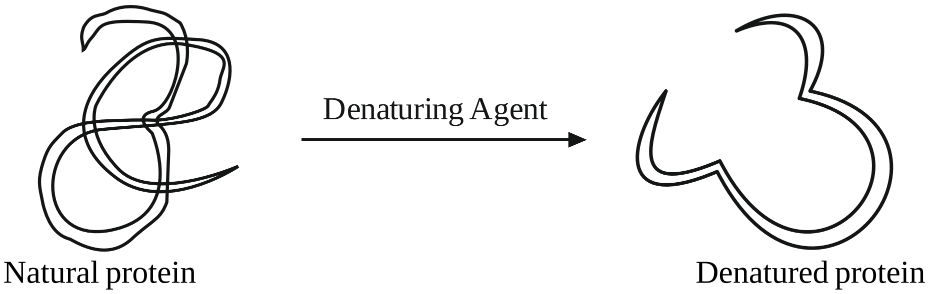
(a) Examples of denaturation :

(i) Boiling of an egg : Coagulation of the white of an egg by the action of heat is a very common example of denaturation.

(ii) Formation of cheese : The coagulation of milk in the presence of an acid (lemon juice) to form cheese is an example of denaturation.

(b) Cause of denaturation :

Denaturation is due to the disruption of the secondary and tertiary structure due to the breaking of hydrogen bonding and salt bridges in proteins causing uncoiling of the protein molecules from an ordered and specific confirmation into a more random conformation resulting into its coagulation from solution.



(c) **Renaturation :**

The reversible process by which the original form of the denatured protein can be regained is known as **renaturation**. Protein denaturation may or may not be reversible. Coagulation of white of an egg on heating is an irreversible process. But in case of reversible denaturation, the protein can be coagulated from their colloidal solution by saturating the solution with soluble salts like ammonium sulphate, or by the addition of water or alcohol thus rejoining the original form.

22.5 ENZYMES :

Enzymes are defined as the complex nitrogenous organic compounds produced by living plants and animals. They are polypeptides i.e. proteins of high molecular mass responsible for catalyzing natural processes prevailing in the bodies of animals and plants, for which the enzymes are also termed as biochemical catalysts and the phenomenon is termed as **biochemical catalysis**.

Some examples of enzyme catalysis are :

(a) **Inversion of cane sugar :** The enzyme invertase converts cane sugar into glucose and fructose.

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(aq)}}$$

(b) **Conversion of milk into curd :** The enzyme lacto bacilli is responsible for the conversion of milk into curd.

(c) **Conversion of glucose into ethyl alcohol :** The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH_{(aq)}} + 2\,CO_{2(g)}$$

(d) **Conversion of starch into maltose :** The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n\,(aq)} + n\,H_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}\,(aq)}$$

(e) **Conversion of maltose into glucose :** The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \xrightarrow{\text{Maltose}} \underset{\text{Glucose}}{2\,C_2H_{12}O_6(aq)}$$

(f) **Decomposition of urea into ammonia and carbon dioxide :** The enzyme urease catalyses the decomposition of urea.

$$NH_2CONH_2\,(aq) + H_2O\,(l) \xrightarrow{\text{Urease}} 2NH_3\,(g) + CO_2(g)$$

(g) In stomach the pepsin enzyme coverts proteins into peptides while in intenstine, pancreatic trypsin converts proteins into amino acids by hydrolysis.

1. NATURE OF ENZYMES :

(i) Enzymes are globular proteins.

(ii) Like proteins enzymes are amphoteric by nature.

(iii) Enzymes also get denatured like proteins.

(iv) When purified enzymes are injected in the body, specific antibodies are produced.

(v) They are generally named after the compound or class of compounds on which they are effective. For example, the enzyme is named maltase which catalyzes hydrolysis of maltose.

$$\text{Maltose} \xrightarrow{\text{Maltase}} 2\ \text{Glucose.}$$

(vi) Enzymes are also named after the reactions. For example the enzymes are named as **oxido reductase** enzymes, when they catalyze the oxidation of one substrate with simultaneous reduction of another substrate. The name of the enzyme always ends with suffix-**ase**.

2. PROPERTIES OF ENZYMES :

(i) **Catlytic efficiency :** Enzymes are very efficient catalysts. A very small quantity of any enzyme is needed to catalyse a reaction. For example, the enzyme rexin coagulate over a million times its weight of milk during cheese formation.

(ii) **Specificity :** Enzymes are highly specific in nature. An enzyme catalyses only a particular reaction.

Invertase can break up **sucrose** into glucose and fractose, but fails to breake up a similar disaccharide, **maltose**, which can only be broken by another enzyme maltase.

Similarly **urease** hydrolyses urea to ammonia and carbon dioxide but does not hydrolyse N-methyl urea which has a similar structure.

$$NH_2CONH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

$$CH_3NHCONH_2 + H_2O \xrightarrow{\text{Urease}} \text{No action}$$

(iii) **Effect of temperature :** Enzymes are most effective near body temperature i.e. the rate of enzyme reaction becomes maximum at the optimum temperature with the range 298 - 310K. In general all the chemical reactions proceed faster with increase in temperature, bu the rate of enzyme catalyzed reaction first increases, become maximum at about 35°C and then decreases at higher temperature.

(iv) **Effect of pH :** The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.

(v) **Effect of co-enzymes and activators :** The enzymatic activity is increased in the presence of small organic molecules called **co-enzymes** which are derived from vitamins such as thiamine, **riboflavin** etc.

Metal ions like Na^+, Mn^{2+}, Co^{2+}, Ca^{2+} etc when weekly bonded to enzyme molecules increase their catalytic activity, for which there are called **activators**. For example **amylase** in presence of **sodium chloride** are catalytically very active.

(vi) **Influence of inhibitors :** The enzyme activity can be reduced or inhibited by the presence of certain compounds known as enzyme inhibitors.

22.6 HORMONES :

A **hormone** is a chemical released by one or more cells that affects cells in other part of the organism. Only a small amount of hormone is required to alter cell metabolism. All multicellular organisms produce hormones. Plant hormones are called **Phytohormones**. Hormones in animals are often transported in the blood. Cells respond to a hormone when they express a specific receptor for that hormone. The hormone binds to the receptor protein, resulting in the activation of a signal transduction mechanism that ultimately leads to cell type - specific responses.

Endocrine hormone molecules are secreted by ductless glands directly into the blood stream whereas **exocrine hormone** molecules are secreted directly into a duct and from the duct they flow into the blood stream. Then they move to different parts of the body and exert strong regulatory influence on the chemical processes taking place there.

Chemical classes of Hormones

Vertebrate hormones fall into three chemical classes.

(i) **Amine derived hormones :** Examples are catecholamines and thyroxine.

(ii) **Peptide hormones :** They are protein hormones and include insulin and growth hormone. More complex protein hormones bear carbohydrate side chains and called glyocoprotein hormones. Luteinizing hormone, follicle stimulating hormones and thyroid stimulating hormones are glycoprotein hormones.

(iii) **Lipid and phospholipid - derived hormones :** They are the derivatives of linoleic acid and arachidonic acid and phospholipids. The main classes are the steroid hormones that derive from cholesterol and cortisol. Calcatriol is a sterol hormone. The adrenal cortex and the gonads are the main sources of steroid hormones.

Some hormones in man are given in the following table.

Hormone	Source	Function
1. Adrenalin -	Adrenal medulla -	Increases pulse rate & blood pressure, releases glucose from glycogen and fatty acids from fats.
2. Testosterone -	Testis -	Normal functions of male sex organ.
3. Estrone or Estradiol	- Ovary -	Normal functioning of female sex organ.
4. Insulin -	Pancreas -	Metabolism of Glucose
5. Cortisone -	Adrenal cortex -	Metabolism of water, fats, proteins and carbohydrates.
6. Pituitary hormone -	Pituitary glands -	Stimulation of thyroid gland, testis, ovary and mammary glands.

Effects of Hormones : A few important effects of hormones are

1. Stimulation or inhibition of growth.
2. Mood swing
3. Induction or suppression of apoptosis (Programmed cell death)
4. Activation or inhibition of immune system.
5. Regulation of metabolism.
6. Preparation of the body for fighting sex, mating and other activity.
7. Preparation of the body for a new phase of life.
8. Control of reproductive cycle.

A hormone may also regulate the production and release of other hormones.

Plant Hormones : An example of plant hormone is a series of substances called **auxins**. Auxins increase the length of most plant cells and thereby contribute to the growth and elongation of the plant.

Another plant hormone is **abscisic acid**, which is produced in mature leaves and inhibits growth in developing leaves and germinating seeds. Another hormone **ethylene** encourages ripening and dropping of leaves and fruits from the trees.

Two important growth regulating hormones are the **gibberellins** and **cytokinins**. Gibberellins affect plants by stimulating their growth via rapid stem elongation. Cytokinins induce plant cells to undergo mitosis, therefore they encourage increased growth in the roots and stems in plants. They also enhance flowering and stimulate some type of seeds to germinate.

22.7 VITAMINS :

Vitamins are defined as the naturally occurring organic compounds required in the diet in very small quantities to maintain the normal health and development of the organism.

Vitamins, themselves do not supply much energy to the body, but in small quantities perform specific and vital functions such as energy transformation reactions in the body. Dificiency of a particular vitamin causes specific disease. Excess of vitamins is also harmful and hence vitamin pills should not be taken without the advice of Doctor.

Classification of vitamins :

Vitamins can be categorized into two groups depending on their solubility in fat or water. These are :

A. Fat soluble vitamins :

Vitamins like A, D, E and K are soluble in fat and oils, but isoluble in water. These are found to be stored in liver and adipose tissues.

B. Water soluble vitamins :

Water soluble vitamins are vitamin C and vitamin B complex. These vitamins must be supplied regularly in diet to our body as they are readily excreted in urine and can not be stored in our body excepting B_{12}.

The sources, properties and functions of some of the important vitamins are discussed here.

1. **Vitamin A (Retinol) :** This belongs to a class of organic compounds called **carotenoids** to which carotenes belong. Vitamin A is a carotene derivative, insoluble in water, but soluble in fats and oils. It is not easily destroyed on heating. It is available in cod liver oil, egg yolk, carrots, milk, butter and green vegetables.

   Function : Deficiency of vitamin A results in the retarded growth and a change in epithelial cells. Deficiency of this vitamin causes **nightblindness, xerosis** in which the skin becomes dry and **xerophthalmia** in which the corneas of eyes become opaque.

2. **Vitamin B Complex :** This consists of a number of complex substances like vitamin B_1 or thiamine, vitamin B_2 or riboflavin, vitamin B_6 and vitamin B_{12} or cyanocobalamine.

   (i) **Vitamin B_1 (Thiamine)** : It is a water-soluble white crystalline compound and stable up to 100^0C in dry condition. Stability to heat decreases in moist condition. Thiamine is available in milk, green vegetables, meat, egg, yeast, cereals, nuts and rice polishings.

   Function : Its deficiency in diet causes loss of appetite, and a severe disease called **beriberi**.

(ii) **Vitamin B_2 (Riboflavin)** : It is an orange yellow water-soluble crystalline compound and quite stable to heat, but sensitive to light. Vitamine B_2 is available in milk, green vegetables, egg, liver and rice polishings.

Function : Deficiency of vitamin B_2 causes skin diseases, sore tongue and anaemia.

(iii) **Vitamin B_6** : It consists of three similar components pyridoxal, pyridoxine and pyridoxamine and is water-soluble. It is easily destroyed by heat and ultraviolet radiation. The chief source of vitamin B_6 is cereal grain, egg yolk, meat, fish, milk and cabbage.

Function : Deficiency of vitamin B_6 causes nervous disturbances and convulsions.

(iv) **Vitamin B_{12} (Cyanocobalamine)** : It is a large complex molecule which has a central cobalt atom coordinated to four nitrogen atoms. Vitamin B_{12} is water-soluble red crystalline solid. It is present in meat, fish, egg and curd.

Function : Lack of this vitamin causes a bad form of **anaemia**.

3. **Vitamin C (Ascorbic acid) :** It is insoluble in fats and oils, but soluble in water. Vitamin C is destroyed in contact with oxygen of air even at room temperature since it undergoes reversible equilibrium. It loses effectiveness upon open storing and therefore, vitamin C tablets are kept in sealed strip foils. A major part of this vitamin is lost when vegetables are cooked in open pans in contact with air. Therefore, cooking of vegetables in closed pans or pressure cookers is considered desirable to avoid loss of vitamin C. It is present in fresh vegetables, citrus fruits (lemon, orange), tomatoes, chillis, amla, papita etc.

Function : Absence of vitamin C is a diet causes **scurvy** and pain in joints.

4. **Vitamin D (Calciferols) :** It is a white crystalline solid soluble in fats and oils only and present in milk, egg, liver, cod liver oil etc. Morning sun rays falling on the skin form vitamin D from the sterols present under the skin.

Function : Vitamin D helps in the development of bones and teeth in growing children. Its deficiency causes **rickets** in which the bones and legs get curved and the teeth get deformed.

5. **Vitamin E (α-Tocopherol) :** This vitamin, also known as **"antisterility"** vitamin is a light yellow oily substance soluble in fats and oils. It is present in animal and vegetable oils, cotton seed oil, maize oil, pea-nut oil, wheat germ oil, sunflower oil etc.

Function : Deficiency of vitamin E causes damage to the reproductive system of both males and females, and increased fragility of RBCs and muscular weakness.

6. **Vitamin K** : This vitamin is a mixture of vitamin K_1 and K_2. It is fat soluble and stable to heat. Vitamin K is present in leafy vegetables, fish, eggyolk and liver.

Function : It plays a vital role in coagulation properties of blood. Its deficiency leads to profuse bleeding even from small wounds and causes disturbances in bleeding time and clotting time of blood.

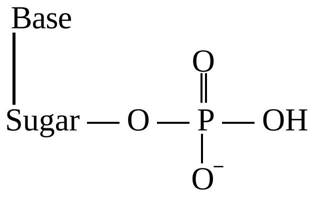
22.8 NUCLEIC ACIDS :

Nucleic acid was first isolated in 1871 by a Swiss physician and chemist *Friedrich Miescher*. He isolated a substance from the nuclei of the pus cells and named it as *nuclein*. This substance was quite different from the carbohydrates and proteins. Later, it was found that the nuclein had acidic properties and it was renamed by **Altman** in 1889 as nucleic acid. **Nucleic acid** is a substance, which is responsible for the transmission of hereditary characters.

Nucleic acids are long chain biopolymers present in most living cells either in the free state or bound to proteins as nucleoproteins. The nucleic acids are biopolymers of high molecular mass with nucleotide as their repeating units. As regards their elemental composition, the nucleic acids contain carbon, hydrogen , oxygen , nitrogen and phosphorous.

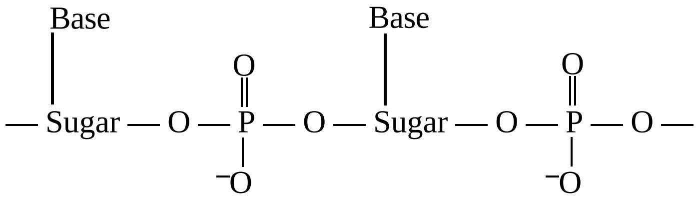
(a) Composition of Nucleic acids :

We know, **nucleotide** is the monomeric unit of nucleic acid. A **nucleotide** is further made up of a **phosphoric acid unit** and a **nucleoside**. A **nucleoside** is made up of two components, that is a pentose sugar and a nitrogen containing heterocyclic base. Thus, in general, a nucleotide and a nucleic acid can be represented as follows:



$$\overset{\displaystyle \text{Base}}{\overset{|}{\text{Sugar}}} - O - \underset{\displaystyle O^-}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{P}}}} - OH$$

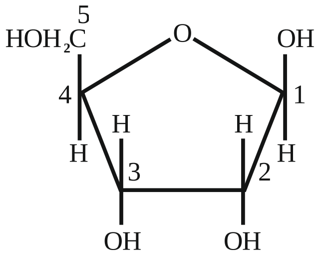
(A nucleotide)



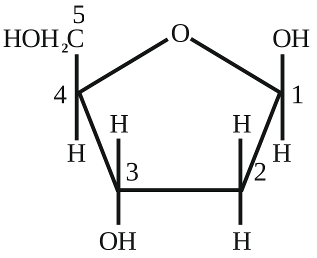
$$- \overset{\displaystyle \text{Base}}{\overset{|}{\text{Sugar}}} - O - \underset{\displaystyle {}^-O}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{P}}}} - O - \overset{\displaystyle \text{Base}}{\overset{|}{\text{Sugar}}} - O - \underset{\displaystyle {}^-O}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{P}}}} - O -$$

(A nucleic acid)

Two types of sugars are present in nucleic acids. They are β-D ribose and β-D-2-deoxyribose. Both these pentose sugars are present in furanose form. The bases present in nucleic acids are purine and pyrimidine.



β-D ribose



β-D-2- deoxyribose

The bases derived from purine are adenine (A) and guanine (G). Similarly, the bases derived from pyrimidine are thymine (T), uracil (U) and cytosine (C).

The nucleic acid which contains only ribose is known as **ribonucleic acid (RNA)** and the nucleic acid which contains deoxyribose is known as **deoxyribonucleic acid (DNA)**. Nucleic acids are long chain polymers of nucleotides and therefore they are known as polynucleotides.

DEOXYRIBONUCLEIC ACID (DNA) :

DNA is composed of two strands of polynucleotides coiled around each other in the form of a double helix resembling a gently twisted ladder. This information was given by James Dewey Watson who received Nobel prize along with Francis Crick and Maurice Wilkins with the foundation of a new field of **Molecular Biology**.

The bases (specific pyrimidine groups) on one strand of DNA are paired with the bases (purine groups) on the other stand with the help of hydrogen bonding, which is highly specific because the structures of bases allow only one mode of pairing. Adenine (A) pairs with only thiamine (T) via two hydrogen bonds while guanine (G) pairs with cytosine (C) through three hydrogen bonds. It is because the sequence of bases in one strand automatically determines that of other.

Double strand helix structure of DNA

The complimentary pairing of nucleotides bases explains how indentical copies of parental DNA pass on to two daughter cells thus transmitting inherent characters (heredity). Har Gobind Khurana, an Indian Scientiest shared the Nobel prize for Medicine and Physiology for cracking the genetic code while working at Cambridge, UK with Marshal Nirenberg and Robert Holley.

DNA FINGER - PRINTING :

Each person has unique finger prints which occur at the tips of the fingers being used for indentification. But unfortunately now fingerprints can be easily altered by surgery.

A sequence of bases on DNA is also unique for a person and information regarding this is called DNA finger printing. It is same for every cell and can not be altered by any treatment. For this reason DNA fingerprinting is now used :

(i) to determine paternity of an individual

(ii) in forensic laboratories for identification of criminals.

(iii) to identify dead bodies in any accident by comparing the DNA's of their parents or children.

(iv) to identify racial groups to rewrite biological evolution.

RIBONUCLEIC ACID (RNA) :

The process of translating coded message into action requires ribonucleic acid (RNA). The chemical constitution of RNA is almost similar to that of DNA except that the sugar in RNA is *ribose* and the base is *uracil* (U) in place of *thymine* (T) as in DNA. The structure of RNA in most organisms is single stranded, but appears helical because at some places it is wound back upon itself.

There are three kinds of RNA

(i) **Messenger RNA (m-RNA) :** This carries the genetic information from that template of DNA chain to the site of protein.

(ii) **Transfer RNA (t-RNA) :** This is the smallest of all the RNAs, single stranded and occurs free in the cytoplasm of the cell, one for each aminoacid found in protein.

(iii) **Ribosomal RNA (r-RNA) :** This is present in ribosome and constitutes about 80% of total RNA. r-RNA helps in protein synthesis and carries no message of DNA.

BIOLOGICAL FUNCTIONS OF NUCLEIC ACIDS :

The two important biological functions of nucleic acids are replication and protein synthesis.

(i) Replication is a process by which a single DNA molecule produces two identical copies of itself. Replication is an enzyme catalysed process. The two identical copies of DNA produced from the original DNA are then passed on to the two new cells resulting from cell division. In this way hereditary characters are tranmitted from one cell to another. DNA is double stranded.

(ii) Another important function of RNA is the synthesis of proteins. The RNA molecule present in the cell nucleus is responsible for the synthesis of all the proteins present in a cell. Protein synthesis is a very fast process.

CHAPTER (22) AT A GLANCE

1. **Carbohydrates :** Carbohydrates are polyhydroxy aldehydes or ketones and their derivatives or substances that yield one of these compounds on hydrolysis.
2. **Aminoacids :** Aminoacids are regarded as building blocks of proteins.
3. **Proteins :** Proteins are linear or branched polymers of α-amino acids linked by peptide bonds. Enzymes, many hormones and antibiotics are also proteins in nature.
4. **Nucleic acids :** Nucleic acids contain long chain of alternating sugar and phosphate units with bases attached to the sugar residue. DNA contains deoxyribose sugar and bases are adenine, guanine, cytosine and thiamine. RNA contains ribose suagr and bases like adenine, guanine, cytosine and uracil. While DNA is present in the molecule of the cell, RNA is

present outside the nucleus in the surrounding fluid called cytoplasm. DNA is the chemical bases of heredity and have the coded message for the proteins to be synthesised in the cell. The three types of RNA i.e. *m*-RNA, *t*-RNA and *r*-RNA carry out the synthesis of proteins in the cell. RNA is single stranded whereas DNA is double stranded.

5. **Vitamins :** Vitamins are specific organic compounds required by animals, bacteria and micro-organisms in small amounts for the maintenance and normal growth of life. Vitamin A, D, E and K are fat soluble while vitamin B and C are water soluble. Deficiency of these vitamins causes diseases.
6. **Enzymes :** They are considered as conjugated proteins. They are globular proteins (soluble in water, acid and alkali).
7. **Hormones :** Chemicals released by one or more cells that affect cells in other part of the organism are called hormones. They may be amine-derived hormones (catecholamines, thyroxine etc), peptide hormones or protein hormones, (insulin, TRH and growth hormones), lipid and phospholipid derived hormones - steroid hormones (testoterone, cortisol, calcitriol etc). Plant hormones are called *auxins*. Other plant hormones are *gibberellins* and *cytokinins*, *ethylene*, *abscisic acid* etc.

QUESTIONS

A. VERY SHORT ANSWER QUESTIONS (1 MARK EACH)

1. Enzymes are ________ type of proteins
2. The carbohydrate present in DNA molecule is ________
3. The general formula of a carbohydrate is ________
4. DNA stands for ________
5. RNA stands for ________
6. Name the nucleic acids which are used in protein synthesis
7. Name the bases present in both RNA and DNA.
8. Which vitamin is Ascorbic acid ?
9. Which vitamin is obtained from sunlight ?
10. Which elements are generally present in proteins ?
11. What are the hydrolysis products of sucrose ?
12. Name two carbohydrates which act as biofuels.
13. What causes the disease sickle cell anaemia ?
14. __________ is the chemical basis of heredity.
15. Name the building blocks of proteins.
16. Which polysaccharide is stored in the liver of animals.

[**Answers**. 1. Conjugated, 2. Deoxyribose, 3. $C_x(H_2O)_y$, 4. Deoxyribonucleic acid, 5. Ribonucleic acid, 6. DNA & RNA, 7. Adenine, guanine and cytosine, 8. Vitamin C 9. Vitamin D, 10. C, H, O, N, S & P., 11. Glucose & Fructose, 12. Starch and glycogen, 13. Defective Haemoglobin, 14. DNA, 15. α - Amino acids, 16. Glycogen]

B. SHORT ANSWER QUESTIONS (2 MARKS EACH) :

1. What are oligosaccharides ? Give one example.
2. What are zwitter ions?
3. What is meant by inversion of sugar?
4. What are polysaccharides? Give one example.
5. What happens when protein is denatured?
6. What is a prosthetic group?
7. What are proteins?
8. What are monosaccharides ? Give one example.
9. Why can not vitamin C be stored in our body?
10. What are the different types of RNA found in the cell?
11. What is the difference between a nucleoside and a nucleotide?
12. What are enzymes?
13. What are anomers?
14. What are nucleic acids?
15. How does glucose differ from fructose?

C. SHORT ANSWER QUESTIONS (3 MARKS EACH) :

1. Classify Carbohydrates giving one example of each class.
2. What are the important units of protein ? What is the name of the bond between these units ?
3. Give two biological functions of nucleic acids.
4. Differentiate between DNA and RNA.
5. Where does the water present in the egg go after boiling the egg?
6. How are the vitamins classified?
7. Explain mutarotation of D-glucose.
8. Name four important vitamins of vitamin B complex. Deficiency of which of these vitamins causes *beriberi* ?
9. Name three hormones from three different classes of vertebrate hormones.
10. Name two plant hormones giving one function of each of them.

11. What are reducing and non-reducing sugars?
12. What is the basic differenc between starch and cellulose?
13. How can you explain the absence of aldehyde group in the pentaacetate of D-glucose.
14. Differentiate between globular and fibrous proteins.
15. Explain why glucose and fructose give the same osazone, on treatment with excess phenyl hydrazine.

D. LONG QUESTIONS :

1. What are proteins ? How are they classfied ? Discuss their primary, secondary and tertiary structures.
2. What are vitamins ? Classify the vitamins along with the roles of various vitamins in our body.
3. How glucose is synthesized? Discuss the ring structure of D-Glucose.
4. What are monosaccharides? Elucidate the structure of D-Fructose.
5. What are hormones? How are they classified. Give one example of each along with its functions.
6. What are plysaccharides? Discuss the structure of starch and cellulose.

E. MULTIPLE CHOICE QUESTIONS :

1. Which one of the following is a disaccharide ?

   (a) glucose (b) starch (c) sucrose (d) cellulose
2. Ascorbic acid is the name of

   (a) a vitamin (b) an enzyme (c) an aminoacid (d) a hormone
3. Which of the following is a monosaccharide ?

   (a) maltose (b) fructose (c) sucrose (d) lactose
4. Ribose is an example of

   (a) ketohexose (b) disaccharide (c) pentose (d) polysaccharide
5. Enzymes are

   (a) proteins (b) minerals (c) oils (d) fatty acids
6. The main structural feature of protein is

   (a) the ester linkage (b) the ether linkage (c) the peptide linkage (d) all of the above
7. In nucleic acids, the sequence is

   (a) phosphate - base - sugar (b) sugar - base - phosphate

   (c) base-sugar - phosphate (d) base- phosphate - sugar
8. $\alpha-$ and $\beta-$ glucose differ in the orientation of –OH group around

   (a) C_1 (b) C_2 (c) C_3 (d) C_4

9. Vitamin A deficiency leads to a disease known as

   (a) Beriberi (b) Night blindness (c) Scurvy (d) All

10. Insulin is

    (a) Antibiotic (b) Antiseptic (c) Hormone (d) Vitamin.

11. Which of the following is known as antiscurvy factor ?

    (a) Vitamin A (b) Vitamin C (c) Vitamin D (d) Vitamin E

12. The fat -soluble vitamin is

    (a) Retinol (b) Thiamine (c) Riboflavin (d) Pyridoxine

13. Vitamin B_1 is called

    (a) Riboflavin (b) Thiamine (c) Pyridoxine (d) Cyanocobalamine

14. Which of the following contains cobalt ?

    (a) Chlorophyll (b) Haemoglobin (c) Vitamin C (d) Vitamin B_{12}

15. Hair, Finger nails, hoofs etc. are all made of

    (a) Fat (b) Vitamins (c) Proteins (d) Iron

16. Proteins are polymers of amino acids. Which of the following is not a protein ?

    (a) Wool (b) Nails (c) Hair (d) DNA

17. The chemical messengers produced in ductless glands are

    (a) Vitamins (b) Hormones (c) Lipids (d) Antibiotics

18. The function of DNA is

    (a) to synthesise RNA (b) to contain message to carry out specific protein synthesis (c) to carry hereditary characteristics from generation to generation (d) all of the above.

19. Adenosine is an example of

    (a) Nucleoside (b) Nucleotide (c) Purine base (d) Pyrimidine base

20. Two purine bases present in both DNA & RNA are

    (a) Guanine & Adenine (b) Guanine and Uracil (c) Adenine & Thiamine (d) Cytosine and Uracil

21. A mixture of amylose and amylopectin is called

    (a) starch (b) cellulose (c) lactose (d) sucrose

22. Which vitamin is water soluble?

    (a) Vitamin-K (b) Vitamin-B (c) Vitamin-E, (d) Vitamin-A

23. The number of chiral carbons in $\beta-$ D(+) glucose are

    (a) three (b) four (c) five (d) six

24. Which hormone contains iodine.

    (a) Thyroxine (b) Insulin (c) Adrenaline (d) Testosterone

25. Sugars have the suffix

(a) –ol (b) –al (c) –ose (d) –one

26. The function of enzymes in the living system is to

(a) provide immunity
(b) provide energy
(c) catalyse biochemical reaction
(d) transport oxygen

27. The helical structure of protein is stabilised by

(a) Hydrogen bonds
(b) Dipetide bonds
(c) Peptide bonds
(d) van der Waals forces.

28. Vitamin A is called

(a) Ascorbic acid
(b) Retinol
(c) Calciferol
(d) Tocopherol

ANSWERS

1. (c) 2. (a) 3. (b) 4. (c)
5. (a) 6. (c) 7. (c) 8. (a)
9. (b) 10. (c) 11. (b) 12. (a)
13. (b) 14. (d) 15. (c) 16. (d)
17. (b) 18. (d) 19. (a) 20. (a)
21. (a) 22. (b) 23. (c) 24. (a)
25. (c) 26. (c) 27. (a) 28. (b)

* * *

UNIT - XV

CHAPTER - 23

POLYMERS

23.1 INTRODUCTION :

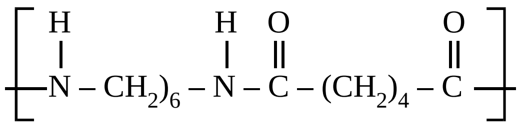
Polymers (Greek words, poly = many and meros = parts) are defined as the large molecules having very high molecular mass consisting of a very large number of repeating structural units joined together through covalent bonds in a regular fashion. The simple molecules from which the repeating structural units are derived are called **monomers** and the process of formation of polymers from their monmers is called **polymerization**.

For example,

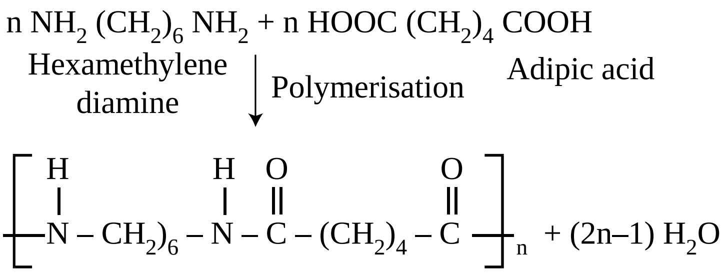
(i) In case of polythene, polymer which is obtained by the polymerization of ethene molecules the repeating structural unit $\left[CH_2 - CH_2 \right]$ is derived from the nonomers ethene.

$$\underset{\text{(Monomer)}}{\underset{\text{Ethene}}{n\,CH_2 = CH_2}} \xrightarrow{\text{Polymerization}} \underset{\text{(Polymer)}}{\underset{\text{Polythene}}{\left(CH_2 - CH_2 \right)_n}}$$

(ii) In case of Nylon 6, 6, two different types of monomers used are hexamethylene diamine and adipic acid interacting with each other with the repeating structural unit



$$\left[-\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - \right]$$



$$\underset{\text{Hexamethylene diamine}}{n\,NH_2\,(CH_2)_6\,NH_2} + \underset{\text{Adipic acid}}{n\,HOOC\,(CH_2)_4\,COOH}$$

$$\downarrow \text{Polymerisation}$$

$$\left[-\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - \right]_n + (2n-1)\,H_2O$$

Nylon 6, 6

Polymers because of their large size are also termed as macromolecules. But the reverse is not true i.e. all polymers are macromolecules but all macromolecules are not polymers. For example, proteins and nucleic acids are regarded as macromolecules but not polymers as these molecules do not contain repeating structural units. Where as polythene can be regarded as both a macromolecule and a polymer as it contains a number of repeating structural units.

23.2 CLASSIFICATION OF POYMERS :

Polymers can be classified into different categories basing upon different factors. These are :

A. Classification based upon the sources :

Depending on the source from which they are derived, poymers can be categorized into three classes, such as;

(a) **Natural polymers :** Polymers which are found in nature i.e. in animals and plants are called natural polymers. Examples are :

(i) Proteins, silk, wool etc.

(ii) Polysacharides : Starch (potatoes, rice etc.), cellulose of cotton and wood.

(iii) Natural rubber

(b) **Semi-synthetic polymers :** These are chemically modified natural polymers. For example cellulose on acetylation with acetic anhydride in presence of con. H_2SO_4 gives cellulose diacetate which is used for making threads of acetate rayon and other materials like films, glasses etc. Other examples are gun cotton and vulcanized rubber.

(c) **Synthetic polymers :** Man made polymers like plastics (polyethylene, polypropylene), fibres (nylon and terylene), rubbers (neoprene) adhesives, paints etc. are called synthetic polymers.

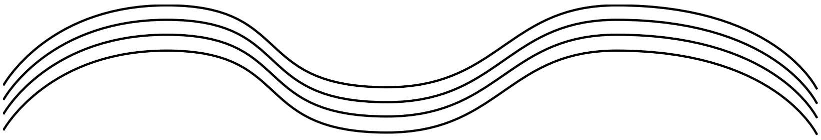
B. Classification based on structure :

On the basis of structures, polymers can be classified into three types. These are:

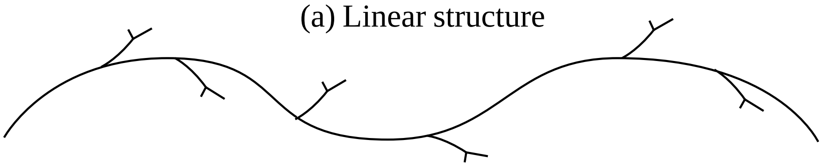
(a) **Linear polymers :** In linear polymers the monomers are joined together to form long straight chains of polymers molecules [Fig. 23.1(a)]. The various polymeric chains are then stacked over one another to give a well packed structure resulting with high melting point, high densities and high tensile strength. Examples of linear polymers are high density polythene, nylon, polyester etc.

(b) **Branched chain polymers :** In these polymers the manomer units not only combine to produce the linear chain called the main chain, but also form branches of different lengths along the main chain [Fig. 23.1(b)]. Due to branching these polymers do not pack well for which they have lower melting points, densities and tensile streangth than that of linear polymers. Examples of this class are low density polythene, starch, glycogen, amylopectin etc.

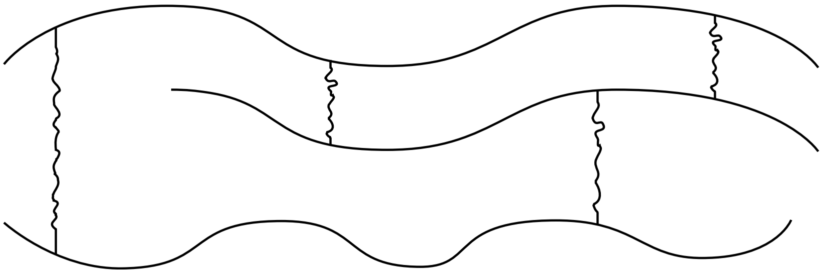
(c) Cross-linked or three demensional network polymers : In these type of polymers the initially formed linear polymer chains are joined together to form a three-dimensional network structure [Fig. 23.1(c)]. Only two cross-links per polymer chain are required to join together all the long chain polymer molecules to form a giant molecule. Because of the presence of cross-links, these polymers are called **cross-linked polymers**, which are usually formed from bifunctional and trinfunctional monomers containing strong covalent bonds between various linear polymer chains. Examples are bakelite, melamine etc.



(a) Linear structure



(b) Branched chain structure



(c) Three dimensional network or cross-linked structure

Fig. 23.1 : Different structures of polymers.

C. Classification based on the nature of repeating structural units :

Depending on the nature of repeating structural units, polymers are of two types:

(a) Homopolymers : Polymers containing only one type of monomers are called homopolymers.

$$n\,CH_2 = CH_2 \xrightarrow{\text{Polymerization}} \left(CH_2 - CH_2 \right)_n$$

Ethene — Polythene

(Monomer) — (Polymer)

Other examples are polyvinyl chloride (PVC), polyacrylonitrile (PAN), polypropylene etc.

(b) **Copolymers :** Polymers whose repeating structural units are derived from two or more types of monomers are called copolymers. Nylon-66 is a copolymers of hexamethylene diamine and adipic acid.

$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH$$

Hexamethylene diamine (Monomer) Adipic acid (Monomer)

$$\downarrow \text{Polymerization}$$

$$\left[HN-(CH_2)_6-NH-CO-(CH_2)_4-CO \right]_n + (2n-1)\,H_2O$$

Nylon 6, 6

(Copolymer)

Other examples are Buna–S–rubber, bakelite, polyethylene terephthalate (PET) etc.

D. **Classification based on mode of polymerization :**

Polymerization i.e. the process of synthesis of polymers can be carried out in two modes. These are addition polymerization and condensation poymerization. Based on these two methods of synthesis, the poymers can be classified into two categories.

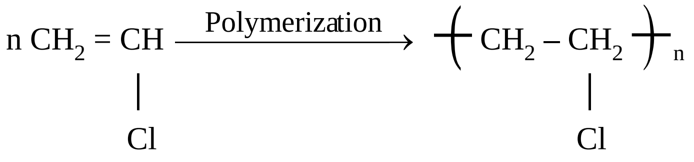
(a) **Addition polymers :** Addition polymers are those polymers which are formed by the repeated addition of monomers molecules possesing double or triple bonds without elemination of simple molecules like water. These are also referred to as chain growth polymers. For examples :

(i) ethene polymerises to from polyethylene.

$$n\,CH_2=CH_2 \xrightarrow{\text{Polymerization}} \left(CH_2-CH_2 \right)_n$$

Ethelene Polyethylene

(ii) Vinyl chloride polymerises to form polyvinylchloride (PVC).

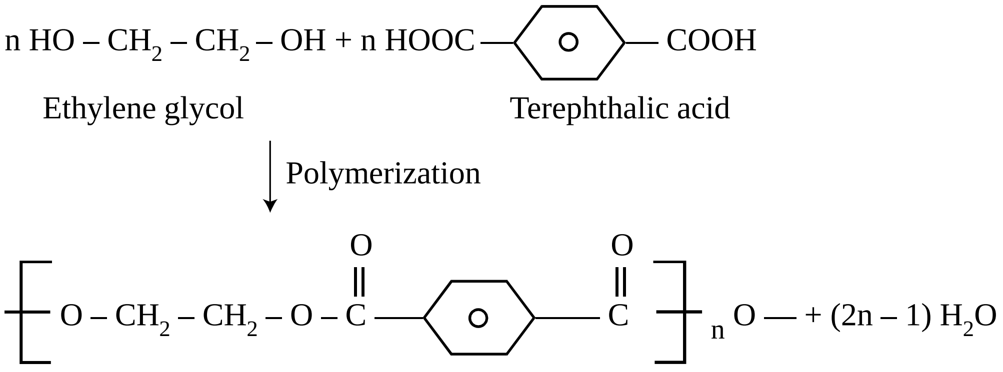


$$n\,\underset{\displaystyle |\atop Cl}{CH_2=CH} \xrightarrow{\text{Polymerization}} \left(\underset{\displaystyle |\atop Cl}{CH_2-CH_2} \right)_n$$

Vinyl chloride PVC

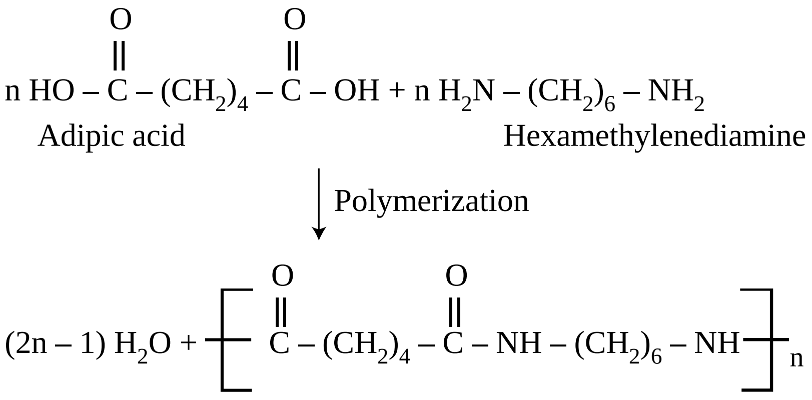
(b) **Condensation polymers :** Polymers which are formed by the codensation reaction of molecules having more than one functional group resulting with the removal of simple molecules like H_2O, NH_3 or CH_3OH. These are also termed as step growth polymers. For examples :

(i) Dacron (polyester) is produced by successive condensation of ethylene glycol molecules and terephthalic acid molecules.



Dacron (polyethylene terephthalate)

(ii) Similarly Nylon – 6, 6 is a condensation polymer.



$$n\,HO-\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-\overset{\overset{O}{\parallel}}{C}-OH + n\,H_2N-(CH_2)_6-NH_2 \xrightarrow{\text{Polymerization}} (2n-1)\,H_2O + \left[\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-\overset{\overset{O}{\parallel}}{C}-NH-(CH_2)_6-NH\right]_n$$

Nylon – 6, 6

E. Classification based on molecular forces :

Depending on the magnitude of intermolecular forces like hydrogen bond, van der Waals forces and dipole–dipole interactions existing between the adjacent polymer chains, the polymers can be classfied into four categories. These are :

(a) Elastomers : Polymers in which the intermolecular forces of attraction between the polymer chains are the weakest resulting with high degree of elasticity are called **elastomers**.

Elastomers are amorphous polymers consisting of randomely coiled molecular chains of irregular shape having a few cross links. Under the application of an external force, these randomly coiled chains straighten out and the polymer is stretched. But as soon as the force is withdrawn, because of very weak van der Waal forces of attraction, the polymers return to its original randomly coiled state. Thus, whereas weak van der Waals forces of attraction permit the polymer chains to be stretched, the cross links help the polymer to come back to the original position when the force is withdrawn. (Fig. 23.2)

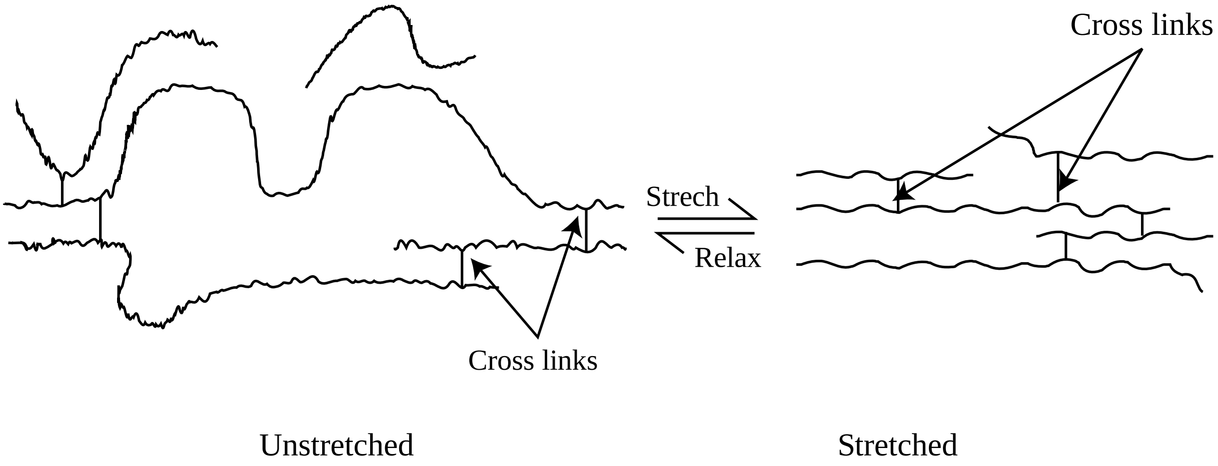


Fig. 23.2 : Unstretched and stretched forms of an elastomer

Most important examples of elastomers are buna-S, buna-N, neoprene etc.

(b) **Fibres :** Fibres are the thread forming polymers possessing very high tensile strength, high modulus, but least elasticity which are attributed due to very strong inter molecular forces of attractions like hydrogen bonding or dipole interactions (Fig. 23.3)

Most important examples are polyamides (nylons), polyesters (terylene, dacron) and polyacrylonitrile (orlon, acrilan).

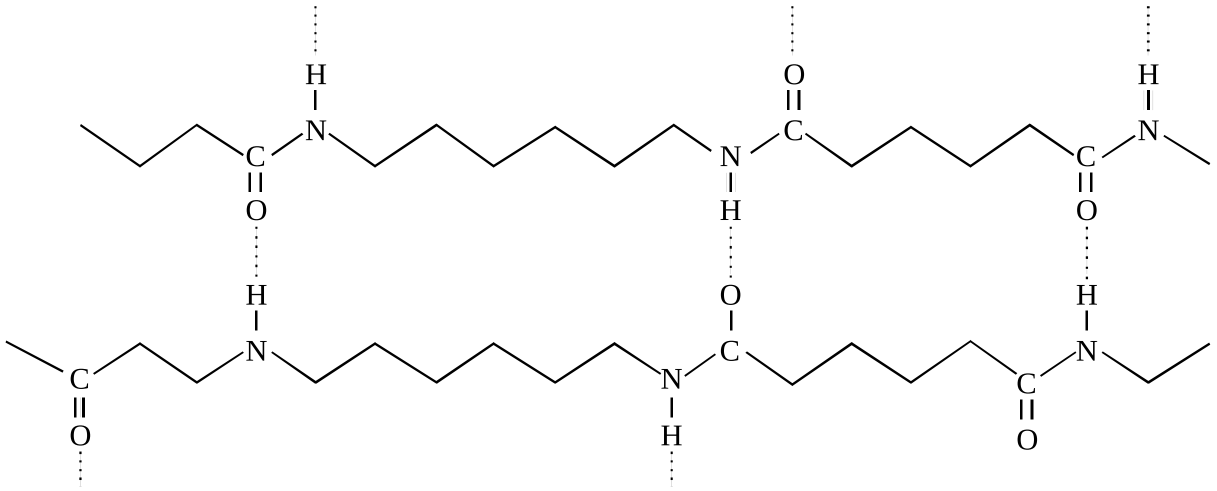


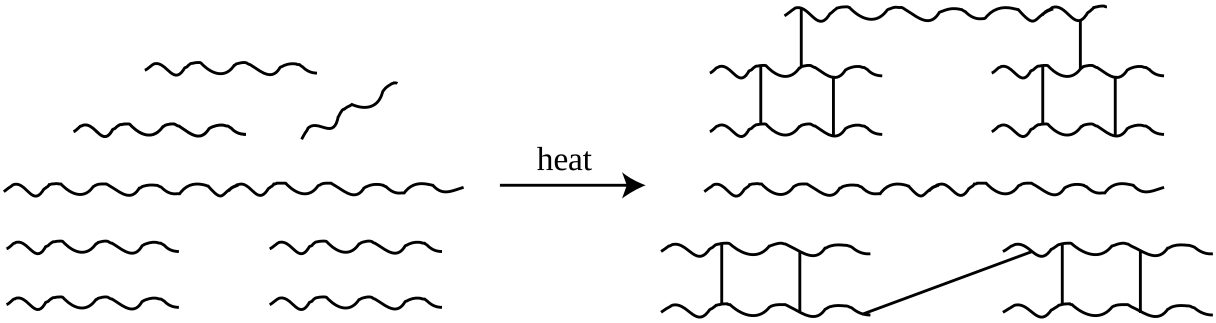
Fig. 23.3: Hydrogen bonding in Nylon-6,6

(c) **Thermoplastic polymers :** Thermoplastic polymers are the linear or slightly branched long chain molecules which can be easily softened repeatedly on heating and hardened on cooling with little change in their properties because of the inter molecular forces being intermediate between elastomers and fibres.

When heated these polymers melt and form a fluid which can be moulded into any desired shapes and then cooled to get the desired product.

Some common examples of thermoplastics are polythene, polypropylene, polystyrene, polyvinyl chloride, teflon, polyacrylonitrile etc.

(d) **Thermosetting polymers :** Thermosetting polymers are semi-fluid substances with low molecular masses which when heated in a mould undergo change in chemical composition to give a hard, infusible and insoluble mass due to extensive cross-linking between different polymer chains to give a three-dimensional network solid. (Fig. 23.4).



Uncrosslinked polymer Highly cross-linked polymer

Fig. 23.4 : Conversion of uncrosslinked polymer into highly cross-linked thermosetting polymer on heating.

In contrast to thermoplastic polymers thermosetting polymers can be heated only once as these undergo prermanent change on melting and set into a new solid which can not be remelted. Thus these can not be reused. Common examples are : phenol-formaldehyde resins (bakelite), urea-formaldehyde resins etc.

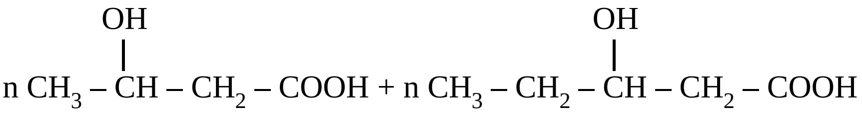
F. **Classification based on the basis of degradability of polymers by micro-organisms:**

Polymers may be classified into biodegradable polymers and non-degradable polymers on the basis of their degradability by micro-organisms.

(a) **Biodegradable polymers :** These are the polymers which are degraded by micro-organisms during a certain period thus not posing any threat to our environment.

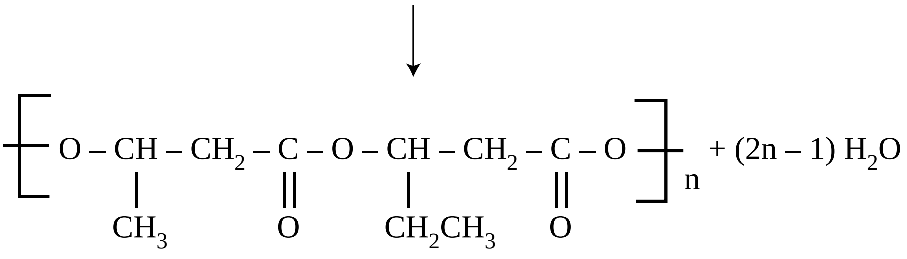
Some new biodegradable synthetic polymers have been designed and developed containing functional groups similar to the functional groups present in biopolymers. Biopolymers like starch, cellulose etc. disintegrate themselves in biological systems during a certain period of time by enzymatic hydrolysis and to some extent by oxidation and hence are biodegradable. Hence they do not cause any pollution. Examples of biodegradable polymers are :

(i) **Poly β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV) :** It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which two monomer units are connected by ester linkages.



$$n\,CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_2-COOH + n\,CH_3-CH_2-\overset{\overset{\large OH}{|}}{C}H-CH_2-COOH$$

3-Hydroxy butanoic acid 3-Hydroxypentanoic acid

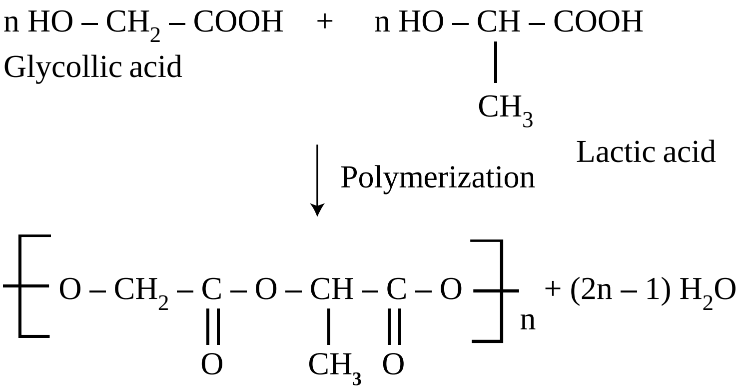


$$\downarrow$$
$$\left[O-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-O \right]_n + (2n-1)\,H_2O$$

PHBV

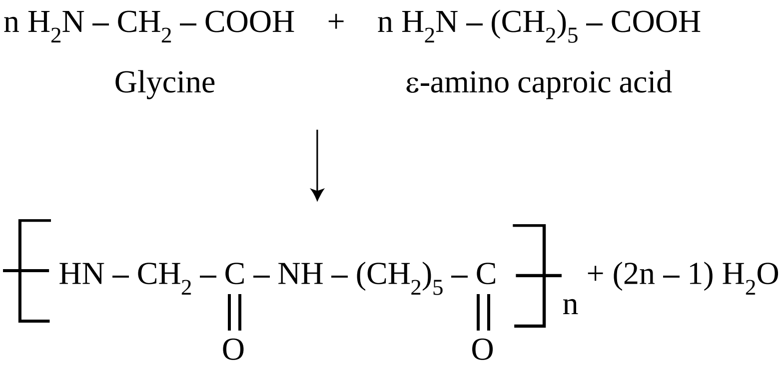
PHBV is used in special packaging, orthopaedic devices and in controlled drug release. When a drug is enclosed in a capsule of PHBV, it is released only when the polymer is degraded in the body.

(ii) **Poly-Glycollic acid - Poly Lactic acid :** This is a copolymer of glycollic acid and lactic acid, commercially called **dextron**. This was the first biodegradable polyester used as sutures, that is for stitching of wounds after operation.



$$\underset{\text{Glycollic acid}}{n\,HO-CH_2-COOH} + \underset{\text{Lactic acid}}{n\,HO-\underset{CH_3}{\underset{|}{CH}}-COOH}$$
$$\Big\downarrow \text{Polymerization}$$
$$\left[O-CH_2-\underset{O}{\underset{\|}{C}}-O-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-O \right]_n + (2n-1)\,H_2O$$

(iii) **Nylon 2 - Nylon 6 :** It is an alternating copolymer of glycine and ε-aminocaproic acid and is biodegradable.



$$\underset{\text{Glycine}}{n\,H_2N-CH_2-COOH} + \underset{\varepsilon\text{-amino caproic acid}}{n\,H_2N-(CH_2)_5-COOH}$$
$$\downarrow$$
$$\left[HN-CH_2-\underset{O}{\underset{\|}{C}}-NH-(CH_2)_5-\underset{O}{\underset{\|}{C}} \right]_n + (2n-1)\,H_2O$$

Nylon 2 - Nylon 6

All the above polymers are plyesters and are therefore, susceptible towards hydrolysis of their ester links. Hence these are completely degraded and absorbed by the body within 15 days to one month for which these are mainly used for medical goods such as surgical sutures, tissue in growth materials or for controlled drug release devices, plasma substitutes etc.

(b) **Non-degradable polymers :** The polymers which are not degraded by micro-organisms within a suitable period and seriously affect the environment leading to environmental pollution are called non-degradable polymers.

Most of the commercially synthesized polymers like polythene, PVC, teflon, nylons, polyesters, bakelite etc are the examples of non-degradable polymers.

23.3 GENERAL METHODS OF POLYMERIZATION :

The process of polymerization can be carried out by two methods.

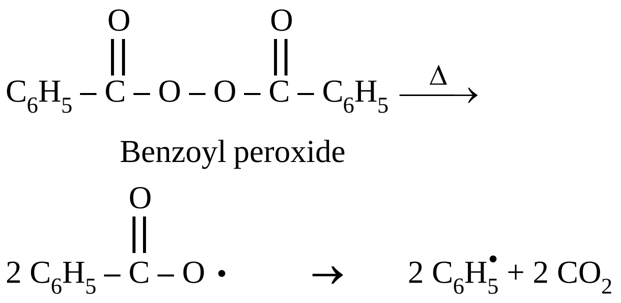
A. ADDITION POLYMERIZATION :

The type of polymerization involving successive addition of monomer units to the growing chain with a reactive intermediate such as a free radical, a carbocation or a carbanion is termed as addition polymerization. This can also be termed as chain growth polymerization as after each act of addition of monomer the reactive intermediate is regenerated leading to increase in chain length.

The monomers used are unsaturated compounds like alkenes, alkadienes, and their derivatives with free radical governed addition polymerization is the most common method.

(a) **Free radical addition polymerization :** Addition polymerization of alkenes or their derivatives involves the chain reactions in which the chain carrier is a free radical formed in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide etc. This vinyl polymerization involves three steps.

(i) **Initiation :** The initiation of polymerization is a two step process. The first step is the decomposition of the initiator to produce a free radical.



$$C_6H_5 - \overset{\overset{\large O}{||}}{C} - O - O - \overset{\overset{\large O}{||}}{C} - C_6H_5 \xrightarrow{\Delta}$$

Benzoyl peroxide

$$2\,C_6H_5 - \overset{\overset{\large O}{||}}{C} - O\,\bullet \rightarrow 2\,C_6\overset{\bullet}{H_5} + 2\,CO_2$$

Bezoyloxy radical Phenyl radical

In the second step, the free radical interacts with the vinyl monomer to give rise the initiated monomer radical.

$$\dot{C}_6H_5 + CH_2 = CH_2 \rightarrow C_6H_5 - CH_2 - \dot{C}H_2$$

Ethene

(ii) Propagation : This step involves the addition of the new monomer radical to the monomer molecules in rapid succession to form a growing polymer chain.

$$C_6H_5 - CH_2 - \dot{C}H_2 + CH_2 = CH_2 \rightarrow C_6H_5 - CH_2 - CH_2 - CH_2 - \dot{C}H_2$$

$$\downarrow + (n-1)\,CH_2 = CH_2$$

$$C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - \dot{C}H_2$$

(iii) Termination : In the termination step, the growing chain radical deactivates either by combination or by disproportionation to form a dead polymer.

Combination :

$$2\,C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - \dot{C}H_2 \longrightarrow$$

$$C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - CH_2 - CH_2 - CH_2 \left(CH_2 - CH_2 \right)_n C_6H_5$$

Polythene (Dead polymer)

Disproportionation :

$$2\,C_6H_5 \left(CH_2 - CH_2 \right)_n CH_2 - \dot{C}H_2 \longrightarrow$$

$$C_6H_5 \left(CH_2 - CH_2 \right)_n CH = CH_2 + C_5H_6 \left(CH_2 - CH_2 \right)_n CH_2CH_3$$

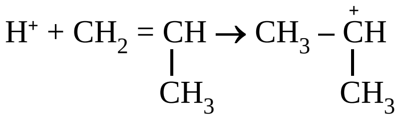
Dead polymers

(b) Cationic polymerization : Cationic polymerization takes place by the addition of a positively charged ion to a vinyl monomer to form a carbocation as the reaction intermedicate. The initiators used for the cationic polymerization include strong protic acids like H_2SO_4 or Lewis acids like $AlCl_3$, BF_3 in the presence of water.

The reaction proceeds through three steps such as initiation, propagation and termination.

(i) Initiation : $HB \rightarrow H^+ + B^-$

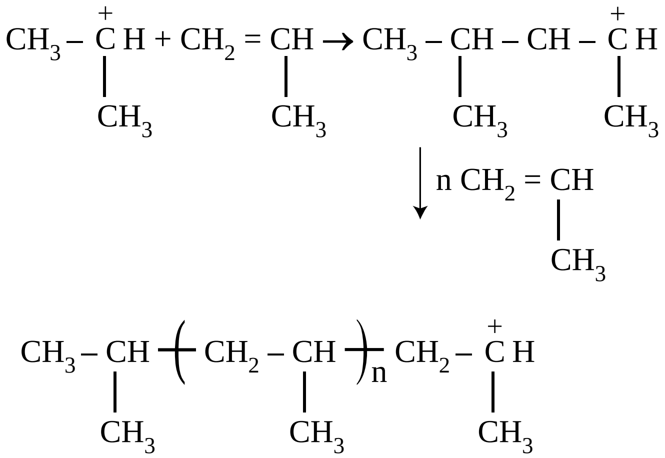
Protic acid



$$H^+ + CH_2 = \underset{\displaystyle CH_3}{\underset{|}{CH}} \rightarrow CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}H}}$$

Propene

(ii) Propagation :

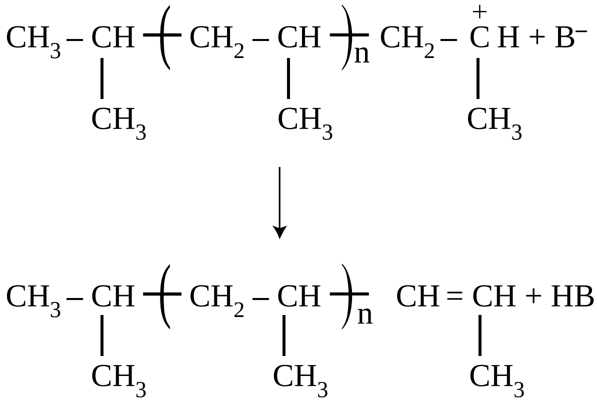


$$CH_3-\underset{CH_3}{\overset{+}{C}}H + CH_2=\underset{CH_3}{CH} \rightarrow CH_3-\underset{CH_3}{CH}-CH-\underset{CH_3}{\overset{+}{C}}H$$

$$\downarrow n\,CH_2=\underset{CH_3}{CH}$$

$$CH_3-\underset{CH_3}{CH}\left(CH_2-\underset{CH_3}{CH}\right)_n CH_2-\underset{CH_3}{\overset{+}{C}}H$$

(iii) Termination : Transfer to counter ion



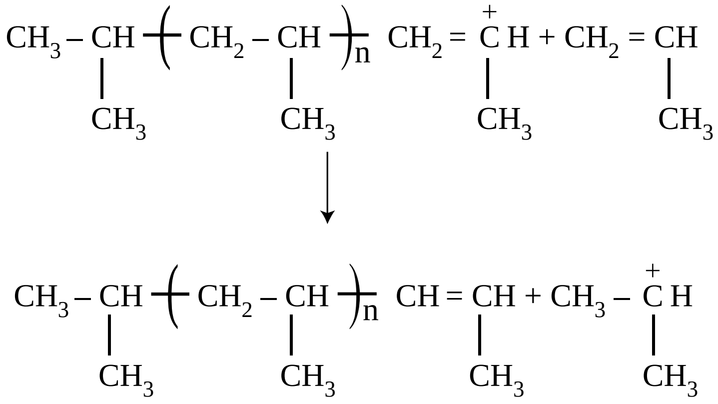
$$CH_3-\underset{CH_3}{CH}\left(CH_2-\underset{CH_3}{CH}\right)_n CH_2-\underset{CH_3}{\overset{+}{C}}H + B^-$$

$$\downarrow$$

$$CH_3-\underset{CH_3}{CH}\left(CH_2-\underset{CH_3}{CH}\right)_n CH=\underset{CH_3}{CH} + HB$$

Polypropene

Transfer to monomer :



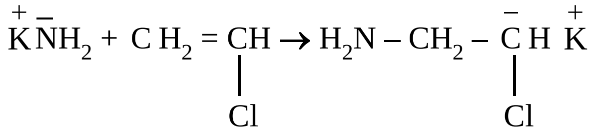
$$CH_3-\underset{CH_3}{CH}\left(CH_2-\underset{CH_3}{CH}\right)_n CH_2=\underset{CH_3}{\overset{+}{C}}H + CH_2=\underset{CH_3}{CH}$$

$$\downarrow$$

$$CH_3-\underset{CH_3}{CH}\left(CH_2-\underset{CH_3}{CH}\right)_n CH=\underset{CH_3}{CH} + CH_3-\underset{CH_3}{\overset{+}{C}}H$$

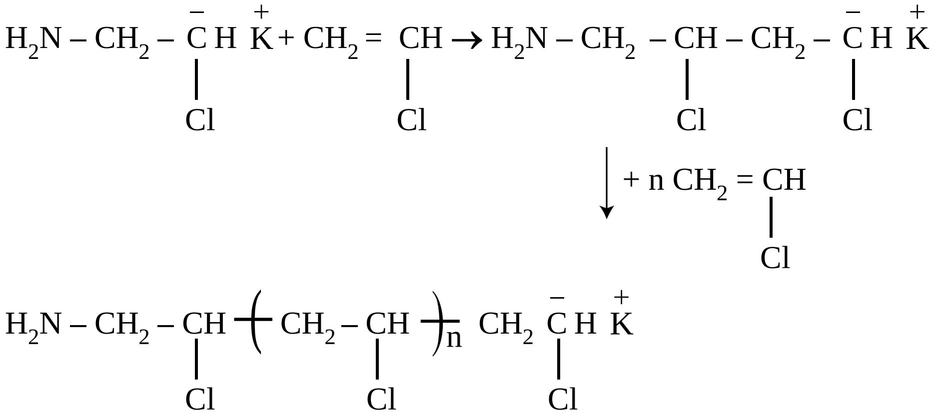
(c) Anionic polymerization : Anionic polymerization involves the successive addition of vinyl monomers to a negatively charged species known as carbanion as reaction intermediate formed by the reaction of a negative ion or group to the monomer molecule. The initiators used for the anionic polymerization are strong bases like potassium amide or lithium amide. The steps involved are :

(i) Initiation :



$$\overset{+}{K}\overset{-}{N}H_2 + CH_2 = \underset{\substack{|\\ Cl}}{CH} \rightarrow H_2N - CH_2 - \underset{\substack{|\\ Cl}}{\overset{-}{C}}H\,\overset{+}{K}$$

(ii) Propagation :



$$H_2N - CH_2 - \underset{\substack{|\\ Cl}}{\overset{-}{C}}H\,\overset{+}{K} + CH_2 = \underset{\substack{|\\ Cl}}{CH} \rightarrow H_2N - CH_2 - \underset{\substack{|\\ Cl}}{CH} - CH_2 - \underset{\substack{|\\ Cl}}{\overset{-}{C}}H\,\overset{+}{K}$$

$$\downarrow + n\,CH_2 = \underset{\substack{|\\ Cl}}{CH}$$

$$H_2N - CH_2 - \underset{\substack{|\\ Cl}}{CH} \left(CH_2 - \underset{\substack{|\\ Cl}}{CH} \right)_n CH_2\,\underset{\substack{|\\ Cl}}{\overset{-}{C}}H\,\overset{+}{K}$$

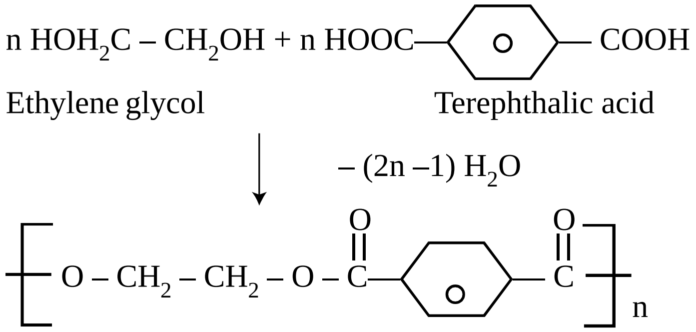
The most important aspect of the anionic plymerization is that the termination is absent in this case. If inert solvents and pure reactants are used, the system will result in the formation of carbanion end-group. Hence the anionic polymers are also termed as **living polymers**.

B. CONDENSATION POLYMERIZATION :

Condensation polymerizaton is the type of polymerization involving the condensation between two bifunctional monomers with the loss of simple molecules like H_2O, NH_3, HCl etc. leading to the formation of high molecular mass polymers.

The reaction regenerates a bifunctional species for which the sequence of condensation goes on till any one of the reactants is totally consumed. This type of polymerization is therefore termed as step growth polymerization.

The simplest example of the condensation polymer is the polyethylene terephthalate (PET) formed by the condensation of ethylene glycol and terephthalic acid with the elimination of water molecules.

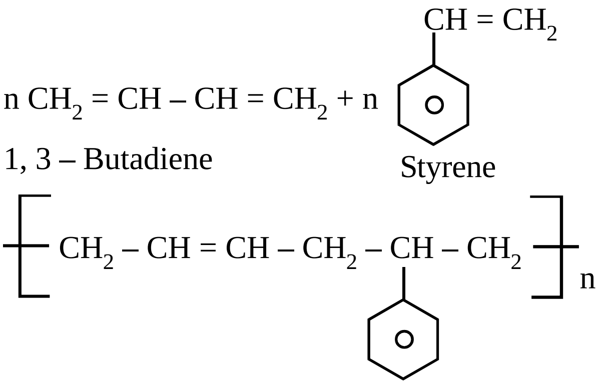


Polyethylene terephthalate (Terylene or Dacron)

23.4 COPOLYMERIZATION :

A polymer consisting of two or more chemically different types of monomer units in the chain is called a copolymer and the process of synthesis of copolymer is called copolymerization which may be a chain growth polymerization or a step growth polymerization.

For example, a mixture of 1, 3 – butadiene and styrene can form a copolymer.



Butadiene-styrene copolymer

The properties of copolymers are quite different from that of homopolymers. For example, butadiene-styrene copolymer is quite tough and is a good substitute for natural rubber and is used for the manufacture of floor tiles, cable insulation, autotyres etc.

Copolymers can be classified into four types basing on the distribution of different monomers in the chain. Suppose A and B are two monomers.

(i) **Random copolymers :** These are the copolymers in which the monomers are randomly arranged.

– A – B – A – A – A – B – B – A –

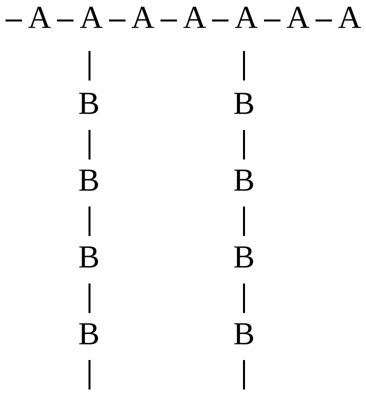
(ii) **Alternating copolymers :** In case of alternating copolymers the monomers are arranged alternately in the chain.

– A – B – A – B – A – B –

(iii) **Block copolymers :** Block copolymers contain long sequence of monomers in a linear chain.

– A – A – A – A – B – B – B – B – A – A – A – A –

(iv) **Graft copolymers :** Graft copolymers consist of main homopolymer chain with branches of another type of homopolymer.



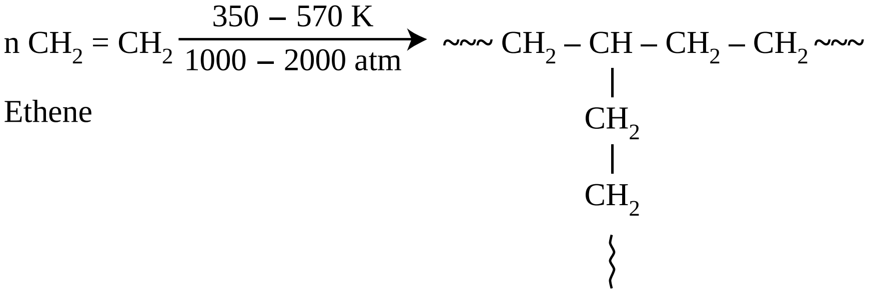
23.5 SOME IMPORTANT POLYMERS :

A. POLYTHENE :

It is a polymer of ethylene. Two types of polythenes can be synthesized depending on the conditions of synthesis with different types of intiators having widely different properties. These are :

(a) Low density polythene : The low density polythene is manufactured by heating pure ethylene to 350 - 570 K under pressure of 1000 - 2000 atmospheres and in presence of a trace of oxygen or peroxide following free radical mechanism.

It consists of highly branched chain molecules, for which these molecules do not pack well resulting with low density and low melting point. Low density polythene is a transparent polymer of moderate tensile strength and high toughness. It is mainly used (i) as a packing material in the form of thin plastic film bags (ii) for insulating wires and cables, and (iii) in manufacturing toys, squeeze bottles and flexible pipes.



$$n\,CH_2 = CH_2 \xrightarrow[1000\,-\,2000\text{ atm}]{350\,-\,570\text{ K}} \sim\sim\sim CH_2 - \underset{\underset{\underset{\wr}{CH_2}}{|}}{\underset{\underset{CH_2}{|}}{CH}} - CH_2 - CH_2 \sim\sim\sim$$

Ethene

Low density polythene

(b) High density polythene : High density polythene is prepared by co-ordination polymerization where ethene is heated to 330 – 350 K under a presure of 6–7 atmospheres in the presence of a catalyst consisting of triethyl aluminium and titanium tetrachloride (Ziegler-Natta catalyst).

$$n\,CH_2 = CH_2 \xrightarrow[(Et)_3\,Al\,+\,TiCl_4]{330\,-\,350\text{ K},\;6\,-\,7\text{ atm.}} \left(CH_2 - CH_2 \right)_n$$

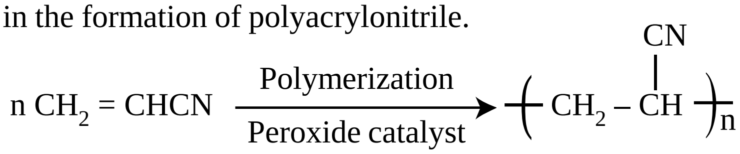
High density polythene

This polymer consists of linear chains, for which the molecules can be closely packed in space resulting in very high density and high melting point. It is quite harder, tougher and has greater tensile strength than low density polythene.

It is used for (i) manufacturing containers like buckets, dustbins, bottles etc and (ii) manufacturing different housewares, pipes etc.

B. POLYACRYLONITRILE (PAN) OR ORLON :

Vinyl cyanide (acrylonitrile) on polymerization in the presence of a peroxide catalyst results in the formation of polyacrylonitrile.



$$n\ CH_2 = CHCN \xrightarrow[\text{Peroxide catalyst}]{\text{Polymerization}} \left(CH_2 - \overset{\overset{CN}{|}}{C}H \right)_n$$

Acrylonitrile Polyacrylonitrile

PAN also known as **acrilon** or **orlon** is used for (i) making blankets, sweaters, bathing suits etc. (ii) for making synthetic carpets.

C. POLYTETRAFLUOROETHYLENE (PTFE) OR TEFLON :

Telfon is an addition polymer of tetrafluoroethylene formed on heating in the presence of a free radical initiator at high pressure.

$$n\ CF_2 = CF_2 \xrightarrow[\text{Heat, High pressure}]{\text{Catalyst}} \left(CF_2 - CF_2 \right)_n$$

Tetrafluoroethene Teflon

Teflon is a very tough meterial and is resistant towards heat, action of chemicals such as acids and bases. it is used:

(i) as material resistant to heat and chemical attack

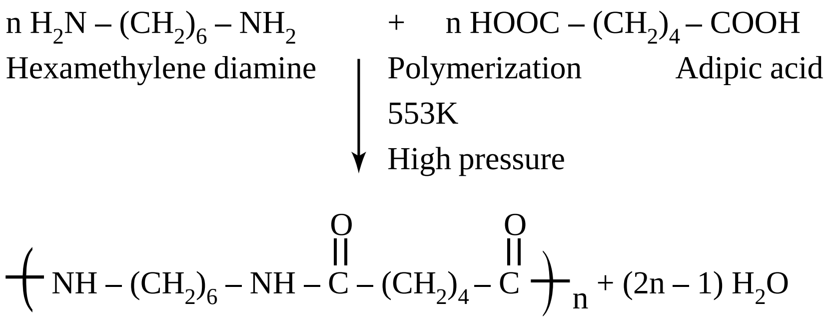
(ii) for coating articles and cookware to make them non-sticky as non-sticky utensils.

(iii) for making gaskets, pump packings, valves, seals etc.

D. POLYAMIDES OR NYLONS

Polyamides with amide linkages (– CO – NH –) in the chain are formed by the condensation polymerization of diamines with dibasic acids and also of amino acids and their lactams. Polyamides popularly known as **nylons** are of different types as follows :

(a) **Nylon - 6, 6 :** Nylon - 6, 6 can be prepared by heating equimolar mixture of hexamethylene diamine and adipic acid under high pressure. It is given the name nylon - 6, 6 since both hexamethylene diamine and adipic acid contain six carbon atoms each.



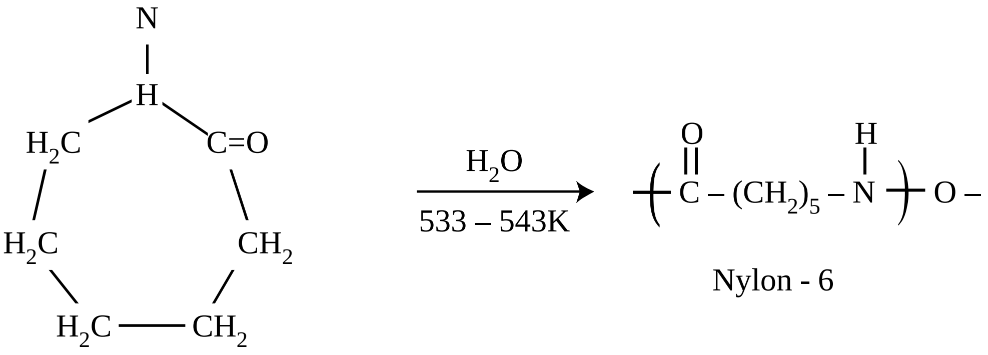
$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH \xrightarrow[\text{553K, High pressure}]{\text{Polymerization}} \left(NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n + (2n-1)\,H_2O$$

Hexamethylene diamine, Adipic acid

Nylon – 6, 6

Nylon - 6, 6 is used for making tyre cord, fishing nets, climbing ropes, strings for sports rackets and bristles for brushes.

(b) **Nylon - 6 :** Nylon -6 can be synthesized by heating caprolactam with water at a high temperature.



Caprolactam

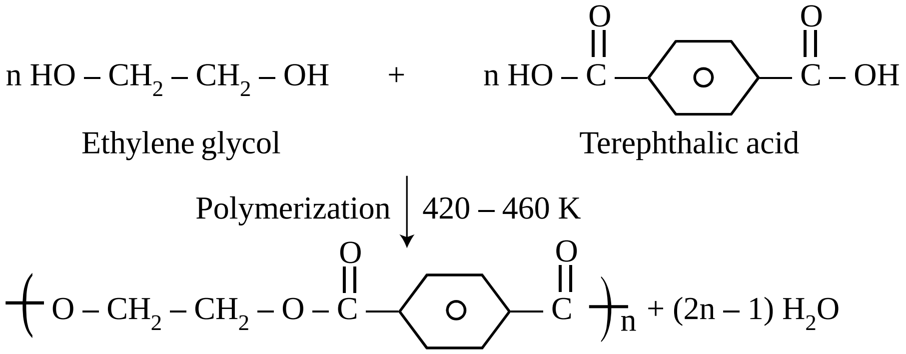
Nylon - 6

Nylon - 6 is used for the manufacture of ropes, tyre cords and fabrics.

E. POLYESTERS :

Polyesters are the polymers with ester linkages $(-\overset{O}{\overset{\|}{C}}-O-)$ which can be formed by the condensation of dicarboxylic acids with diols.

Dacron or terylene is the best example of polyester, being prepared by the condensation of ethylene glycol and terephthalic acid with elimination of water at 420 – 460 K in the presence of a catalyst consisting of a mixture of zinc acetate and antimony trioxide.



Ethylene glycol

Terephthalic acid

Terylene or Dacron

It is used for (i) making textile, sarees, dress materials and curtains.

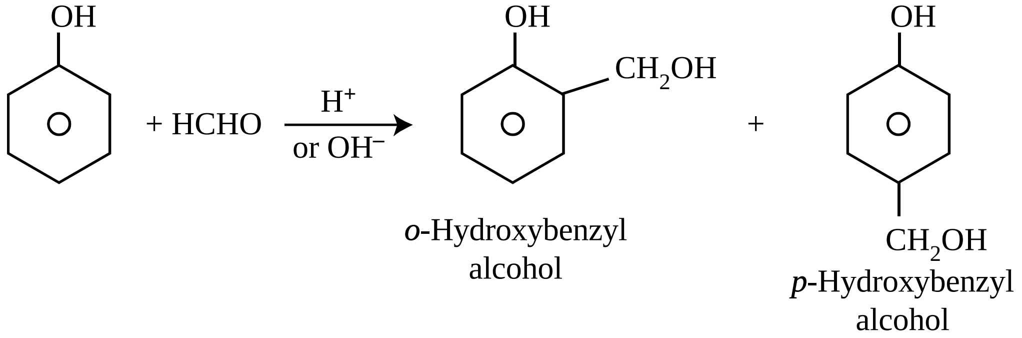
(ii) making sails of sail-boats.

(iii) making water houses for fire-fighting operations.

(iv) making conveyor belts.

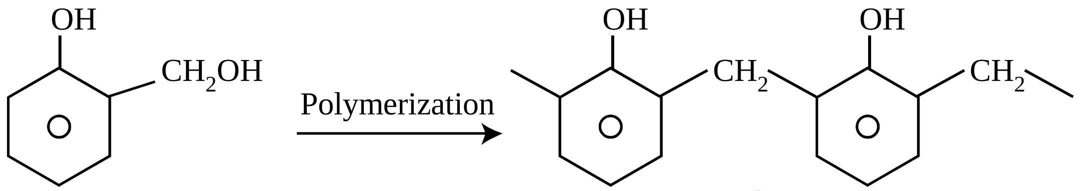
F. PHENOL-FORMALDEHYDE RESIN (BAKELITE) :

When phenol reacts with formaldehyde in the presence of either an acid or a base catalyst, polymer of high molecular mass is obtained. The process starts with the initial formation of *ortho* and *para* hydroxymethyl phenol derivatives which further react with phenol to form compounds having rings joined to each other through methylene bridges resulting initially with a linear polymer called **Novolac**.



o-Hydroxybenzyl alcohol

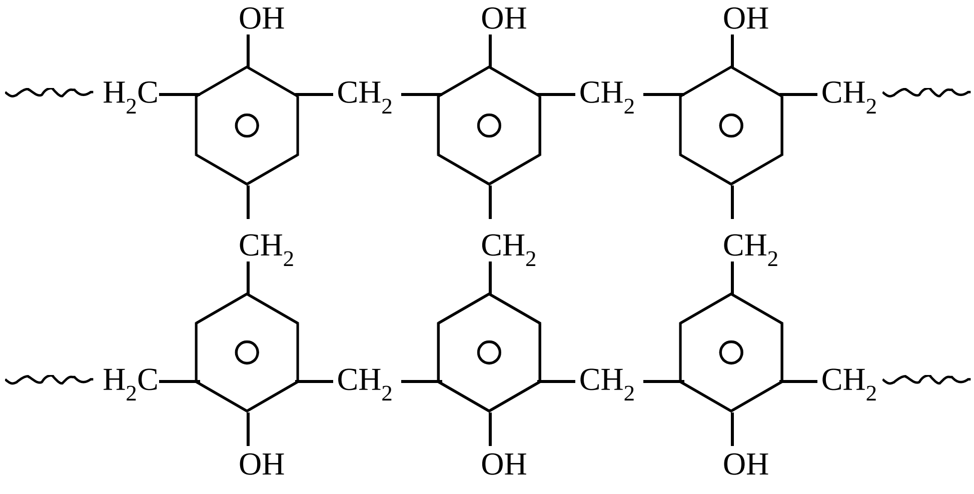
p-Hydroxybenzyl alcohol



Novolac

Novolac an heating with formaldehyde undergoes cross linking to form an infusible solid mass called **Bakelite**.

$$\text{Novolac} + \text{n HCHO} \xrightarrow[-\text{n } H_2O]{\Delta}$$



Bakelite

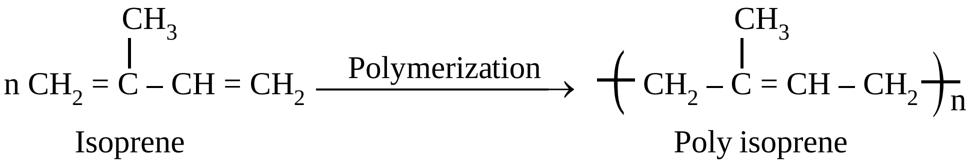
Bakelite is used for

(i) making combs, fountain pen barrels, gramophone records etc.

(ii) making electrical goods like switches, plugs etc.

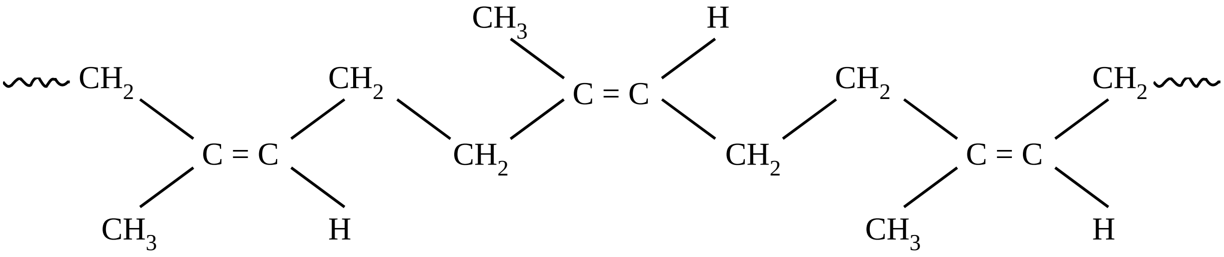
G. RUBBER

(a) Natural Rubber : Rubber is a natural linear polymer of isoprene (2-methy - 1, 3 - butadiene)



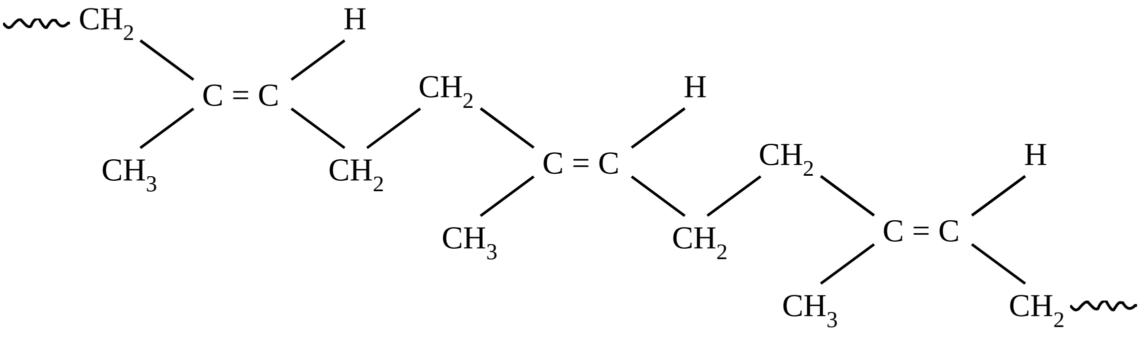
$$n\,CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerization}} \left(CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right)_n$$

In polyisoprene each repeating unit contains a double bond, it exhibits cis-trans isomerism. Natural rubber has all cis-configuration having weak van der Waals interactions between various chains thus resulting with a coiled structure. Hence natural rubber can be stretched like a spring and exhibits elastic properties.



Cis-polyisoprene
(Natural rubber)

In contrast synthetic rubber (gutta percha) obtained by free radical plymerization isoprene has all trans-configurations.



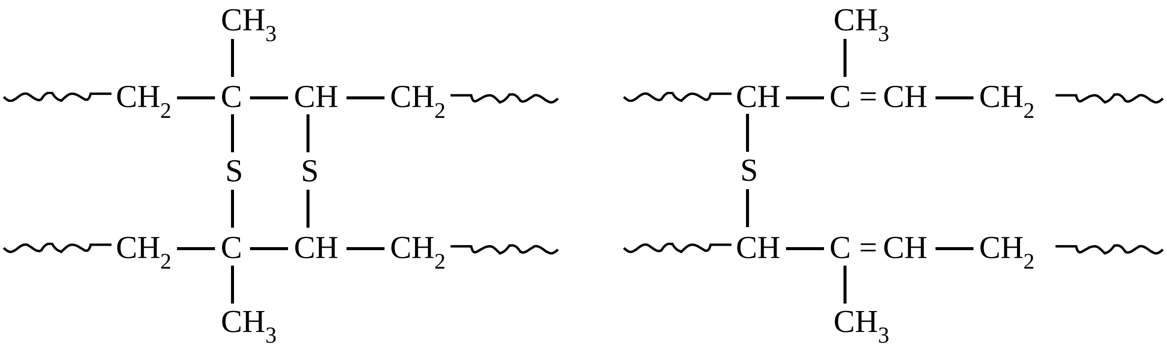
Trans-isoprene
(Gutta-percha)

Vulcanization of rubber :

The process of heating natural rubber with sulphur and an appropriate additive like zinc oxide at temperature 373K to 415K to improve its properties is called **vulcanization**. The vulcanized rubber has exclient elasticity, low water absorption tendency and resistant to the action of organic solvents and oxidising agents in contrast to the natural rubber which is soft and sticky, having high water absorption capactiy, low tensile strength and resistance to abrasion.

During vulcanization linear chains of isoprene units present in natural rubber get cross-linked through sulphur bridges at the allylic positions, which make rubber hard and stronger removing sticky quality of the natural rubber since the individual chains can no longer slip over the other because of locking together in a giant size molecule.

The structures of vulvanized rubber can be represented as :



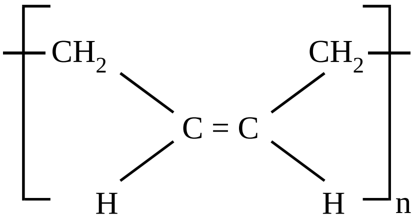
The extent of hardness or toughness depends on the amount of sulphur added. For making tyre rubber 5% sulphur is used, whereas for ebonite 20 – 25% sulphur and for making battery case rubber 30% sulphur is used.

(B) Synthetic Rubber :

(i) **Cis-polybutadiene** : Polymerization of 1, 3-butadiene in the presence of Zeigler - Natta catalyst results with cis-polybutadiene having properties similar to that of natural rubber. It is used for making footwear, tyres and toys etc.

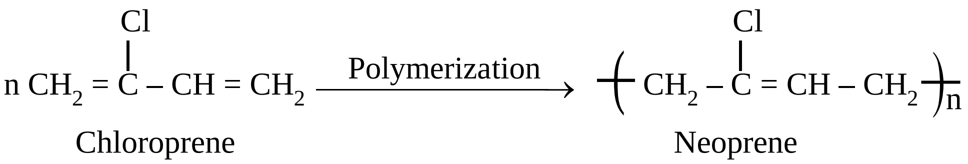
$$n\,CH_2=CH-CH=CH_2 \xrightarrow[(C_2H_5)_3Al\,+\,TiCl_3]{\text{Zeigler - Natta catalyst}}$$

1, 3 - Butadiene



Cis - 1, 4 - Polybutadiene

(ii) **Neoprene :** Neoprene is prepared by the free radical polymerization of chloroprene (2-chloro -1, 3- butadiene).



$$\underset{\text{Chloroprene}}{n\,CH_2 = \overset{\overset{\displaystyle Cl}{|}}{C} - CH = CH_2} \xrightarrow{\text{Polymerization}} \underset{\text{Neoprene}}{\left(CH_2 - \overset{\overset{\displaystyle Cl}{|}}{C} = CH - CH_2 \right)_n}$$

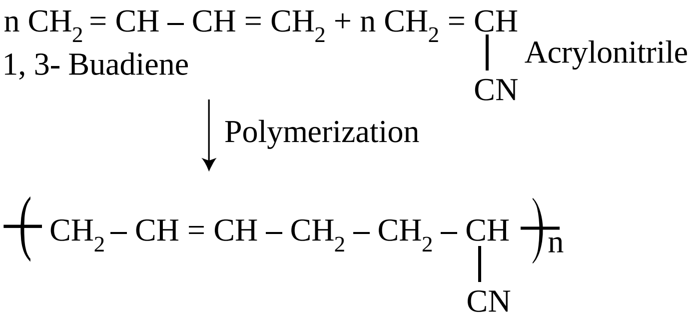
Neoprene is used

(i) for manufacturing hoses, shoes heel, stoppers etc as it is resistant to oils, gasoline and other solvents and stable towards aerial oxidation.

(ii) as an insulator.

(iii) for making conveyer belts and printing rollers.

(iii) **Buna-N :** Buna-N is a copolymer of 1, 3-butadiene and acrylonitrile prepared by free radical polymerization.



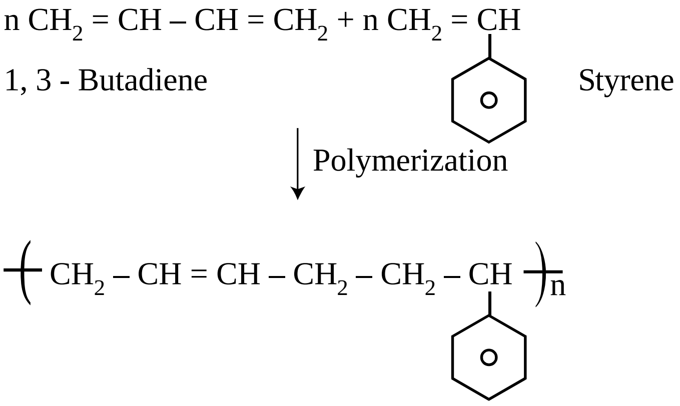
$$\underset{\text{1, 3- Buadiene}}{n\,CH_2 = CH - CH = CH_2} + n\,CH_2 = \underset{\underset{\displaystyle CN}{|}}{CH} \ \text{Acrylonitrile}$$

$$\Big\downarrow \text{Polymerization}$$

$$\left(CH_2 - CH = CH - CH_2 - CH_2 - \underset{\underset{\displaystyle CN}{|}}{CH} \right)_n$$

Buna - N is used for making oil seals, manufacture of hoses and tank linings.

(iii) **Buna-S :** It is a copolymer of 1, 3 butadiene and styrene.



$$\underset{\text{1, 3 - Butadiene}}{n\,CH_2 = CH - CH = CH_2} + n\,CH_2 = \underset{\underset{\displaystyle C_6H_5}{|}}{CH} \ \text{Styrene}$$

$$\Big\downarrow \text{Polymerization}$$

$$\left(CH_2 - CH = CH - CH_2 - CH_2 - \underset{\underset{\displaystyle C_6H_5}{|}}{CH} \right)_n$$

Buna - S

It is used for the manufacture of automobile tyres, rubber soles, water proof shoes, belts etc.

CHAPTER (23) AT A GLANCE

1. **Polymers** are macromolecules built up by repeating structural units joined by the covalent bonds, whereas all macromolecules are not polymers.
2. **Monomers** are the simple raw materials (molecules) from which polymers are synthesized.
3. Polymers can be classfied on different basis i.e. **natural** or **synthetic**, **homopolymer** or **copolymer**, **linear** or **branched** chain polymer etc.
4. The process of polymerization may be **addition polymerization** or **chain growth polymerization** and **condensation polymerization** or **step growth polymerization**.
5. **Polythene**, **polystyrene**, **teflon**, **orlon** etc are examples of **addition** polymers where as **Nylon**, **Bakelite** and **Dacron** are the examples of **condensation** polymers.
6. **Bifunctionality** is the minimum criterion for a molecule to act as monomer.
7. **Natural rubber** is a **cis-1,4-polyisoprene** the properties of which can be modified by **vulvanization** process on heating with sulphur. **Neoprene**, **Buna-S** & **Buna-N** are the examples of **synthetic rubbers**.
8. In order to avoid the hazardous effect of polymeric wastes, **biodegradable polymers** like **PHBV, Nylon-2, Nylon-6** have been synthesized successfully.

QUESTIONS

A. VERY SHORT QUESTIONS (1 mark each) :

(a) Bakelite is formed by the chemical combination of phenol and ——.
(b) Name the linkage (bond) prevailing in the proteins.
(c) Write any two uses of Neoprene.
(d) Mention two uses of Buna-S.
(e) What is Buna-N?
(f) What is neoprene?
(g) Name the monomer used for the preparation of Teflon.
(h) What is PHBV?
(i) What is a copolymer?
(j) Name the monomer of Nylon-6
(k) What are thermosetting polymers?
(l) Name the monomers used for Novolac.
(m) What are the monomers required for terylene?
(n) Define the term polymerization.

B. SHORT ANSWER QUESTIONS (2 marks each) :

(a) What are polymers ? Give two examples.

(b) What is Tefflon ? Give one of its uses.

(c) What is natural rubber? Why it can not be used for making foot-ball bladders?

(d) What is terylene? How is it prepared?

(e) What are biodegradable polymers? Give two examples.

(f) What is Nylon-6, 6? How is it prepared?

(g) What are natural and synthetic polymers? Give one example of each.

(h) What do you mean by vulvanization of rubber?

(i) Define copolymerization and give one example.

(j) What do you mean by free radical polymerization ? Name one initiator used for it.

C. SHORT ANSWER QUESTIONS (3 marks each) :

Distinguish between

(a) Thermoplastic and thermosetting polymers.

(b) Homopolymers and copolymers.

(c) Natural rubber and synthetic rubber.

(d) Addition polymerization and condensation polymerization.

(e) Nylon-6 and Nylon-6, 6

(f) Buna-N and Buna-S

(g) Novolac and Bakelite

D. LONG QUESTIONS (7 marks each) :

(a) What are polymers ? What are the different methods of their preparation? Name an important polymer and describe a method of its preparation with chemical equation.

(b) What are polymers? How are they classified on the basis of

(i) structure (ii) synthesis and (iii) molecular forces involved. Give one example of each kind.

(c) What are natural rubbers and what are synthetic rubbers? What is vulcanisation? How does it improve the characteristics of rubbers?

(d) What is free radical addition polymerization? What are the intiators used for it? Discuss the mechanism of free radical polymerization taking one example.

E. MULTIPLE CHOICE QUESTIONS :

1. Chloroprene is the repeating unit in
   (a) PVC
   (b) Polythene
   (c) Neoprene
   (d) Polystyrene
2. Orlon is a polymer of
   (a) Vinyl chloride
   (b) Styrene
   (c) Butadiene and adipic acid
   (d) Acrylonitrile
3. Which of the following is a condensation polymer?
   (a) Teflon
   (b) Bakelite
   (c) Buna-S
   (d) Neoprene
4. Natural rubber is a polymer of
   (a) Acrylonitrile
   (b) Isoprene
   (c) Vinyl chloride
   (d) Tetrafluoroethylene
5. Which of the following is not a condensation polymer?
   (a) Bakelite
   (b) Nylon
   (c) Dacron
   (d) Teflon
6. Teflon is a type of
   (a) Condensation polymer
   (b) Synthetic rubber
   (c) Addition polymer
   (d) None of these
7. Which of the following is synthetic rubber?
   (a) Buna-S
   (b) Polyisoprene
   (c) Dacron
   (d) None of these
8. Which is naturally occurring polymer?
   (a) Rayon
   (b) Nylon
   (c) Protein
   (d) PVC
9. Which of the followings is called a polyamide?
   (a) Rayon
   (b) Terylene
   (c) Nylon
   (d) Teflon
10. A raw material used in making nylon is
    (a) Adipic acid
    (b) Butadiene
    (c) Ethylene
    (d) Methyl methacrylate
11. Teflon is a polymer of
    (a) Monofuoroethene
    (b) Difluoroethene
    (c) Trifluoroethene
    (d) Tetrafluorethene
12. Which of the following is used to make non-stick cookware?
    (a) PVC
    (b) PET
    (c) Teflon
    (d) Nylon

13. Nylon-6,6 is obtained from

(a) Propene and adipic acid (b) Phenol and formalehyde

(c) Hexmethylene diamine and adipic acid (d) Adipic acid and phthalic acid

14. Nylon-6 is made from

(a) 1, 3 - Butadiene (b) Chloroprene

(c) Adipic acid (d) Caprolactam

15. Baby feeding bottles are generally made up

(a) Polystyrene (b) Polyurethane

(c) Polyamide (d) Polyester

16. Teflon, styrene and neoprene are all

(a) Monomers (b) Homopolymers

(c) Copolymers (d) Condesation polymers

ANSWER FOR MULTICPLE CHOICE QUESTIONS

1. (c) 2. (d) 3. (b) 4. (b) 5. (d) 6. (c) 7. (a) 8. (c) 9. (c) 10. (a)

11. (d) 12. (c) 13. (c) 14. (d) 15. (a) 16. (b)

* * *

UNIT - XVI

CHAPTER - 24

CHEMISTRY IN EVERYDAY LIFE

24.1 INTRODUCTION :

Life without Chemistry is totally impossible, because the basic needs of human being i.e. food, cloth and shelter involve the basic principle of Chemistry. Thus Chemistry has played a vital role in everyday life. For example, clothes like wool, silk, cotton, nylon etc. we wear, soaps and detergents used to wash them are all organic compounds. The food (carbohydrates, proteins, oils and fats etc.) we eat to nourish and build up our body are organic in nature. The house where we live uses cement, paints, adhesives, marbles etc., all involving the chemical processes. The medicines protecting us from diseases like antibiotics, sulphadrugs etc. are also boon of Chemistry. So the basic principles of Chemistry have influenced every sphere of human life.

24.2 CHEMICALS IN MEDICINE :

Chemical substances of natural or synthetic origin used for curing diseases and reducing suffering from pain are called **medicines** or **drugs**. The branch of science which deals with the treatment of diseases using suitable chemicals is known as **chemotherapy**.

Though all drugs are medicines and all medicines are drugs, medicine is safer to use having negiligible toxicity without causing addiction, whereas drug causes addiction with serious side effects.

Medicines are generally classified basing on the purpose for which they are used. Different classes of medicines are :

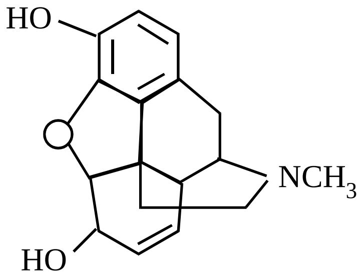
A. ANALGESICS

An analgesic may be defined as a drug that selectively relieves pain by acting on the central nervous system and on peripheral (external) pain mechanisms without significantly altering consciousness. Simply analgesics may be referred to the medicines used for getting relief form pain.

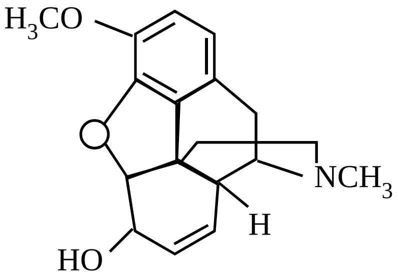
Analgesics are categorized into two classes :

(a) Narcotics : Drugs which produce sleep and unconsciousness are called narcotics, and are mainly used for the relief of post-operative pain, cardiac pain, pains of terminal cancer and in child birth.

Narcotic analgesics are mostly opium products which contains **morphine** and **codeine**. These are very effictive analgesics, but regular doses cause addiction. Other examples are **heroin** and **marijuana**.

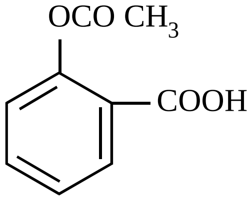


MORPHINE

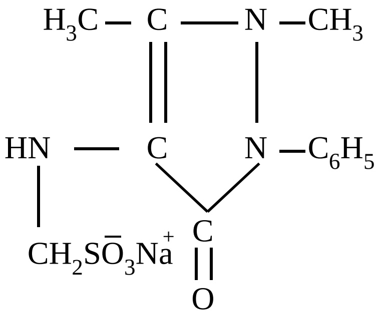


CODEIN

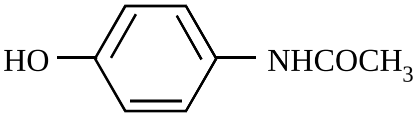
(b) Non-narcotics : Regular doses of this type of analgesics do not cause addiction. They give temporary relief from pain and possess anti-inflammatory property. Examples of non-narctoic analgesies are aspirin, analgin and paracetamol.



ASPIRIN



ANALGIN



PARACETAMOL

There have antipyretic properties also. Aspirin is the commonly used analgesic which gives relief from headache, muscular pain and toothache. The toxic side effect of using aspirin is gastric irritation leading to ulceration. Thus it should not be administered in empty stomach. But its calcium salt i.e. **DISPRIN** which is water soluble, is better than Aspirin having few side effects. Because of the side effects other analgesics like ibuprofen, naproxen are now being used. However because of anti blood clotting action af aspirin, it is still the drug of choice for prevention of **heart attacks** and reliever of **angina pains**.

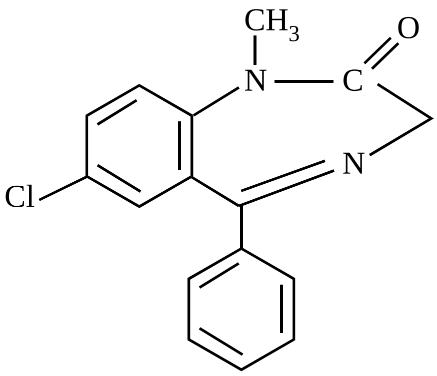
B. TRANQUILIZERS

Tranquilizers may be defined as the neurologically active drugs which help in reducing stress and fatigue by inducing a sense of well being.

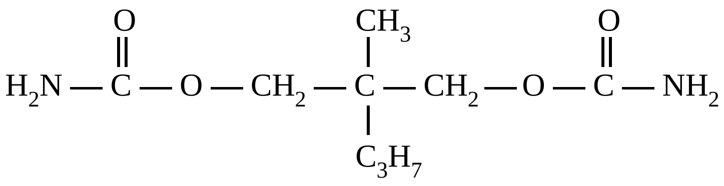
These affect the message transfer mechanisms from nerve to receptor for which they are used for the treatment of mild or even severe mental diseases. They form an essential component of sleeping pills.

Tranquilizers are of different types. Such as :

(a) Sedatives : These drugs are suitable for violent patients who are mentally upset. Examples are **calmpose** and **equanil**.



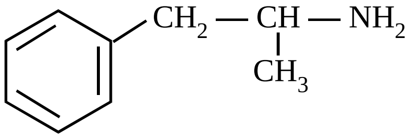
CALMPOSE



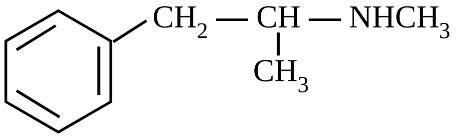
$$H_2N-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{C_3H_7}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-NH_2$$

EQUANIL

(b) Antidepressants : These drugs are also called mood elevators, which are given to those patients who lose self-confidence and are much depressed, thus improving their efficiency. Examples are **amphetamine** and **methamphetamine**.

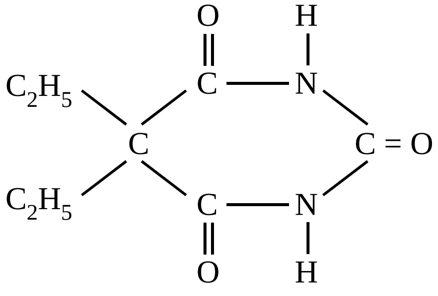


AMPHETAMINE
(Benzedrine)

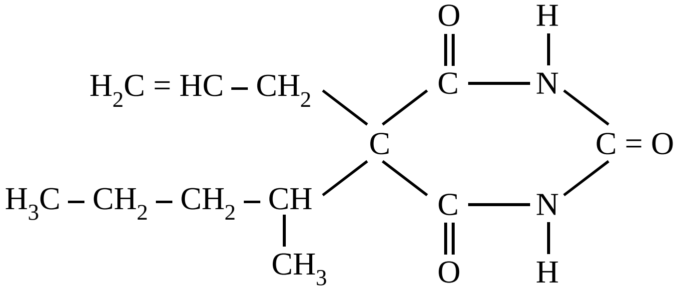


METHAMPHETAMINE
(Methedrine)

(c) Hypnotics : Luminal and **Seconal** are some important hypnotics producing sleep which are the derivative of barbituric acid called barbiturates. These are habit forming drugs.



LUMINAL



SECONAL

C. ANTISEPTICS AND DISINFECTANTS :

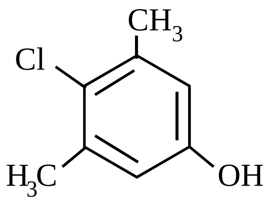
Antiseptics and disinfectants are the chemicals which either kill or prevent the growth of micro-organisms.

(a) Antiseptics : Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surface in order to kill or prevent the growth of micro-organisms in the form of antiseptic creams like **furacin**, **soframycin** etc.

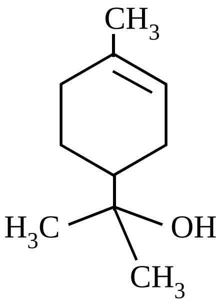
Antiseptics has the ability to reduce the odour produced as a result of bacterial decomposition of organic matter on the body or in the mouth for which they are added to face powders and breath purifiers.

More examples of antiseptics are :

(i) **Dettol,** most commonly used antiseptic, is a mixture of chloroxylenol and terpineol.



CHLOROXYLENOL



TERPINEOL

(ii) **Bithional** is added to soaps to impart antiseptic properties to reduce the odour produced by bacterial decomposition of organic matter on the skin.

(iii) **Iodine** is a very powerful antiseptic used as tincture of iodine which is 2–3% solution of iodine in alcohol and water.

(iv) Very dilute aqueous solution of **boric acid** is used as a mild antiseptic for eye wash.

(v) **Iodoform** is used as antiseptic powder for wounds.

(vi) 2–5% **mercurochrome** solution is a very good antiseptic for skin, mucous surfaces and wounds.

(vii) **Salol** is used as an intenstial antiseptic for throat ailments.

(b) Disinfectants : Disinfectants are the chemical substances which kill micro-organisms but are not safe to be applied to the living tissues, but can be applied to abiotic objects such as floors, drains, toilets, instruments etc. Examples are :

(i) Solution of cresols : (i.e. *o*–, *m*– and *p*– methyl phenols) in soapy water is called **lysol** which is used as a disinfectant.

(ii) Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution is a disinfectant.

(iii) SO_2 in very low concentration acts an disinfectant.

(iv) One percent solution of phenol is disinfectant whereas 0.2 percent solution acts as an antiseptic.

D. ANTIMICROBIALS

Antimicrobials are defined as the drugs used to destroy or prevent development or inhibit the pathogenic action of micro-organisms such as bacteria, viruses, fungi or other parasites.

Microbial diseases can be controlled by the following ways :

(i) By using a bactericidal drug which kills the organisms in our body.

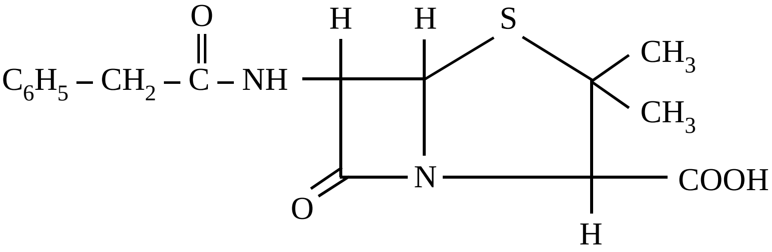
(ii) By checking the growth of organisms using a bacteriostatic drug.

(iii) By improving the resistance power of the body towards infection i.e. increasing the immunity power.

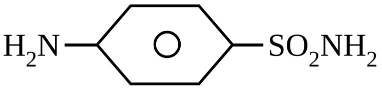
Examples of antimicrobial drugs are

(i) antibiotics- **Penicillin**, **Tetracycline**, **Ofloxacin**

(ii) Sulpha drugs - **Sulphanilamide**, **Sulphapyridine**.



Pencillin - G



Sulphanilamide

E. ANTIBIOTICS

The term antibiotic has been derived from the word "antibiosis" which means survival of fittest i.e. a process in which one organism may destroy another to preserve itself. That means antibiotics are chemical substances produced by or derived from living cells which is capable in small concentration of inhibiting the life proceses or even destroying the micro-organisms.

But with development of synthetic methods producing compounds which are same as derived from micro-oganisms, the definition of antibiotics needs modification.

An antibiotic is now defined as the chemical substance produced wholly or partially by chemical synthesis, which in low concentration either kills or inhibits the growth of micro-ogranisms by intervening in their metabolic processes.

I. Conditions for a chemical substance to be an antibiotic :

All chemical substances produced by or derived from living cells can not be antibiotics. These have to satisfy the following conditions.

(i) Antibiotics must be a product of metabolism although it might have been synthesized.

(ii) If the antibiotic is a synthetic product, it should be a structural analogue of naturally occurring antibiotic.

(iii) It must be effective at low concentrations.

(iv) In order to act as therapeutic agent, it must have the following characteristics.

  (a) It must be effective against a pathogen.

  (b) It should not have any toxic side effects.

  (c) It should be stable and can be stored for a longer time.

II. Classification of anibiotics :

(a) Basing on their action on micro-organism antibiotics are of two types:

  (i) **Bactericidals** which kill the organisms in the body. Examples : **Penicillin**, Ofloxacin.

  (ii) **Bacteriostatic** which checks the growth of micro-organisms. Examples : **Erythromycin** and **Tetracycline**.

(b) The broad based classification of antibiotics classifies them into two types :

  (i) **Broad spectrum antibiotics :** These include the antibiotics which are effective for a number of microbial diseases.

  Examples are **penicillin**, **chloramphenicol** etc.

  (ii) **Narrow spectrum antibiotics :** These are the antibiotics which are highly specific in their action. Examples are **bacitracin** and **nystatin**.

(c) On the basis of the type of bacteria the antibiotic can destroy, the antibiotics are of two types. These are :

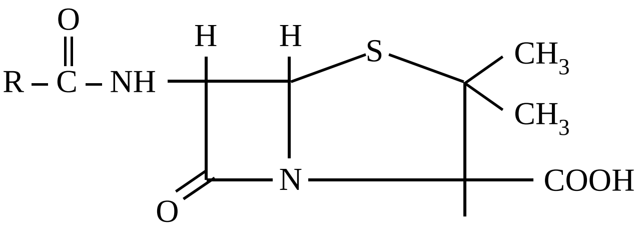
  (i) Gram positive bacteria and

  (ii) Gram negative bacteria.

III. Examples of antibiotics :

(i) **Penicillin** : The first antibiotic penicillin was discovered by Alexander Fleming in 1929, who along with H.W. Florey received Nobel Prize for medicine in 1945 for their contribution to the development of penicillin.

Penicillin can not be taken orally. To persons who are allergic, it can cause fatal coma. The general structure of pencillins can be represented as :



For Penicillin - G $R = -CH_2 - C_6H_5$
and Penicillin - V $R = -CH_2 - O - C_6H_5$

Penicillin is very much effective for pneumonia, bronchitis, sore throat, and other infectious diseases caused by various cocci and some gram positive bacteria.

(ii) **Streptomycin :** Streptomycin is a very effective drug for the treatment of tuberculosis, meningitis, pneumonia and also for common infections like throat, lungs etc.

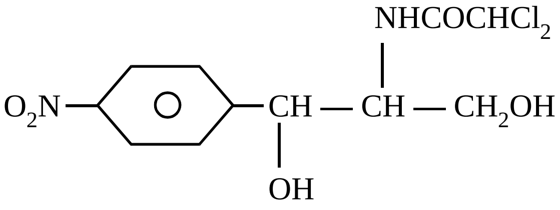
(iii) **Tetracyclines : Terramycin** and **Auromycin** are the best examples of tetracyclines, which are highly effective against a number of bacteria, viruses, protozoa, parasites etc. Unlike penicillin and streptomycin tetracyclines can be taken orally as these are absorbed from the gastrointestinal tract. Due to this advantage streptomycin is largely replaced by tetracyclines.

(iv) **Chloramphenicol (Chloromycetin) :** As an antibiotic chloramphenicol is having certain advantages over others. These are :

(a) Chemically it is the first antibiotic to be synthesized on a commercial scale.

(b) It can be taken orally and very effective in the treatment of typhoid, dysentry, acute fever, urinary infections, meningitis and pneumonia.

(c) It is the first natural compound found to contain a nitro group and the presence of $-CHCl_2$ group is most unusual.



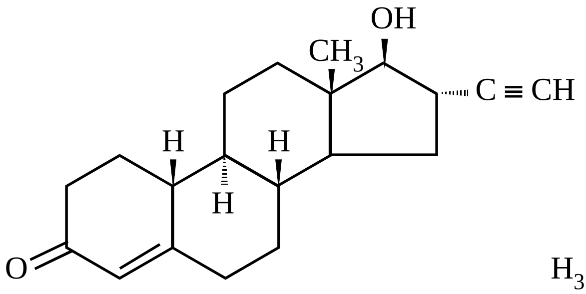
CHLORAMPHENICOL

F. ANTIFERTILITY DRUGS

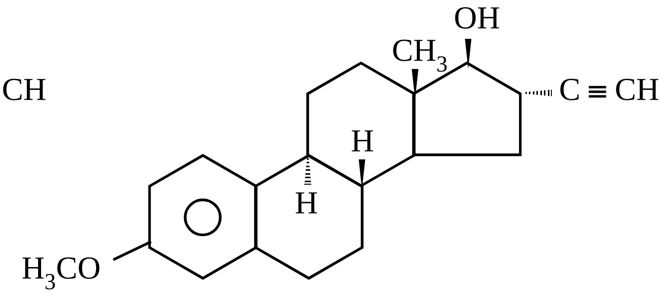
Antifertility drugs may be defined as the chemical substances which are used to check pregnancy in women having control over the female menstrual cycle and ovulation.

Rising social problems like environmental pollution, insufficient food resources, unemployment etc. due to high population growth have become serious global problems which gave birth to the idea of family planning which is possible by birth control pills or oral contraceptives.

These antifertility drugs contain a mixture of synthetic estrogen and a progesterone derivative which are more potent than the natural hormones. For example, a common brand name **Enovid E** contains **norethindrone** (a progesterone derivative) and mestranol (an estrogen). However all these drugs have side effects and should be used only under doctor's advice.

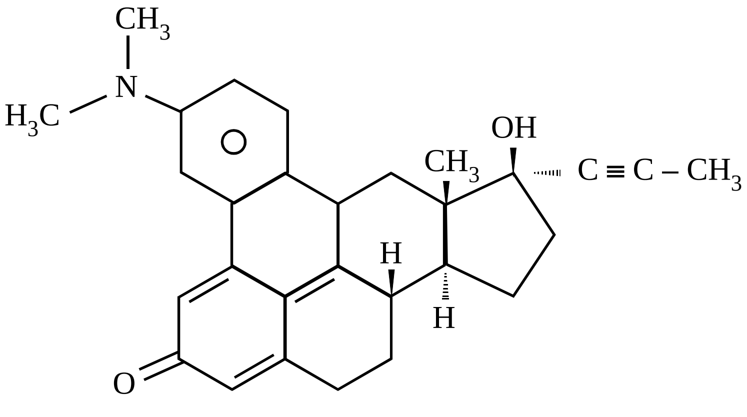


Norethindrone



Mestranol

Mifepristone the synthetic steroid is now widely used as "morning after pill" that blocks the effects of progesterone.



Mifepristone

G. ANTACIDS

Antacids are defined as the chemical substances which neutralize the acid secreted in the stomach and raise the pH to an appropriate level.

The most common disease now the people are suffering is **gastritis**, which is due to the presence of excess hydrochloric acid in the gastric juice. Over productions of acid in the stomach causes irritation and pain with the development of ulcers. The various antacids used to check the gastritis are :

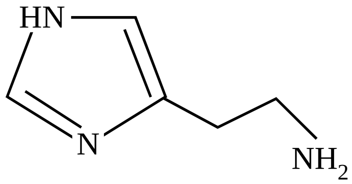
(i) **Sodium hydrogen carbonate.** But excessive use of it may make the stomach alkaline and accelerates the production of more acid.

(ii) **Metal hydroxides:-** a mixture of aluminium and magnesium hydroxide.

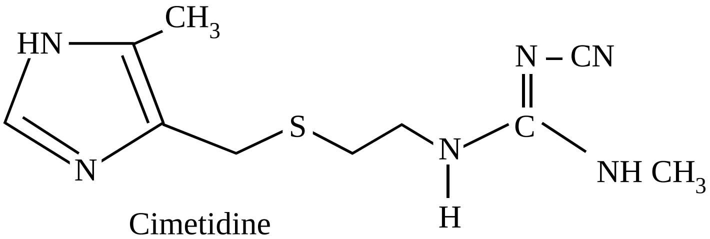
(iii) The drug **cimetidine (Tegamet)** was a better invention in the field of antacids as it prevents the interaction of **histamine** which actually stimulates the secretion of pepsin and hydrochloric acid in the stomach, with the receptors present in the stomach wall resulting in the production of low amount of acid.

(iv) Now another drug **ranitidine (Zantac)** has now prevailed in the medicinal field as a very effective antacid.

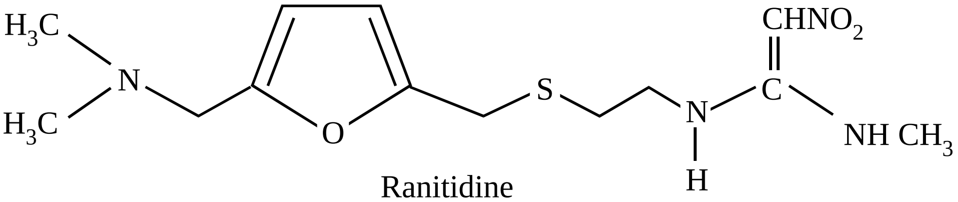
(v) Recently **omeprazole** and **lansoprazole** have been used as antacids preventing the formation of acid in the stomach.



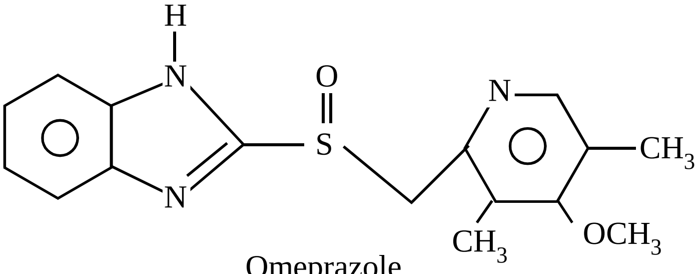
Histamine



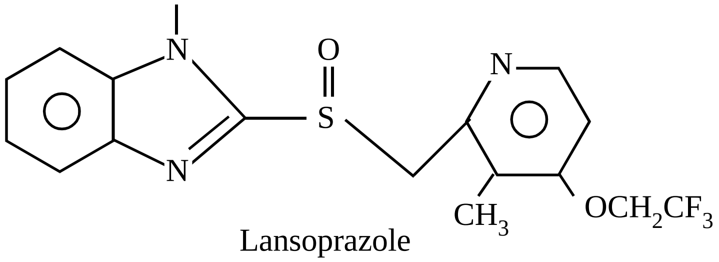
Cimetidine



Ranitidine



Omeprazole



Lansoprazole

H. ANTIHISTAMINES

Antihistamines are defined as the antiallergy drugs used to treat allergy such as skin rashes, inflammation of tissues, asthma and itching of hives due to the release of histamine is the body.

Histamine is a potent vasodilator with various functions. These are :

(i) It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels.

(ii) It is also responsible for the nasal congestion associated with common cold.

Antihistamines work on different receptors for which these are completely different from antacids. They interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine has its impact. These are mainly used for treatment of

(i) hay fever

(ii) conjuctivitis

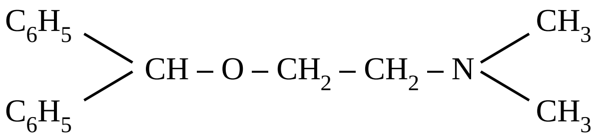
(iii) seasonal rhinitis (inflammation of nasal mucosa) i.e. sneezing, nasal discharge

(iv) itching of eyes, nose and throat

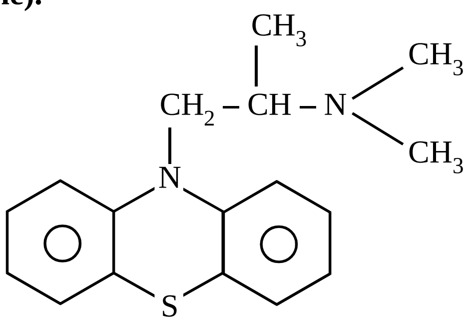
(v) nausea in pregnancy

(vi) post operative vomiting.

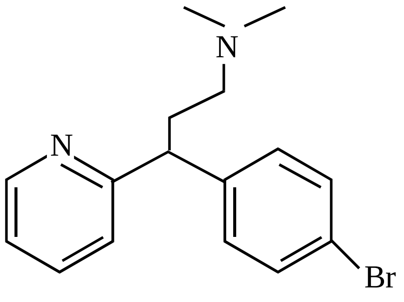
Commonly used antihistmine drugs are : **diphenylhydramine, cetrizine, promethazine, brompheniramine (Dimetapp)** and **terfenadine (Seldane).**



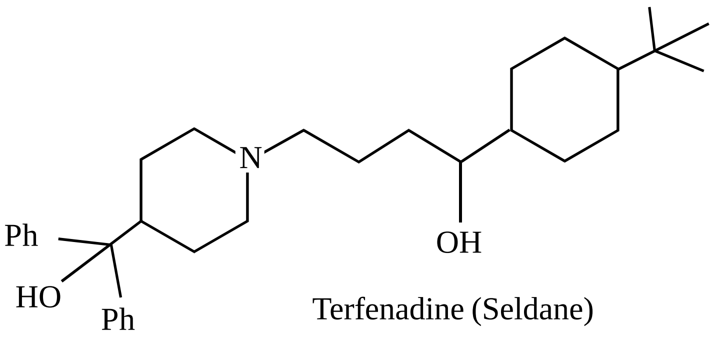
Diphenylhydramine



Promethazine



Brompheniramine
(Dimetapp)



Terfenadine (Seldane)

24.3 CHEMICALS IN FOOD :

All those chemicals which are added to food to improve its shelf life, taste, appearance, odour and nutritive (food) value are termed as **food additives**. Main types of food additives are:

(i) preservatives

(ii) food colours

(iii) flavouring agents

(iv) artificial sweetners

(v) antioxidants

(vi) fortifiers

(vii) emulsifiers

(viii) antifoaming agents

(ix) nutritional supplements such as minerals, vitamins and amino acids.

I. PRESERVATIVES

Preservatives may be defined as the chemicals which are capable of inhibiting or arresting the process of fermentation, acidification or other decomposition of food caused by bacteria, yeasts and moulds.

(a) Preservatives used in a common man's house are salt, sugar, spices and oil to check the growth of micro-organisms in food.

(i) The preservation of food like raw mango, amla, fish, meat etc by adding excess salt is called **salting** which prevents the availability of water for bacterial growth.

(ii) **Sugar syrup** is used for the preservation of fruits like mango, apples, carrot etc, which checks the growth of micro-organisms by dehydrating them.

(iii) Oil and spices are commonly used as preservaties for pickles, jams, squashes etc.

(b) Sodium benzoate : Sodium benzoate is used as preservative in soft drinks and acidic foods. It is metabolized by conversion into hippuric acid, $C_6H_5CONHCH_2COOH$ which is ultimately excreted in urine.

(c) Sodium metabisulphite ($Na_2S_2O_5$) : Sodium or potassium metabisulphite is used as a preservative for pickles, jams and squashes. Its preservative action is due to SO_2 which dissolves in water to give sulphurous acid.

$$Na_2S_2O_5 \rightarrow Na_2SO_3 + SO_2$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

Sulphurous acid inhibits the growth of yeasts, moulds and bacteria.

(d) Epoxides : Epoxides such as ethylene oxide and propylene oxide are used to preserve low moisture foods such as spices, dried fruits and nuts. These foods are expossed to these gaseous chemicals in closed chamber for sufficient time when all types of micro-organisms including spores and viruses get killed.

(e) Sodium and Calcium propionate : These are used in bread and cakes to inhibit the growth of moulds.

(f) Sorbic acid and its salts : Sodium and potassium sorbates are now used for controlling the growth of yeasts and moulds in processed cheese, pickles, baked food items, certain meat and fish products.

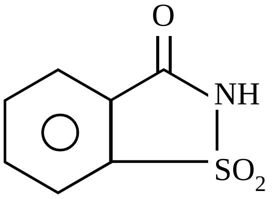
(g) *p*-Hydroxy benzoate esters : The methyl, ethyl, propyl and heptyl esters of *p*-hydroxy benzoic acid are used to preserve baked food, beer, soft drinks and syrups. They are highly effective in inhibiting the growth of moulds and yeasts but less effective on bacteria.

II. ARTIFICIAL SWEETENING AGENTS :

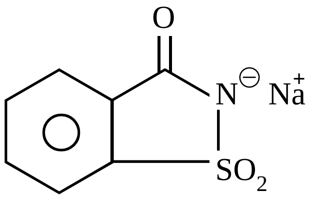
Most commonly used natural sweetners are sucrose and fructose which not only add to our calorie intake, but also causes tooth decay. Particularly for diabetic patients who want to control their sugar intake, calorie free artificial sweetners have been synthesised. Some commonly used artificial sweetners are :

(a) Saccharin : *Ortho*-sulphobenzoimide also called **saccharin** is the first most popular sweetening agent which is about 550 times as sweet as cane sugar.

It is insoluble in water but its soidum salt is soluble in water. Chemically it is 1, 2 - benzisothiazolin - 3 - one - 1, 1 - dioxide (o-sulphobenzoimide) and accurs as white crystals.



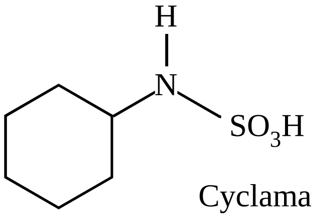
Saccharin
(Insoluble in water)



Sodium salt of Saccharin
(Soluble in water)

It is not biodegradable and is excreted as such in urine. So it does not possess any calorific value and is used as sweetening agent by diabetic patients.

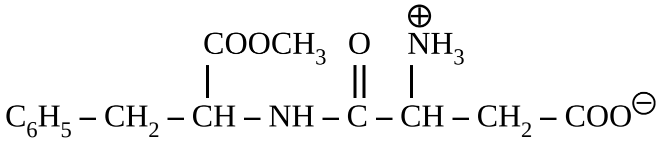
(b) Cyclamate : Cyclamate is seven times sweeter than sucrose. However a mixture of cyclamate and saccharin in the ratio 10:1 is found to be sweeter than either of the two individual compounds. Its structure is:



Cyclamate or N - cyclohexylsulphamate

Its use has been banned because of its suspected link with cancer.

(c) Aspartame : Aspartame is the most efficient and widely used artificial sweetner which is the methyl ester of the dipeptide derived from phenylalanine and aspartic acid.

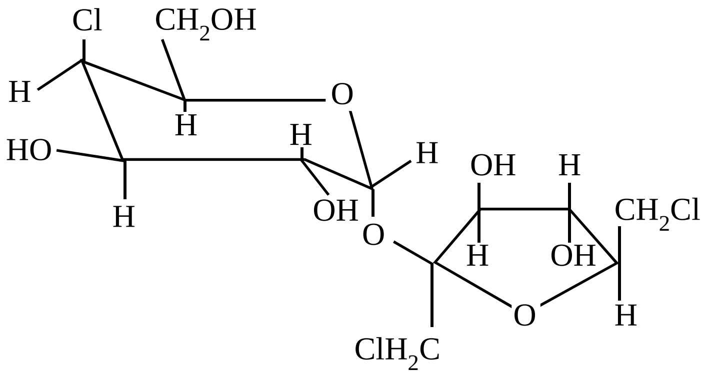


$$C_6H_5-CH_2-\overset{\overset{COOCH_3}{|}}{CH}-NH-\overset{\overset{O}{\|}}{C}-\overset{\overset{\oplus}{NH_3}}{\underset{}{CH}}-CH_2-COO^{\ominus}$$

Aspartame

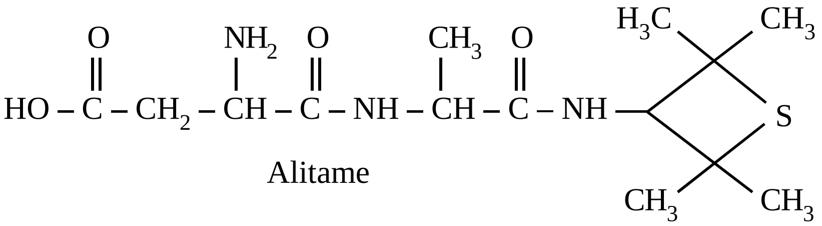
It is approximately 100 times as sweet as cane sugar, but it has short shelf life. It decomposes at baking or cooking temperature and its use is limited to cold foods and soft drinks. Again people suffering from the disease phenylketone urea are advised not to use aspartame since their metabolism converts it to phenylpyruvic acid, accumulation of which is harmful especially to infants due to mental retardation and brain damage.

(d) Sucralose : Sucralose is a trichloro derivative of sucrose which is roughly 600 times as sweet as sucrose. It tastes and looks like sucrose and is quite stable at baking and cooking temperature. It neither provides calories nor causes tooth decay.



Sucralose

(e) Alitame : Alitame is 2000 times as sweet as sucrose. It is a high potency sweetner, but it is very difficult to control the sweetness of the food to which it is added.

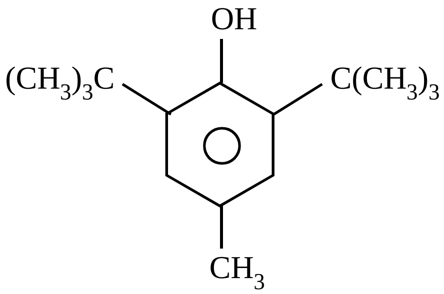


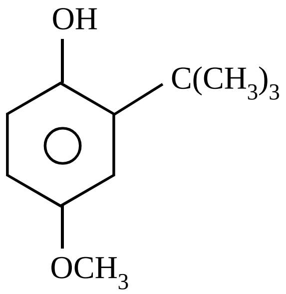
Alitame

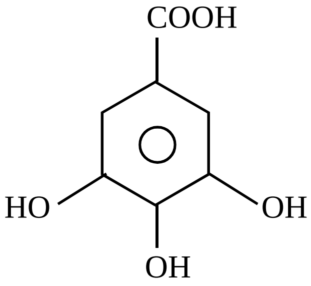
III. ANTIOXIDANTS

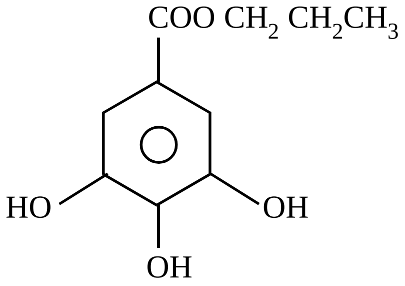
Antioxidants are defined as the chemicals which are added to processed foods like potato chips, biscuits, breakfast cereals etc. to prevent the oxidation of fats and subsequent spoilage of the food.

(i) The most common antioxidants are butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and several esters of gallic acid such as propyl gallate.


Butylated hydroxytoluene
(BHT)


Butylated hydroxyanisole
(BHA)


Gallic acid


Propyl gallate

(ii) Antioxidants are also termed as sacrificial materials as they are more reactive towards oxygen than the materials they are protecting. They also reduce the rate of involvement of free radicals in the ageing process.

(iii) The addition of BHA to butter increases its shelf-life from months to years.

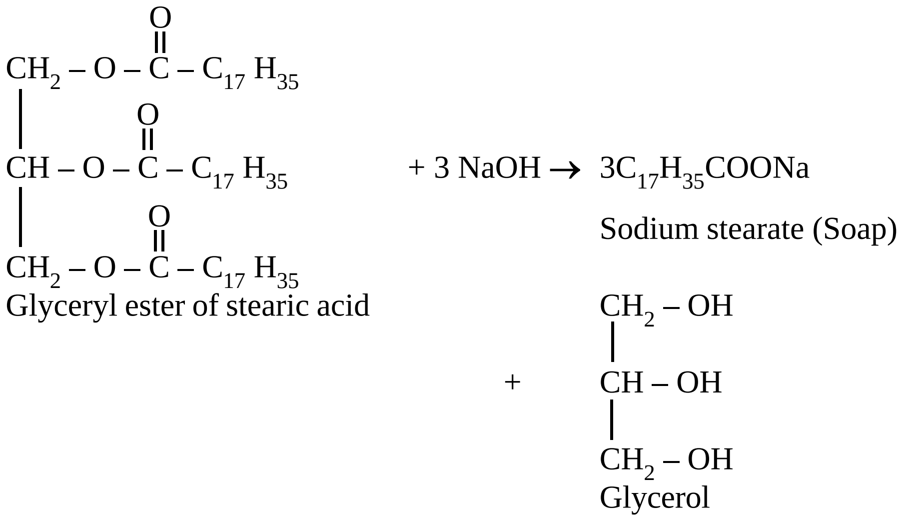
(iv) Sulphur dioxide and sodium metabisulphite which are used as preservatives, are also used an antioxidants for wine, beer, sugar syrups, dried fruits and vegetables.

(v) Ascorbic acid prevents browning caused by enzymatic oxidation of phenolic compounds.

24.4 CLEANSING AGENTS :

I. (a) Soaps : Soaps are the sodium or the potassium salts of higher fatty acids like stearic acid, palmitic acid, oleic acid etc. They are prepared by the alkaline hydrolysis i.e. saponification of oils and fats. Soaps may also be obtained by the direct neutralisation of higher fatty acids, like stearic acid, palmitic acid and oleic acids with alkali, such as NaOH or KOH.

(i)



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \end{array} + 3\,NaOH \rightarrow 3C_{17}H_{35}COONa + \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Glyceryl ester of stearic acid

Sodium stearate (Soap)

Glycerol

(ii) $C_{17}H_{35}-COOH + NaOH \xrightarrow{\text{Direct neutralization}} C_{17}H_{35}\,COONa + H_2O$

Stearic acid Soap (Sodium stearate)

The saturated fats and oils give hard soaps than the unsaturated one. Also sodium salts of a given fat or oil is harder and less soluble than the potassium salts. Hence, soft soaps are particularly of potassium salts of higher unsaturated fatty acids and hard soaps are sodium salts of higher saturated falty acids.

(b) Types of soaps : Saponification of oils or fats produces soap. However, different soaps are prepard by varying diffeent raw materials.

(i) **Washing soaps :** These are made from cheaper fats like mohwa oil, rosin etc using caustic soda for their saponification. Sodium silicate is added to these soaps as a filler. Some cheap starch or white clay is added to increase the weight and reduce the cost.

(ii) **Toilet soaps :** Toilet soaps are made from best animal or vegetable fats or mixture of both with removal of excess alkali. Then colour, perfume and germicide etc. are added to the soap during crutching or shredding.

(iii) **Transparent soaps :** These are made by dissolving the soap in ethanol followed by evaporation of the excess solvent.

(iv) **Shaving soaps :** During preparation of shaving soaps glycerol is added to prevent rapid drying. Rosin, a gum is added while making them which forms sodium rosinate responsible for lather.

(v) **Laundry soaps :** These soaps contain fillers like sodium silicate, sodium rosinate, borax and sodium carbonate.

(c) Advantages and disadvantages of soaps : Soap is an effective cleaning agent and is completely biodegradable. Micro-organisms present in sewage water can oxidise soap completely to carbon dioxdes and hence does not create any pollution.

However soaps are having the following limitations.

(i) Ordinary soaps are unsuitable for washing of silk, wool etc. as the alkali present causes harm to the fibre.

(ii) Soaps can not be used in acidic medium because they change the soaps into free carboxylic acids which strick to the fabrics being incapable of removing oil and grease from fabrics.

(iii) Soaps can not be used in hard water because hard water contains calcium and magnesium ions which form insoluble calcium and magnesium soaps when sodium or potassium soaps are dissolved in hard water.

$$\underset{\substack{\text{Sodium stearate}\\\text{(Soap) (Soluble)}}}{2\,C_{17}H_{35}COONa} + CaCl_2 \rightarrow 2NaCl + \underset{\substack{\text{Calcium stearate}\\\text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Ca}$$

Insoluble soaps separate as scum in water and are hindrance to good washing. This causes wastage of soap and also discolours and hardens the fabric being washed.

II. SYNTHETIC DETERGENTS :

Synthetic detergents are generally sodium salts of long-chain alkyl hyrogen sulphate or sodium salts of long chain alkyl benzene sulphonic acids which act as cleansing agents having all the properties of soaps, but do not contain any soap. These are also referred to as **syndets** or **soapless soaps**.

In contrast to soaps, synthetic detergents can be efficiently used even with hard water, because calcium and magnesium salts of synthetic detergents like their sodium and potassium salts are also soluble in water. Hence they do not form curdy white precipitates with hard water. Again they can also be used for acidic solutions. However, unlike soaps they are not completely biodegradable and hence result in water pollution.

Synthetic detergents are of three types. These are :

(a) Anionic detergents : These are so called because a large part of their molecules are anions. These are of two types:

(i) **Sodium alkyl suphates :** These are the sodium salts of sulphonated long chain alcohols formed by the treatment of long chain alcohol with concentrated sulphuric acid followed by neutralisation with sodium hydroxide. Examples are sodium lauryl sulphate and sodium stearyl sulphate.

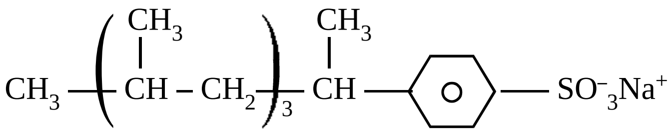
$$\underset{\text{Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2OH} \xrightarrow[-H_2O]{H_2SO_4} \underset{\text{Lauryl hydrogen sulphate}}{CH_3(CH_2)_{10}CH_2OSO_3H}$$

$$-H_2O \downarrow NaOH_{(aq)}$$

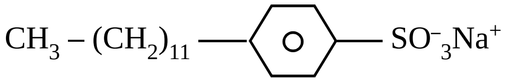
$$\underset{\text{Sodium lauryl sulphate}}{CH_3(CH_2)_{10}\,CH_2O\,SO^-_3Na^+}$$

These sodium alkyl sulphates are 100% biodegradable.

(ii) **Sodium alkyl benzene sulphonates :** These are obtained by Friedel-Craft's alkylation of benzene with a long chain alkyl halide or an alkene or an alcohol followed by sulphonation and neutralization with NaOH. Most widely used detergent is sodium n–dodecylbenzenesulphonate (SDS), which is also referred to as LAS detergents (linear alkyl sulphonates) where as an example of ABS detergents (alkyl benzene sulphonates) with a branched chain alkyl groups is



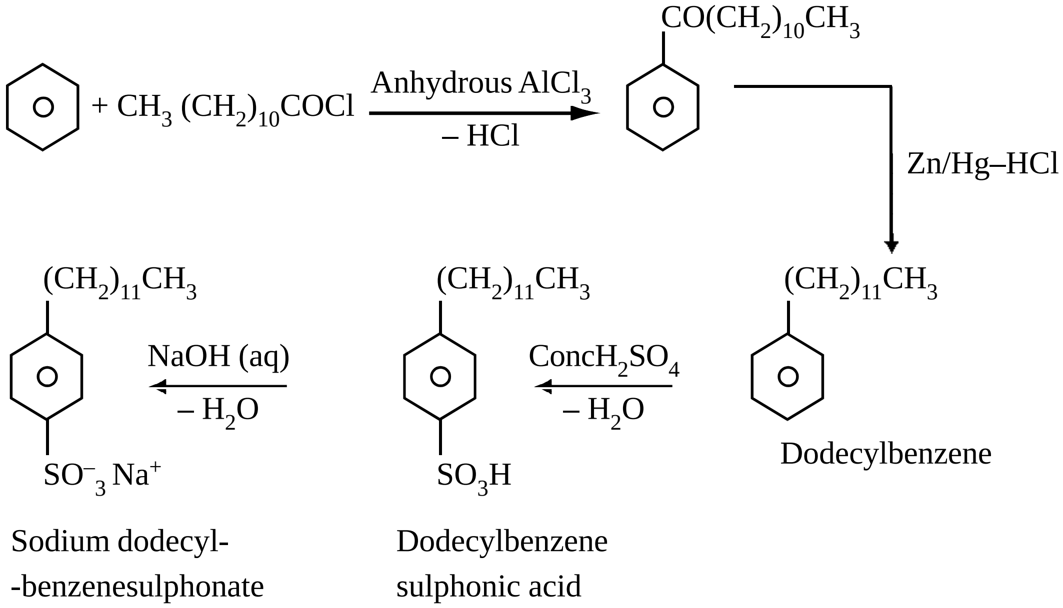
Hard or non-biodegradable ABS detergent



Soft or biodegradable LAS detergent.

(Sodium n-dodecylbenzene sulphonate)

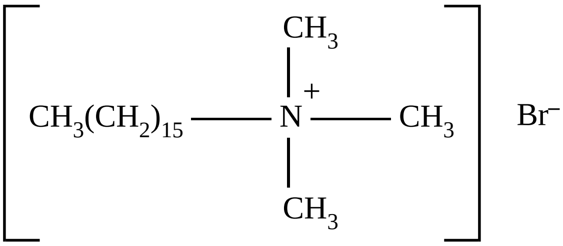
Sodium n-dodecylbenzene sulphonate can be prepared as follows:



(b) Cationic detergents : Cationic detergents are quarternary ammonium salts of amines with chlorides, bromides or acetates as anions containing one or more long chain alkyl groups and a positive charge on nitrogen atom, for which these are called cationic detergents.

Being more expensive than the anionic detergents, they find limited use. However they are extensively used as germicides.

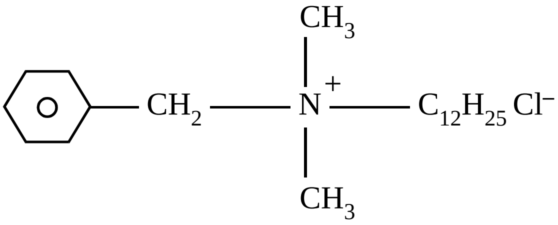
Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.



$$\left[CH_3(CH_2)_{15} - \overset{CH_3}{\underset{CH_3}{\overset{+}{N}}} - CH_3 \right] Br^-$$

Cetyltrimethyl ammonium bromide (germicide)

Other examples of cationic detergents are:

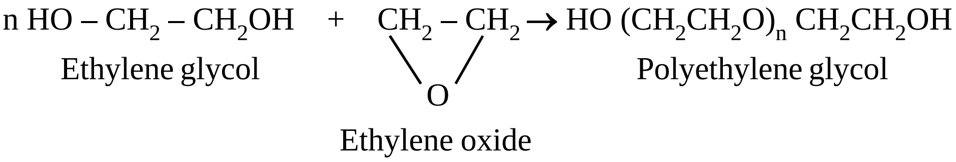


Benzalkonium chloride
(an antibacterial)

$(CH_3)_3\ N^+\ (C_{18}H_{37})\ Br^-$

Trimethyl stearyl
ammonium bromide

(c) Neutral or non-ionic detergents : Non-ionic detergents do not contain any ion in their structure. One most widely used neutral detergent is formed when stearic acid reacts with polyethylene glycol.



$$n\ HO - CH_2 - CH_2OH + CH_2 - CH_2 (O) \rightarrow HO\ (CH_2CH_2O)_n\ CH_2CH_2OH$$

Ethylene glycol — Ethylene oxide — Polyethylene glycol

$CH_3\ (CH_2)_{16}\ COOH\ +\ HO\ (CH_2CH_2O)_n\ CH_2CH_2OH$

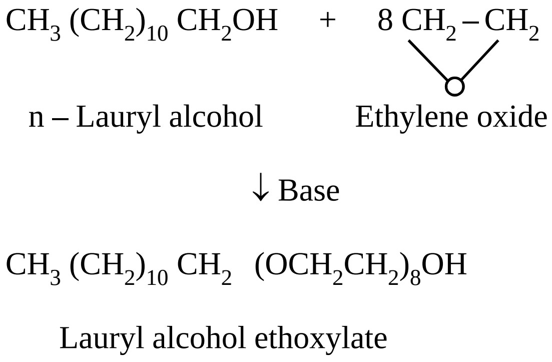
Stearic acid Polyethylene glycol

$\downarrow - H_2O$

$CH_3\ (CH_2)_{16}\ COO\ (CH_2CH_2O)_n\ CH_2CH_2OH$

Non-ionic detergent

Another example of non-ionic detergent is **lauryl alcohol ethoxylate** which is 100% biodegradable. This can be synthesized as follows :



$CH_3(CH_2)_{10}CH_2OH + 8\ CH_2-CH_2$ (ethylene oxide ring)

n – Lauryl alcohol Ethylene oxide

$\downarrow$ Base

$CH_3(CH_2)_{10}CH_2\ (OCH_2CH_2)_8OH$

Lauryl alcohol ethoxylate

Non-ionic detergents are liquid dish washing detergents.

Advantages and disadvantages of synthetic detergents over soaps :

(a) Advantages : Synthetic detergents find wide application these days as cleasing agents having the following advantages over soaps.

(i) Synthetic detergents can be used even in hard water.

(ii) Synthetic detergents can be used even in acidic medium because these are the salts of strong acids and are not decomposed in the acidic medium.

(iii) These are more soluble in water than soaps.

(iv) They have stronger cleansing power than soaps.

(v) Synthetic detergents are prepared from the hydrocarbons obtained from petroleum. This saves vegetable oils used as food.

(b) Disadvantages of synthetic detergents over soaps :

Synthetic detergents having branched chain hydrocarbon chains are not biodegradable and cause water pollution making it unfit for use by the aquatic life. However, this difficulty has been overcome now by using a straight chain hydrocarbon in the detergent instead of branched chain hydrocarbon making it biodegradable. But all soaps are biodegradable.

Difference between Soaps and Detergents :

Main points of difference between soaps and synthetic detergents are given in Table 24.1.

Table 24.1
Difference between soaps and synthetic detergents.

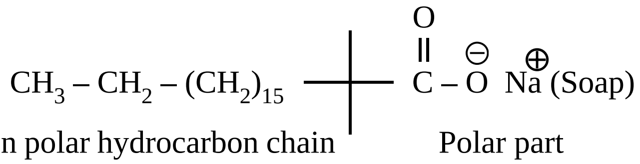
Soaps	Synthetic detergents
1 These are alkali metal salts of long chain fatty acids	1. There are sodium salts of long chain alkyl sulphates or long chain alkylbenzene sulphonates.
2. These can not be used in hard water.	2. These can be used even in hard water
3. These can not be used in acidic solutions.	3. These can be used even in acidic solutions.
4. These are obtained from vegetable oils.	4. These are prepared from hydrocarbons obtained from petroleum.
5. These are biodegradable.	5. Some of the synthetic detergents are not biodegradable.

III. CLEANSING ACTION OF SOAPS AND DETERGENTS :

The cleaning action of a soap or a detergent is called its detergent action or **detergency**. All the soaps and detergents contains two characteristics groups i.e.

(i) Non-polar hydrocarbon chain which is oil soluble (lyophilic or lipophilic) and is called hydrocarbon tail or oil-soluble non-polar part of the soap or detergent molecule.

(ii) Polar end which is water soluble (hydrophilic) and is called negative end or water soluble polar part of the soap or detergent molecule.



$$CH_3-CH_2-(CH_2)_{15} \,\Big|\, \overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\ \overset{\oplus}{Na}\ \text{(Soap)}$$

Non polar hydrocarbon chain — Polar part

(Oil soluble) — (Water soluble)

$$CH_3-(CH_2)_{10}-CH_2 \,\Big|\, O\,SO_2\,\overset{\ominus}{O}\ \ \overset{\oplus}{Na}\ \text{(Detergent)}$$

Oil soluble non-polar part — Water soluble polar part

Cleansing action of soaps and detergents takes place in two steps :

(i) **Wetting :** This results from lowering of surface tesnsion of water by mixing soap with it. As a result the oil droplets of the dirt are wetted on the surface and form a colloidal suspension in the medium of water. The soap forms a protective film on their surface to prevent coagulation. Such colloidal particles are then washed away with water.

(ii) **Emulsification :** When dirty cloth is immersed into the mixture of soap and water, the non-polar part of the soap or detergent dissolves in oil or grease and the polar part of the soap or detergent is held by the surrounding water as shown in Fig. 24.1. The grease layer is then dislodged from skin by rubbing or from garment by tumbling and strirring.

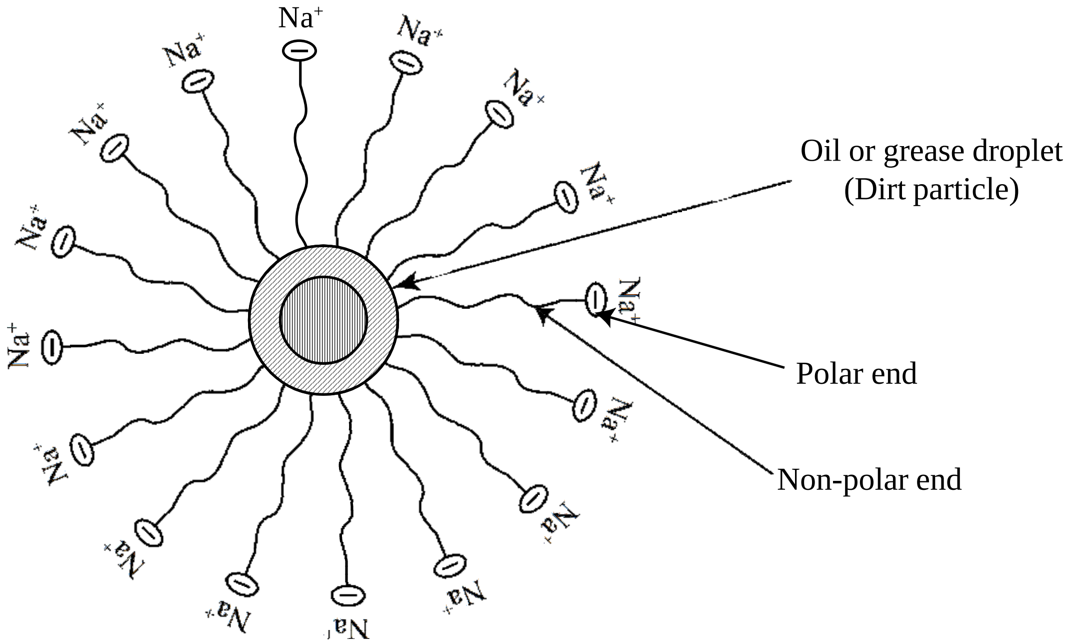


Fig. 24.1 : Cleansing action of soap and detergents

Each oil droplet is surrounded by an ionic atmosphere with negative heads outwards in water. Due to repulsion between similar charges, oil or grease particles change into very small drops and a stable emulsion of oil in water is obtained. The emulsified grease particles bearing dirt can be easily washed with water. Thus soap and detergent clean by emulsifying the fat and grease containing the dirt.

CHAPTER (24) AT A GLANCE

1. **Chemicals in medicine :** Chemical substances used for curing diseases and reducing suffering from pain are called medicines or drugs. The branch of science which deals with the treatment of diseases using suitable chemicals is known as chemotheraphy.

   (a) **Analgesics :** Analgesics decrease pain. These are of two types. (i) Narcotics : Examples are morphine and heroin. (ii) Non-narcotics : Examples are aspirin and phenacetin.

   (b) **Tranquilizers :** These are medicines used to treat mental diseases. Examples are equanil, seconal and luminal.

(c) **Antiseptics :** These are applied to skin, on wounds and cuts to kill or prevent the growth of micro-organisms. Examples are dettol, savlon and acriflavin.

(d) **Disinfectants :** These are the chemicals which kill micro-organisms, but not safe for human beings.

(e) **Antimicrobials :** Drugs used to cure diseases caused by fungi, bacteria and viruses are called antimicrobials. Examples are penicillin, streptomycin and AZT widely used against AIDS.

(f) **Antifertility drugs :** These are used to check pregnancy in women. Example is Enovid E.

(g) **Antibiotics :** These are chemical substances produced by some micro-organisms and can be used to kill other micro-organisms which cause infections. Examples are tetracyclin, chloramphenicol, penicillin.

(h) **Antacids :** These are the chemicals used to remove the excess acid and raise the pH to on appropriate level in stomach. Examples are omeprazole and lansoprazole.

(i) **Antihistamines :** Allergy is caused by liberation of histamines. The drugs used to treat allergy are called antihistamines. Examples are diphenylhydramine and promethazine.

2. **Chemicals in food :** Food additives are those chemicals which are added to food to improve its keeping qualities, appearance, taste, colour, odour and food value. These are :

(a) **Preservatives :** These are used to protect food against bacteria, yeasts and moulds. Examples are: Sodium metabisulphite, Sorbic acid and Sodium benzoate.

(b) **Artificial sweetening agents :** Aspartame, Alitame and Saccharin are the artificial sweetners having no calorie intake for which used by the diabetic patients.

(c) **Antioxidants :** These are used to prevent oxidation of fats in processed foods such as potato chips, biscuits etc. Examples are BHT and BHA.

3. **Cleansing Agents (Soaps and Detergents)**

(a) **Soaps** are sodium and potassium salts of higher fatty acids like stearic acid, palmitic acid, oleic acid etc. Washing soaps contain sodium salts of fatty acids while soft soaps contain potassium salts.

(b) **Synthetic detergents** are generally sodium salts of long chain alkyl hydrogen sulphates or sodium salts of long chain alkyl benzene sulphonic acids.

QUESTIONS

A. VERY SHORT QUESTIONS (One mark each) :

(a) Give the name of the first antibiotic.

(b) Name a substance which can be used as an antiseptic as well as disinfectant.

(c) What are tranquilizers?

(d) What type of medicine chloramphenicol is?

(e) Name two antipyretic drugs.

(f) Name two analgesic drugs.

(g) Aspirin is an ——— .

(h) Streptomycin is a ——— spectrum antibiotic.

(i) What is the name given to medicines used for getting relief from pain?

(j) Name the antibiotic used specifically for treatment of typhoid fever.

(k) Name one broad spectrum antibiotic.

(l) What is the difference between a preservative and an antioxidant?

(m) Name an antacid which prevents the formation of acid in the stomach.

(n) What structural unit makes detergents non-biodegradable?

(o) What type of detergents are used for dish washing?

(p) Give an example of a bactericidal antibiotic.

(g) In transparent soaps ——— is used.

(h) Name two artificial sweetening agents.

(i) ——— is the sweetening agent used in the preparation of sweets for a diabetic patient.

B. SHORT QUESTIONS (Two marks each) :

(a) What are detergents? Name one from each type of detergent.

(b) Write down the difference between soap and detergent.

(c) What are broad spectrum antibiotics? Give two examples.

(d) What are antipyretics? give two examples.

(e) Whay soap is not used for hard water?

(f) What are antifertility drugs? Give one example.

(g) What are the main constituents of Dettol?

(h) What are food preservatives? Give two examples.

(i) Why are Cimetidine and Ranitidine better antiacids than sodium hydrogen carbonate or magnesium hydroxide?

(j) Why is the use of aspartame limited to cold foods and drinks?

(k) What problem arises in using alitame as artificial sweetener?

C. SHORT QUESTIONS (Three marks each) :

(a) How are antiseptics different from disinfectants ? Give one example of each of them.

(b) What are soaps and detergents?

(c) Discuss the cleansing action of soaps?

(d) Why does a detergent act even with hard water? Is it always biodegradable?

(e) Give the composition of one oral contraceptine.

(f) What are detergents? Give their scheme of classification.

(g) What are antioxidants? How do they differ from preservatives.

(h) What is tincture of iodine? What is its use?

(i) What are biodegradale and non-biodegradable detergents? Give one example of each.

(j) Low level of noradrenaline is the cause of depression. What type of drugs are needed to cure this problem? Name two drugs.

D. LONG QUESTIONS (7 marks each) :

(a) What are food additives? Discuss briefly the various types of food additives.

(b) What are soaps and synthetic detergents? In what respects detergents preferred over soaps? Discuss the cleansing action of soaps and detergents.

(c) Write notes on :

(i) Antibiotics

(ii) Antacids

(iii) Analgesics

E. MULTIPLE CHOICE QUESTIONS :

1. The oils from which soaps are prepared belong to a class of compounds known as

(a) Amine (b) Acid

(c) Hydrocarbon (d) Ester

2. Novalgin is a common

(a) Analgesic (b) Antibiotic

(c) Antipyretic (d) Antimalarial

3. Equanil is a drug to control

(a) Pneumonia (b) Malaria

(c) Ordinary fever (d) Mental disease

4. Medicine which is an antibiotic is

(a) Ampicilin
(b) Aspirin
(c) Calmpose
(d) Chloroquine

5. A detergent is a

(a) Drug
(b) Catalyst
(c) Surface active agent
(d) Soap

6. Which of the following is used as a preservative to protect processed food?

(a) Saccharin
(b) BHT
(c) Sodium sulphate
(d) Sodium metabisulphite

7. The drugs used to get relief from pain are called.

(a) Antibiotics
(b) Antipyretics
(c) Analgeics
(d) Antiseptics

8. Which of the following is an antihistamine drug?

(a) Ciprofloxacin
(b) Chloroquine
(c) Chloramphenicol
(d) Chlorpheniramine maleate

9. Which of the following is a tranquilizer?

(a) Morphine
(b) Seconal
(c) Phenacetin
(d) Streptomycin

10. 2-Acetoxy benzoic acid is called

(a) Mordant dye
(b) Aspirin
(c) Antiseptic
(d) Antibiotic

11. Morphine is

(a) Antiseptic
(b) Antibiotics
(c) Analgesics
(d) Antimalarial

12. Heroin is a derivative of

(a) Nicotine
(b) Morphine
(c) Caffeine
(d) Cocains

13. Which of the followings is used as germicide?

(a) Sodium lauryl sulphate
(b) Cetyltrimethylammonium chloride
(c) Lauryl alcohol ethoxylate
(d) Sodium-2-dodecylbenzene sulphonate

14. Which of the followings is an anionic detergent?

(a) $C_6H_5 - SO_3Na$
(b) $CH_3\,(CH_2)_{16}\,N^+\,(CH_3)_3\,Cl^-$
(b) $CH_3\,(CH_2)_{16}\,CH_2OSO_3Na$
(d) $CH_3\,(CH_2)_{16}\,COO\,(CH_2CH_2O)_n -$
$- CH_2CH_2\text{–}OH$

15. The oxidant which is used as an antiseptic is

(a) $KMnO_4$ (b) $KBrO_3$

(c) CrO_3 (d) KNO_3

16. Which of the followings is used as a "morning after pill"?

(a) Norethindrone (b) Mifepristone

(c) Promethazine (d) Bithional

17. Tincture of iodine is

(a) aqueous solution of I_2 (b) alcoholic solution of I_2

(c) aqueous solution of KI (d) solution I_2 in aqueous KI

18. Pick out the wrong statement.

(a) BHT is an antioxidant (b) Alitame is an artificial sweetener

(c) Sodium alkyl sulphate is a cationic detergent (d) Tetrazine is a harmful edible colour.

19. Pick out the wrong statement for a detergent molecule.

(a) It is not easily biodegraded. (b) It is sodium salt of fatty acid.

(c) It is a source of active agent. (d) It has both non-polar organic part and a polar group.

20. Detergents can be made biodegradable by taking

(a) Cyclic hydrocarbon chain (b) Unbranched hydrocarbon chain

(c) Benzenoid with hydrocarbons (d) Hydrocarbon with more branching

ANSWERS FOR MULTIPLE CHOICE QUESTIONS

1. (d) 2. (a) 3. (d) 4. (a) 5. (c) 6. (d) 7. (c) 8. (d) 9. (b) 10. (b)
11. (c) 12. (b) 13. (b) 14. (c) 15. (a) 16. (b) 17. (b) 18. (c) 19. (b) 20 (b)

❑❑❑

I. LOGARITHMS

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						0202	0253	0294	0334	0374	4	8	12	16	20	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
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						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
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						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
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26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4320	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4963	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
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48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6002	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

II. LOGARITHMS

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51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	8316	1	2	2	3	4	5	6	6	7
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55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
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60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
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73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
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92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9998	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

III. ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	3
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2383	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2788	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

IV. ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	10
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	12
.79	6166	6180	6194	6209	6223	6237	6252	6266	6284	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	9	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	8	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	16	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	15	17	19
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	10	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20