313

Intermediate (TOSS) Course
Senior Secondary Course

CHEMISTRY

2

(CORE MODULES)

Telangana Open School Society (TOSS), Hyderabad

SCERT Campus, Opp. to L.B. Stadium, Basheerbagh, Hyderabad-500
001Telangana. Phone: 040-23299568, website; telanganaopenschool.org
E-mail: dirtoshyd@gmail.com

Telangana Open School Society

Print: 2023

No of Copies:

Printed in India

at
For the Director at Telangana Govt. Text Book Press, Mint
Compound, Khairatabad, Hyderabad, Telangana.

SENIOR SECONDARY COURSE
INTERMEDIATE (TOSS) COURSE
CHEMISTRY-ADDITIONAL CURRICULUM

Chief Advisor	
Smt. Vakati Karuna, IAS Secretary to Government, Department of Education, Government of Telangana, Hyderabad	
Text Book Printing Council	
Smt. A. Sridevasena, IAS Director of School Education, Telangana, Hyderabad	
Sri. P. V. Srihari Director, TOSS, Telangana, Hyderabad	
Sri. S. Srinivasa Chary Director, Textbook Press, Telangana, Hyderabad	
Chief Coordinator	
Sri. Marasani Somi Reddy Joint Director, TOSS, Telangana, Hyderabad	
Coordinators	
Sri. B. Venkateswar Rao State Coordinator, TOSS, Telangana, Hyderabad	**Smt. Ganta Sarita** State Coordinator, TOSS, Telangana, Hyderabad

Telangana Open School Society (TOSS), Hyderabad

SCERT Campus, Opp. to L.B. Stadium, Basheerbagh, Hyderabad-500 001Telangana. Phone: 040-23299568, website; telanganaopenschool.org
E-mail: dirtoshyd@gmail.com

SENIOR SECONDARY COURSE
INTERMEDIATE (TOSS) COURSE
CHEMISTRY-ADDITIONAL CURRICULUM
CONTENT DEVELOPMENT TEAM

EDITOR

Dr. Viplav Duth Shukla,
Associate Professor of Chemistry,
Department of Chemistry, Govt City College

WRITERS

Inorganic Chemistry

Dr. Abhijit Kantankar

Assistant Professor,
Department of Chemistry,
Tara Govt College, Sangareddy Dist,

Dr. K. Vani

Assistant Professor,
Department of Chemistry,
Tara Govt College, Sangareddy,

Dr. A. Dayanand

Assistant Professor,
Department of Chemistry,
Govt. City College, Hyderabad

Dr. K. Ashwini

Assistant Professor,
Department of Chemistry,
Telangana Mahila University,

Organic Chemistry

Dr. P. Sarita Rajender

Senior Assistant Professor,
Head, Dept. of Chemistry,
Univ. College of Engineering, O.U.,

Dr. S. Gururaj

Assistant Professor,
Department of Chemistry,
Nizam College, O.U.,

Dr. Viplav Duth Shukla

Associate Professor,
Department of Chemistry,
Govt City College, Hyderabad.

Physical Chemistry

Dr. A. Hari Padmasri

Professor,
Department of Chemistry,
Univ. College of Science, O.U.,

Sri. Busi Anil Kumar

Assistant Professor,
Department of Chemistry,
Govt City College, Hyderabad.

Dr. Eluri Yadaiah

Associate Professor,
Department of Chemistry,
Govt City College, Hyderabad.

Smt. Malathi

Assistant Professor,
Department of Chemistry,
N B Science College, Hyderabad.

General Chemistry

Dr. P. Pallavi

Assistant Professor,
Department of Chemistry,
Nizam College, OU.

Dr. B. Kavita

Assistant Professor,
Department of Chemistry,
Nizam College, OU.

Layout Designing

Dr. S. Gururaj
grsomadi@gmail.com

Cover page designing & Illustrations

Sri. K. Sudhakara Chary
MPUPS, Maripeda, Mulugu

FOREWORD

Dear Learner,

The Department of Education is giving equal importance to non-formal education through Open Distance Learning (ODL) mode of the lines of formal education. This is the first State Open School established in the country in the year 1991 offering courses up to Upper primary Level till 2008. From the academic year 2008-2009 SSC Course was introduced and Intermediate Course from the year 2010-2011. The qualified learners from the Open School are eligible for both higher studies and employment. So far **4,88,853** learners were enrolled in the Open Schools and **2,86,663** learners have successfully completed their courses. The Open School system is providing a second chance of learning for those who could not fulfil their dreams of formal education.

Government of Telangana is keen in providing quality education by supplying study materials along with the text books to enable the learners to take the exam with ease. Highly experienced professionals and subject experts are involved in preparing curriculum and study material based on subject wise blue prints. The study material for the academic year 2023-24 is being printed and supplied to all the learners throughout the state.

Welcome to the Revised Chemistry Course of Telangana Open Schooling System (TOSS) based on the National Institute of Open Schooling and the National Common Core Curriculum. This Course has four volumes I, II and III consist of theory portion and volume IV is a practical manual. The first book is in your hands. This book comprises one lesson of module 1 on Some Basic Concepts of Chemistry, three lessons of Module 2 on Atomic Structure and Chemical Bonding, five lessons of Module 3 on States of Matter, two lessons of Module 4 on Chemical Energetics and five lessons of module 5 on Chemical Dynamics. In Module 1 you will learn about the various units used to calculate the number of atoms, molecules and ions involved in chemical reactions. Module 2 will enlighten you about what lies inside the atoms and the different types of chemical bonds through which atoms combine. Module 3 deals with the various aspects of three states of matter *viz*, solid, liquid and gas. You will also learn about the properties of solutions and colloids. Module 4 deals with chemical reactions accompanied with energy changes and basic concepts like internal energy, enthalpy, entropy and spontaneity. Module 5 highlights on the Characteristics of Chemical Dynamics, catalysis inter conversion of Chemical energy into electrical energy in electrochemistry, electrochemical cells and fuel cell. We hope you will enjoy the course and find it interesting.

WE wish the learners of Open School make best use of the study material to brighten their future opportunities and rise up to the occasion in building Bangaru Telangana.

Wishing you happy chemistry learning ….

With best wishes.....

-WRITERS

HOW TO USE THE STUDY MATERIAL

Your learning material has been developed by a team of chemistry experts in open and distance learning. A consistent format has been developed for self-study. The following points will give you an idea on how to make best use of the print material.

Title is an advance organiser and conveys an idea about the contents of the lesson. *Reflect on it.*

Introduction highlights the contents of the lesson and correlates it with your prior knowledge as well as the natural phenomena in operation in our immediate environment. *Read it thoroughly.*

Objectives relate the contents to your desired achievements after you have learnt the lesson. Remember these.

Content of the lesson has been divided into sections and sub-sections depending on thematic unity of concepts. Read the text carefully and make notes on the side margin of the page. After completing each section, answer intext questions and solve numerical problems yourself. This will give you an opportunity to check your understanding. You should continue reading a section till such time that you gain mastery over it. At some places you will find some text in ***italics and bold***. This indicates that it is important. You must learn them.

Solved Examples will help you to understand the concepts and fix your ideas. In fact, problem solving is an integral part of training in physics. Do them yourself and note the main concept being taught through a particular example.

Activities are simple experiments which you can perform at your home or work placeusing readily available (low cost) materials. These will help you to understand physics by doing. Do them yourself and correlate your findings with your observations.

Intext questions are based on the concepts discussed in every section. Answer these questions yourself in the space given below the question and then check your answers with the model answers given at the end of the lesson. This will help you to judge your progress. If you are not satisfied with the quality and authenticity of your answers, turn the pages back and study the section again.

What have you learnt is essentially summary of the learning points for quick recapitulation. You may like to add more points in this list.

Terminal exercises in the form of short, long and numerical question will help you to develop a perspective of the subject, if you answer these meticulously. Discuss your responses with your peers or counsellors.

Answers to in text questions: These will help you to know how correctly you have answered the intext questions.

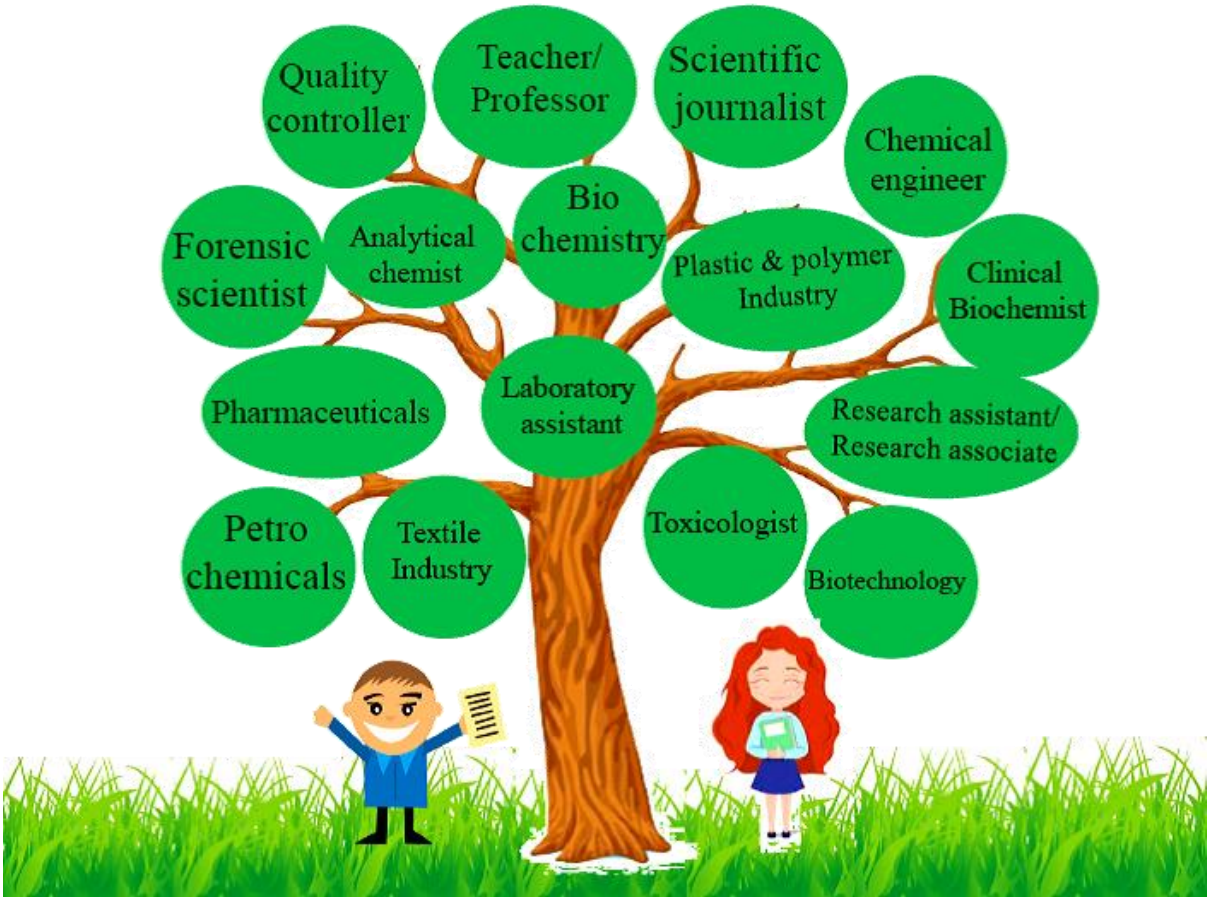
Audio: For understanding difficult or abstract concepts, audio programmes are available on certain content areas. You may listen to these on FM Gyanvani or may buy the CDs from Priced Publication Unit, NIOS.

Video: Video programmes on certain elements related to your subject have been made to clarify certain concepts. You may watch these at your study centre or may purchase these CDs from Priced Publication Unit, NIOS.

www. These are few selected websites that you can access for extended learning. Studying at a distance requires self-motivation, self-discipline and self-regulation. Therefore, you must develop regular study habit. Drawing a daily schedule will help you in this endeavour. You should earmark a well-ventilated and well-lighted space in your home for your study. However, it should not be noisy or distract your concentration from your work.

CAREER OPPORTUNITIES AFTER STUDYING CHEMISTRY

Chemical sciences (Chemistry) offer access to a wide range of careers. Chemistry is the study of substances, their makeup and applications. In fact, it is the study of all materials and is vital to every aspect of our lives. Organic Chemistry, Inorganic Chemistry, Analytical chemistry and Biochemistry are the main branches of chemistry. The career options in chemistry are practically endless! However, employment options depend on how far the education, training and experience taken. A chemistry or biochemistry degree can lead to career paths in professions such as Medicine, pharmacology, agriculture, chemical engineering, forensic science, etc. Some of the important career opportunities after studying chemistry at senior secondary level is as



RATIONALE

According to present scheme of school education at Senior Secondary stage, chemistry emerges out as a separate discipline. It is this stage where major emphasis is to be laid on providing suitable conceptual foundation. The present Senior secondary level Chemistry (313) course at TOSS has now been revised as per the NIOS (National Institute of Open Schooling), Common Core Curriculum developed by COBSE (Council of Boards of School Education) and NCERT (National Council for Educational Research and Training) making it current and need based.

The present chemistry course has been developed basically around the themes: Why do chemical reactions occur? What is the quantitative relationship among reacting constituents in a chemical reaction? How far and how fast will a chemical reaction proceed under a given set of conditions? Can we predict whether a chemical reaction will occur or not? What is the relation between the structure of a chemical substance and its functions/properties? In what way is a chemical reaction relevant for getting new types of substances and materials for daily life and chemical industries? Some interdisciplinary aspects have also been provided to make the course more meaningful and functional.

OBJECTIVES OF THE COURSE

It is expected that a learner will be able to:

Understand the principles, theories and laws of chemistry responsible for various chemical processes/reactions,

- realise the role of chemistry in production of many elements (metals/non-metals) and compounds useful in industries and daily life,
- appreciate the chemical nature of inorganic and organic substances around him/her, choose various vocational, professional and applied courses of his/her choice based on knowledge of chemistry gained.
- Apart from this, the present course also aims at developing the following capacity in the learner:
- perform chemical calculations to know about the chemical reactions and chemical compounds,
- explain chemical reactions, concepts and phenomenon,
- develop awareness about uses and abuses of chemical substances,
- develop skills arranging/setting apparatus, handling apparatus and chemicals properly, and
- analyse and synthesise simple compounds.

SPECIAL FEATURES OF THE COURSE

The academic standard of the present chemistry course in comparable with the chemistry course of any State Education Board or Central Board of Secondary Education. The rationale behind the course is that every lesson has a role to play in understanding the holistic view of chemistry. The present course provides eight modules and a laboratory manual. A student appearing for senior secondary examination is expected to offer all the eight modules and practical.

COURSE STRUCTURE

The Revised Chemistry Course has three parts, I, II and III consist of theory portion and part IV is a practical manual. Part I, II and III of theory portion has eight modules. Part-I consists of five modules namely as: Some basic concepts of chemistry, Atomic Structure and Chemical Bonding, States of matter, Chemical Energetics, and Chemical Dynamics. Part-II consists of three modules namely: Chemistry of Elements and Chemistry of Organic Compounds, Part-III consists of two modules namely: Environmental Chemistry and Chemistry and Industry. Each module is further divided into different lessons.

Overview of the Learning Material

Book - 1

Module - I: Atoms, Molecules and Chemical Arithmetics

01. Mole Concept
02. Chemical Arithmatics

Module - II: Atomic Structure and Chemical Bonding

03. Atomic Structure
04. Periodic Table and Atomic Properties
05. Chemical Bonding

Module - III: State of Matter

06. The Gaseous state
07. The Liquid State
08. The Solid State
09. Solutions
10. Colloids

Module - IV: Chemical Energetics

11.Chemical Thermodynamics
12. Spontaneity of Chemical reactions

Module - V: Chemical Dynamics

13. Chemical Equilibrium
14. Ionic Equilibrium
15. Electro Chemistry
16. Chemical Kinetics
17. Adsorption and Catalysis

Book - 2

Module - VI: Chemistry of Elements

18. Occurance and Extraction of Metals
19. Hydrogen and *s* - block Elements
20. General Characteristics of the *p*-block Elements
21. *p*-block Elements and their Compounds - I
22. *p*-block Elements and their Compounds - II
23. d-block and f-block Elements
24. Coordination Compounds

Module - VII: Chemistry of Organic Compounds

25. Nomenclature and General Principles
26. Hydrocarbons
27. Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)
28. Alcohols, Phenols and Ethers
29. Aldehydes, Ketones and CarboxylicAcids
30. Compounds of Carbon Containing Nitrogen
31. Biomlecules

Book - 3

Module VIIIA: Environmental Chemistry

32. Environmental Concerns
33. Air Pollution
34. Water Pollution
35. Heavy Metal Contamination
36. Radioactive Pollution

Module VIIIB: Chemistry and Industry

32. Petrochemicals
33. Polymers
34. Dyes, Paints and Pigments
35. Drugs and Medicines
36. Building Materials

CONTENTS

Module - VI

Chemistry of Elements

18. Occurrence and Extraction of Metals

19. Hydrogen and *s* - block Elements

20. General Characteristics of the *p*-block Elements

21. *p*-block Elements and their Compounds - I

22. *p*-block Elements and their Compounds - II

23. d-block and f-block Elements

24. Coordination Compounds

Chapter 18

OCCURRENCE AND EXTRACTION OF METALS

Metals and their alloys are extensively used in our day-to-day life. They are used for making machines, railways, motor vehicles, bridges, buildings, agricultural tools, aircrafts, ships etc. Therefore, production of a variety of metals in large quantities is necessary for the economic growth of a country. Only a few metals such as gold, silver, mercury etc. occur in free state in nature. Most of the other metals, however, occur in the earth's crust in the combined form, i.e., as compounds with different anions such as oxides, sulphides, halides etc. In view of this, the study of recovery of metals from their ores is very important. In this lesson, you shall learn about some of the processes of extraction of metals from their ores, called metallurgical processes.

Objectives

After reading this lesson, you will be able to:

- differentiate between minerals and ores;
- recall the occurrence of metals in native form and in combined form as oxides, sulphides, carbonates and chlorides;
- list the names and formulae of some common ores of Na, Al, Sn, Pb, Ti, Fe, Cu, Ag, and Zn;
- list the occurrence of minerals of different metals in India;
- list different steps involved in the extraction of metals;
- list and explain various methods for concentration of ores (gravity separation, magnetic separation, froth floatation, and chemical method);
- explain different metallurgical operations: roasting, calcination, and smelting with suitable examples;
- choose the reducing agent for a given ore;
- differentiate between flux and slag, and
- explain different methods for refining of metals : poling, liquation, distillation and electrolytic refining.

* An alloy is a material consisting of two or more metals, or a metal and a non-metal. For example, brass is an alloy of copper and zinc; steel is an alloy of iron and carbon.

18.1 Occurrence of Metals

Metals occur in nature in free as well as combined form. Metals having low reactivity show little affinity for air, moisture, carbon dioxide, or other non-metals present in nature.

Such metals may remain in elemental or native (free) state in nature. Such metals are called 'noble metals' as they show the least chemical reactivity. For example, gold, silver, mercury, and platinum occur in free state.

On the other hand, most of the metals are reactive and combine with air, moisture, carbon dioxide, and non-metals like oxygen, sulphur, halogens, etc., to form their compounds, like oxides, sulphides, carbonates, halides, and silicates, i.e., they occur in nature in a combined state.

A naturally occurring material in which a metal or its compound occurs is called a mineral. A mineral from which a metal can be extracted economically is called an ore.

An ore is that mineral in which a metal is present in appreciable quantities and from which the metal can be extracted economically.

The main active substances present in nature, especially in the atmosphere, are oxygen and carbon dioxide. In the earth’s crust, sulphur and silicon are found in large quantities. Sea-water contains large quantities of chloride ions (obtained from dissolved sodium chloride). Most active metals are highly electropositive and therefore exist as ions. It is for this reason that most of the important ores of these metals occur as (i) oxides, (ii) sulphides, (iii) carbonates, (iv) halides, and (v) silicates. Some sulphide ores undergo oxidation by air to form sulphates. This explains the occurrence of sulphate ores.

Ores are invariably found in nature in contact with rocky materials. These rocky ore earthy impurities accompanying the ores are termed as gangue or matrix. Some important ores and the metals present in these ores are listed in Table 18.1.

Table18.1 Some Important Ores

Type of Ore	**Metals (Common Ores)**
Native Metals	Gold(Au), silver(Ag)
Oxide ores	Iron(Haematite, Fe_2O_3); Aluminium (Bauxite, Al_2O_3,$2H_2O$); Tin (Cassiterite, SnO_2); Copper (Cuprite, Cu_2O); Zinc (Zincite, ZnO); Titanium (Ilmenite, $FeTiO_3$, Rutile, TiO_2)
Sulphide ores	Zinc (Zincblende, ZnS); Lead (Galena, PbS); Copper (Copperglance, Cu_2S); Silver (Silverglance or Argentite, Ag_2S); Iron(Iron pyrites, FeS_2)
Carbonate ores	Iron (Siferite, $FeCO_3$); Zinc (Calamine, $ZnCO_3$), Lead (Cerrusite, $PbCO_3$)
Sulphateores	Lead(Anglesite,$PbSO_4$)
Halideores	Silver (Hornsilver, AgCl); Sodium (Common salt or Rock salt, NaCl); Aluminium(Cryolite,Na_3AlF_6)
Silicateores	Zinc(Hemimorphite,$2ZnO.SiO_2H_2O$)

18.2 General Principles of Extraction of Metals

The process of extracting the metals from their ores and refining them is called *metallurgy*. The choice of the process depends upon the nature of the ore and the type of the metal. The metal content in the ore can vary depending upon the impurities present and chemical composition of the ore. Some common steps involved in the extraction of metals from their ores are:

(i) Crushing and pulverization
(ii) Concentration or dressing of the ore
(iii) Calcination or roasting of the ore
(iv) Reduction of metal oxides to free metal
(v) Purification and refining of metal.

18.2.1. Crushing and Pulverization

The ore is generally obtained as big rock pieces. These big lumps of the ore are crushed to smaller pieces by using jaw crushers and grinders. It is easier to work with crushed ore. The big lumps of the ore are brought in between the plates of a crusher forming a jaw. One of the plates of the crusher is stationary while the other moves to and fro, and the crushed pieces are collected below (Fig. 18.1).

The crushed pieces of the ore are then pulverized (powdered) in a stamp mill shown in Fig. 18.2. The heavy stamp rises and falls on a hard die to powder the ore. The powdered ore is then taken out through a screen by a stream of water.

Pulverization can also be carried out in a ball mill. The crushed ore is taken in a steel cylinder containing iron balls. The cylinder is set into revolving motion. The striking balls pulverize the crushed ore into fine powder.

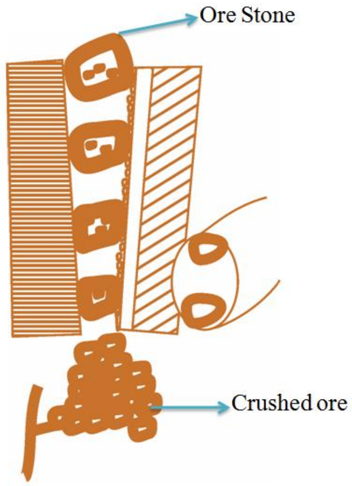


Fig. 18.1 :Jaw Crusher

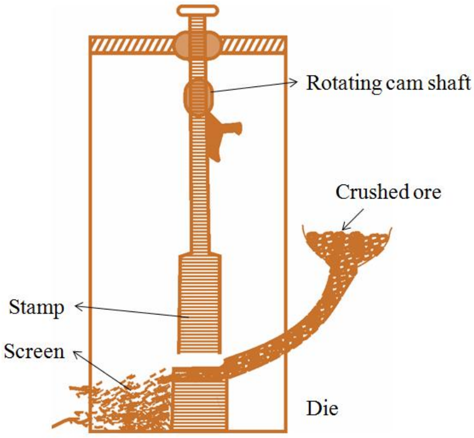


Fig. 18.2:The Stamp mill

18.2.2 Concentration or Dressing of the Ore

Generally, the ores are found mixed with earthy impurities like sand, clay, limestone, etc. These unwanted impurities in the ore are called gangue or matrix.

The process of removal of gangue from powdered ore is called concentration or ore dressing. There are several methods for concentrating the ores. The choice of method depends on the nature of the ore. Some important methods are:

(i) Gravity separation (Hydraulic washing): In this method, the light (low specific gravity) earthy impurities are removed from the heavier metallic ore particles by washing with water. It is therefore used for the concentration of heavier oxide ores, like haematite (FeO_3), tinstone (SnO_2), and gold (Au). In this method, as shown in Fig. 18.3, the powdered ore is agitated with water or washed with a strong current of water. The heavier ore settles down rapidly in the grooves and the lighter sandy and earthy materials (gangue particles) are washed away.

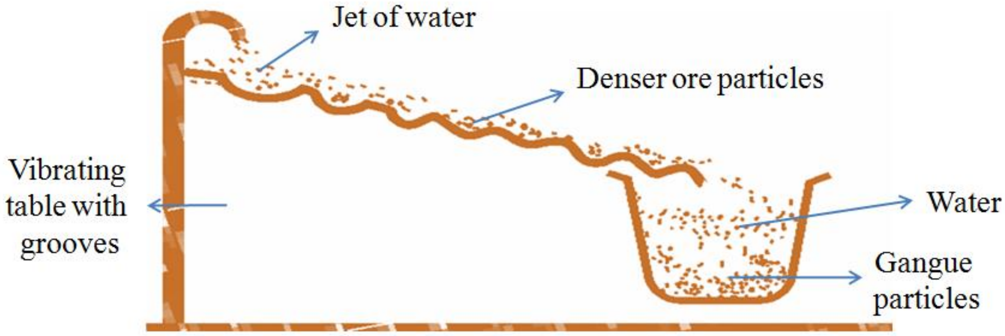


Fig.18.3: Gravity Separation(Hydraulic Washing)

(ii) Magnetic separation method: By this method, those ores can be concentrated which either contain impurities which are magnetic or are themselves magnetic in nature. For example, the tin ore, tinstone (SnO_2), itself is non-magnetic but contains magnetic impurities such as iron tungstate ($FeWO_4$) and manganese tungstate ($MnWO_4$).

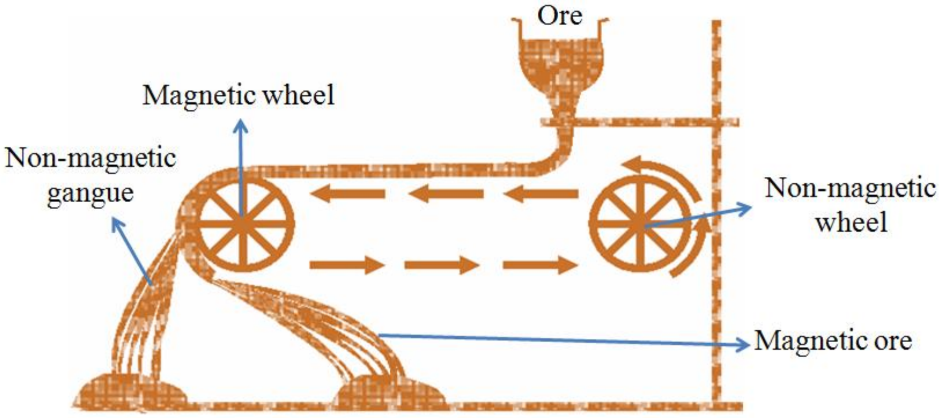


Fig.18.4.:Magnetic Separation

The finely powdered ore is passed over a conveyor belt moving over two rollers, one of which is fitted with an electromagnet (Fig. 18.4). The magnetic material is attracted by the magnet and falls in a separate heap. In this way, magnetic impurities are separated from non-magnetic material.

(iii) Froth floatation method:

This method is especially applied to sulphide ores, such as galena (PbS), zinc blende (ZnS), or copper pyrites (CuFeS2). It is based on the different wetting properties of the surface of the ore and gangue particles. The sulphide ore particles are wetted preferentially by oil and gangue particles by water. In this process, finely powdered ore is mixed with either pine oil or eucalyptus oil. It is then mixed with water. Air is blown through the mixture with a great force. Froth is produced in this process which carries the wetted ore upwards with it. Impurities (gangue particles) are left in water and sink to the bottom from which these are drawn off (Fig. 18.5). Sometimes, to separate a mixture of two sulphide ores, depressants are used or by adjusting the proportion of oil to water. For example, in the separation of an ore containing ZnS and PbS, NaCN depressant is used. It selectively prevents ZnS from coming to the froth.

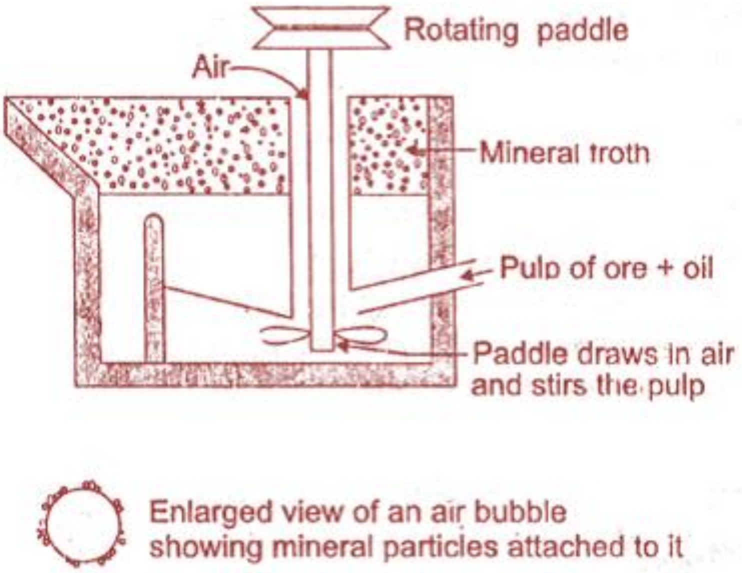


Fig.18.5: Froth floatation

(iv) Chemical method (leaching):

In this method, the ore is treated with a suitable chemical reagent which dissolves the ore, leaving behind insoluble impurities. The ore is then recovered from the solution by a suitable chemical method. This is applied for the extraction of aluminium from bauxite ($Al_2O_3 \cdot 2H_2O$). Bauxite is contaminated with iron(III) oxide (Fe_2O_3), titanium(IV) oxide (TiO_2), and silica (SiO_2). These impurities are removed by digesting the powdered ore with an aqueous solution of sodium hydroxide at 420K under pressure. Aluminium oxide dissolves in sodium hydroxide, whereas iron(III) oxide, silica, and titanium(IV) oxide remain insoluble and are removed by filtration.

$$Al_2O_3 + 6NaOH \longrightarrow \underset{\text{Sodiumaluminate}}{2Na_3AlO_3} + 3H_2O$$

Sodium aluminate is diluted with water to obtain a precipitate of aluminium hydroxide. It is filtered and ignited to obtain pure alumina.

$$Na_3AlO_3 + 3H_2O \longrightarrow Al(OH)_3 + 3NaOH$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Intext Questions18.1

1. What is the difference between an ore and a mineral?

....

2. Name some important methods of concentrating the ores.

....

3. Which metal is extracted from the mineral zinc blene?

....

18.2.3 Calcination and Roasting of the Ore

The concentrated ore is converted into metal oxide by calcination or roasting.

(A) Calcination: Calcination involves heating of the concentrated ore in a limited supply of air so that it loses moisture, water of hydration, and gaseous volatile substances. The ore is heated to a temperature so that it does not melt. Two examples of calcination are given below:

(i) Removal of water of hydration

$$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$$

(ii) Expulsion of CO_2 from carbonate

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

(B) Roasting: Roasting is a process in which the concentrated ore is heated in a free supply of air at a temperature insufficient to melt it. The following changes take place during roasting:

(i) Drying of the ore.

(ii) Removal of the volatile impurities like arsenic, sulphur, phosphorus, and organic matter.

$$4As + 3O_2 \longrightarrow 2As_2O_3(g)$$
$$S + O_2 \longrightarrow SO_2(g)$$
$$4P + 5O_2 \longrightarrow P_4O_{10}(g)$$

(iii) Conversion of the sulphide ores into oxides.

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

Calcination and roasting are generally carried out in a reverberatory furnace or in a multiple hearth furnace.

18.2.4 Reduction of the Metal Oxides to Free Metal

This process is carried out after calcination or roasting of ores. In this process called *smelting*, the oxide ores are converted into the metallic state by reduction.

(A) Smelting: Smelting is a process in which the oxide ore in molten state is reduced by carbon or other reducing agents to free metal.

(i) by using carbon as a reducing agent:

This method is used for the isolation of iron, tin, and zinc metals from their respective oxides. The oxide ores are strongly heated with charcoal or coke. Reduction occurs by the action of carbon and/or carbon monoxide which is produced by the partial combustion of coke or charcoal.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$
$$SnO_2 + 2C \longrightarrow Sn + 2CO$$
$$ZnO + C \longrightarrow Zn + CO$$

(ii) Other reducing agents:

Oxide ores which cannot be reduced by carbon or metals which show affinity to carbon by forming metal carbides, are reduced by reducing agents like aluminium, sodium, magnesium, or hydrogen. *Oxides* like chromium oxide (Cr_2O_3) or manganese oxide (Mn_3O_4) are reduced by aluminium powder in a highly exothermic reaction. This process is known as *Goldschmidt's Alumino-thermic Reduction* method.

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + \text{Heat}$$

$$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3 + \text{Heat}$$

Heat is generated in the process due to the formation of Al_2O_3 which is a highly exothermic reaction.

Titanium is obtained by the reduction of $TiCl_4$ (produced by the action of carbon and chlorine on TiO_2) by Mg in an inert atmosphere of argon (Kroll process).

$$TiCl_4 + 2Mg \xrightarrow[1103K]{Heat} Ti + 2MgCl_2$$

Titanium can also be obtained by the reduction of TiO_2 by sodium.

$$TiO_2 + 4Na \xrightarrow[1103K]{Heat} Ti + 2Na_2O$$

Tungsten and molybdenum can be obtained by the reduction of their oxides by hydrogen.

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

(iii) Self-reduction:

This is applied to the sulphide ores of copper, mercury, and lead. The ores are heated in air, a part of these sulphide ores is changed into the oxide or sulphate which then reacts with the remaining part of the sulphide ore to give the metal and sulphur dioxide. The reactions showing their extraction are given below:

(1) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

Copperglance

$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

(2) Copper produced at this stage is called Blister copper. The evolution of sulphur dioxide produces blisters on the surface of solidified copper metal.

$2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$

Cinnabar

$2HgO + HgS \longrightarrow 3Hg + SO_2$

(3) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

Galena

$PbS + 2O_2 \longrightarrow PbSO_4$

$PbS + 2PbO \longrightarrow 3Pb + SO_2$

$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$

(B) Reduction of concentrated ores by other methods:

Some metals cannot be obtained from their ores by using common reducing agents such as C, CO, H_2, etc. Other methods of reduction are used for such cases.

(i) Reduction by precipitation:

Noble metals like silver and gold are extracted from their concentrated ores by dissolving metal ions in the form of their soluble complexes. The metal ions are then regenerated by adding a suitable reagent. For example, concentrated argentite ore (Ag_2S) is treated with a dilute solution of sodium cyanide (NaCN) to form a soluble complex:

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

This solution is decanted off and treated with zinc to precipitate silver,

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

(ii) Electrolytic Reduction:

Active metals like sodium, potassium, and aluminium, etc., are extracted by the electrolysis of their fused (molten) salts. For example, sodium is obtained by the electrolysis of fused sodium chloride (Down's process). The reactions taking place in the electrolytic cell are:

$$NaCl \rightleftharpoons Na^+ + Cl$$

Na^+ ions move towards the cathode and Cl ions move towards the anode. Following reactions take place at the electrodes:

At the Cathode $Na^+ + e^- \longrightarrow Na$ (Reduction)
(Negative electrode) (metal)

At the Anode $Cl^- \longrightarrow Cl + e^-$ (Oxidation)
(Positive electrode)

$$Cl + Cl \longrightarrow Cl_2$$

Aluminium is extracted from molten alumina (Al_2O_3) by electrolysis. The melting point of alumina is quite high (2323K) which is inconvenient for electrolysis. It dissolves in molten cryolite (Na_3AlF_6) at around 1273K. The reactions which take place in the cell are:

At the Cathode $Al^{3+} + 3e^- \longrightarrow Al$ (metal)

At the Anode $C + 2O^{2-} \longrightarrow CO_2 + 4e^-$

Intext Questions18.2

1. Explain the following terms: Calcination, Roasting, Smelting, Fluxand Slag.

....

2. Which is the cheapest and most abundant reducing agent employed in the extraction of metals?

....

3. Name the process which is used for converting sulphide ores in to oxides.

....

4. What happens to (i) Bauxite and (ii) Calamine ores during calcination?

....

18.2.5 Refining of Metals

Except in the electrolytic reduction method, metals produced by any other method are generally impure. The impurities may be in the form of (i) other metals (ii) unreduced oxide of the metal (iii) non-metals like carbon, silicon, phosphorus, sulphur, etc., and (iv) flux or slag. Crude metal may be refined by using one or more of the following methods:

(i) Liquation: Easily fusible metals like tin, lead, etc., are refined by this process. In this method, the impure metal is poured onto the sloping hearth of a reverberatory furnace (Fig. 18.6) and heated slowly to a temperature little above the melting point of the metal. The pure metal drains out leaving behind infusible impurities.

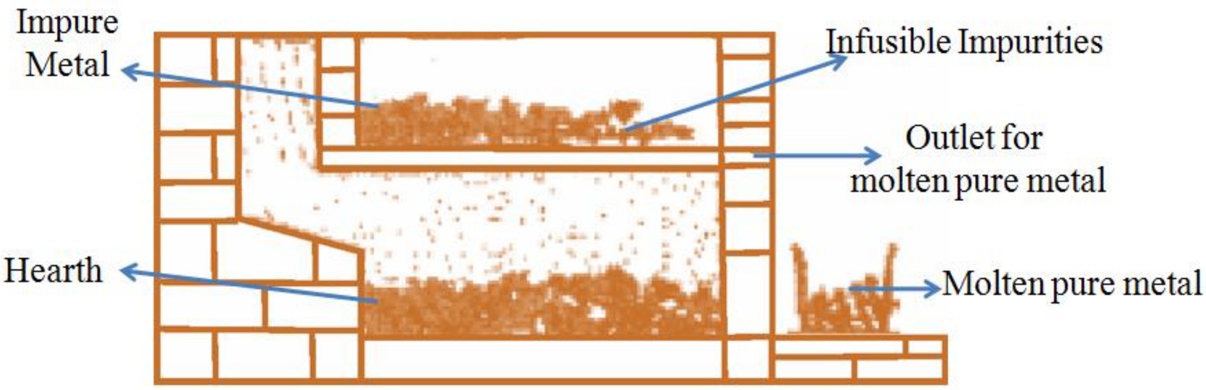


Fig.18.6:Liquation

(ii) Poling: Poling involves stirring the impure molten metal with green logs or bamboo. The hydrocarbons contained in the pole reduce any metal oxide present as impurity. Copper and tin are refined by this method (Fig. 18.7).

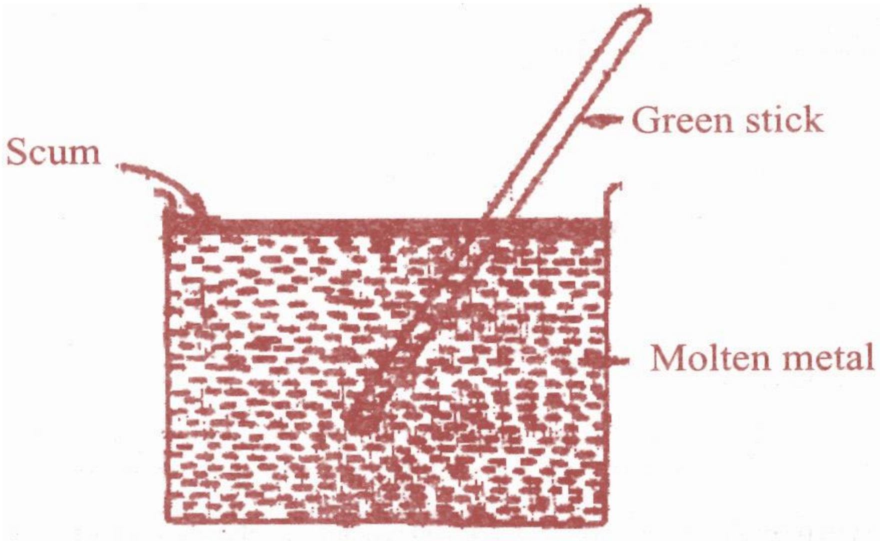


Fig.18.7: Poling

(iii) Distillation: Volatile metals like zinc and mercury are purified by distillation. The pure metal distils over, leaving behind non-volatile impurities.

(iv) Electrolytic Refining: A large number of metals like copper, silver, zinc, tin etc. are refined by electrolysis. A block of impure metal is made the anode and a thin sheet of pure metal forms the cathode of the electrolytic cell containing a suitable metal salt solution which acts as an electrolyte (Fig. 18.8). On passing current, pure metal deposits at the cathode sheet while more electropositive impurities are left in solution. Less electropositive metals do not dissolve and fall away from the anode to settle below it as anode mud.

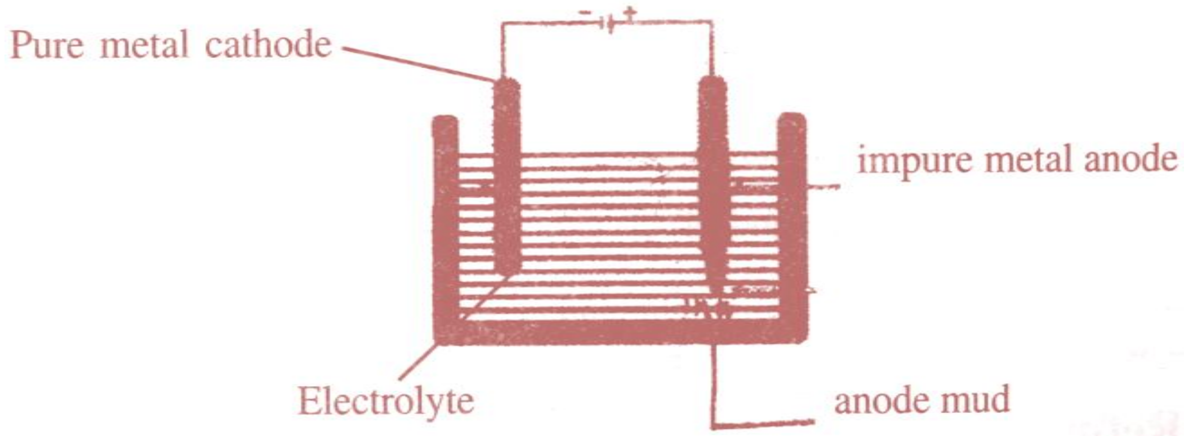


Fig.18.8: Electrolytic Refining

For example, in the electrolytic refining of crude copper (blister copper), a large piece of impure copper is made the anode and a thin piece of pure copper is made the cathode. An acidified solution of copper sulphate is used as an electrolyte. On passing an electric current of low voltage through the solution, copper(II) ions obtained from copper sulphate solution go to the cathode where they are reduced to the free copper metal and get deposited.

$$Cu^{2+} + 2e^- \longrightarrow Cu \text{ (at cathode)}$$

An equivalent amount of the metal from the anode dissolves into the electrolyte as Cu^{2+} ions.

$$Cu \longrightarrow Cu^{2+} + 2e^- \text{ (at anode)}$$

As the process goes on, the anode becomes thinner while the cathode becomes thicker. The impurities like silver, gold settled down at the bottom of the cell as 'anode mud'.

(v) Zone refining: This approach is designed on the idea that impurities are more soluble in the ‘melt’ of the metal than in its solid state. A rod made of impure metal with a circular mobile heater attached to one end (Fig. 18.9). The heater is permitted to advance while the molten zone travels with it. The heater was moved from one end to the other multiple times in the same direction. Impurities are concentrated at one end, and this end is chopped to remove impurities.

This procedure is conveniently used to purify low-melting metals like Ge, Si, Ga, B and In.

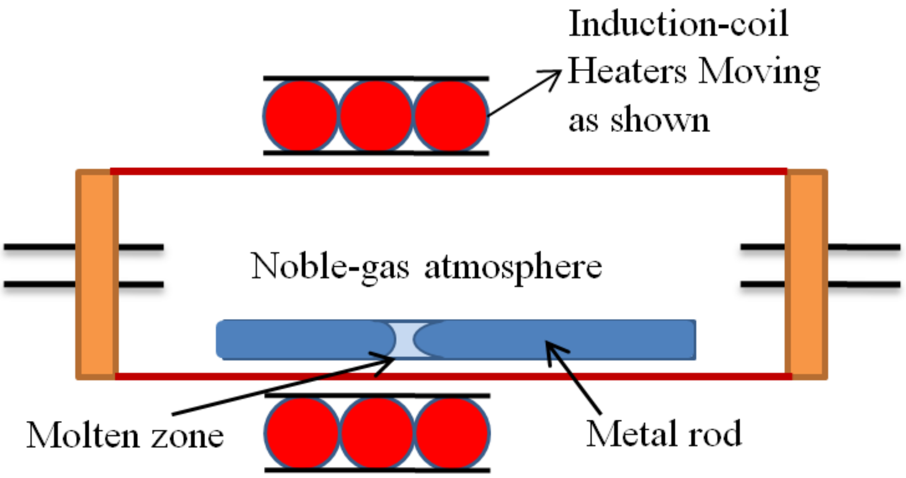


Fig. 18.9: Process of Zone refining.

(vi) Vapour phase refining:

In this process, impure metal is chemically transformed into its volatile compound, which is subsequently collected somewhere and degraded to produce pure metal. This procedure is feasible only, when the metal can form a volatile compound with accessible chemical reagents and thus formed compound should be easily decomposed.

Impure Ni can be refined using the ‘Mond Process’ in which Ni is initially converted into its tetra carbonyl which on pyrolytic decomposition gives refined Ni.

$$Ni + 4CO \xrightarrow{330\text{-}350K} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450\text{-}470K} Ni + 4CO$$

Zr and Ti can be refined using the “van Arkel Method” in which these metals are heated with iodine under the vacuum condition to form their volatile iodides. These iodides are decomposed by an electrical arc using a tungsten filament to produce the temperature over 1800K to give refined metals.

$$Zr + 2I_2 \rightarrow ZrI_4$$

$$ZrI_4 \rightarrow Zr + 2I_2$$

18.3 Intext Questions

1. Which method is used for the refining of metals that are easily fused?

....

2. Which metals are refined by poling?

....

3. Name a metal which is purified by distillation.

....

4. Name any three elements which are refined by electrolytic refining

....

5. Which metals were purified using the Zone refining method?

……………………………………………………………………………………………

6. In the purification of Ni using the Mond process, Ni metal is converted into which compound?

……………………………………………………………………………………………..

18.3. Advanced Metallurgy

Several principles of chemical sciences were applied in the field of metallurgy for the feasible extraction of metals from their ores conveniently. These principles are mainly based on Chemical Thermodynamics and Electrochemistry.

18.3.1 Thermodynamic principles involved in metallurgy:

Chemical transformations in metallurgy can be explained using core concepts of thermodynamics. The change in Gibbs free energy for any chemical process at a certain specified temperature is denoted by using the following equation;

$$\Delta G = \Delta H - T\Delta S \quad \text{……….} \ (1)$$

Where, ΔH is the enthalpy change and is the entropy change for the chemical transformation.

The equation can also be expressed in the following form;

$$\Delta G- = -RT\ln K \quad \text{………..}(2)$$

Where, K is the equilibrium constant of chemical reaction at a particular temperature T. The negative sign of ΔG- indicates a positive temperature which further indicates the feasibility of a forward reaction. Similarly if ΔS and ΔH are positive, TΔS directly proportional to an increase in the temperature.

When two chemical transformations are simultaneously carried out in a single system, the net sum of ΔG- these chemical transformations is negative which indicates the feasibility of the reaction and the coupling of the reaction is possible. The relation between ΔG- and Temperature could be explained using Ellingham Diagrams.

18.3.1 a.Ellingham Diagram:

H.J.T. Ellingham proposed the graphical representation of Gibbs free energy (ΔG-) with variable temperatures (T) to provide significant information for the selection of appropriate reducing agents in the metallurgical transformation of metal oxides into metals which is known as the “Ellingham Diagram”. These diagrams are useful to evaluate the role of various reducing agents in the reductive transformation of metal ores. For a particular chemical transformation, if the ΔG is negative, that chemical reaction is feasible.

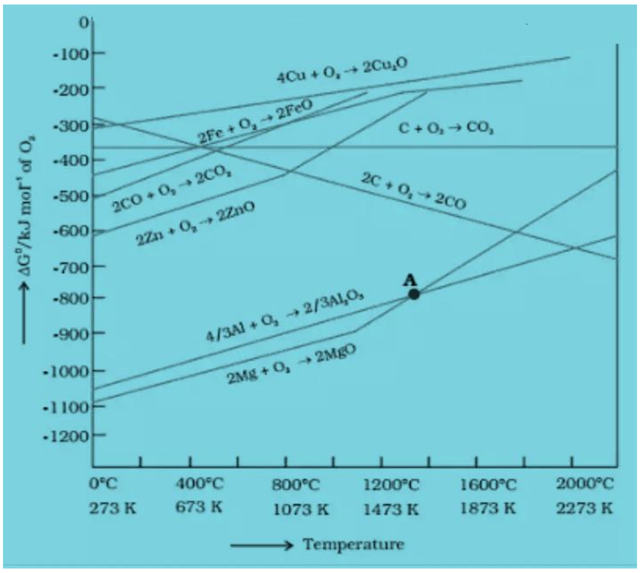


Fig. 18.20: Gibbs free energy (ΔG-) vs T curves for the formation of metal oxides (Ellingham diagram)

18.3.1 b. Applications:

i. Extraction of Fe from FeO:

Iron is extracted from FeO on treatment with coke powder in the blast furnace. the following chemical reaction is carried out in this process.

$$FeO(s) + C(s) \rightarrow Fe(s/l) + CO(g)$$

$$FeO(s) \rightarrow Fe(s) + \frac{1}{2} O_2\,(g)\ [\Delta G^{-}_{(FeO,\ Fe)}]$$

$$C(s) + \frac{1}{2} O_2\,(g) \rightarrow CO(g)\ [\Delta G_{(C,CO)}]$$

$$\Delta G_{(C,CO)} + \Delta G^{-}_{(FeO,\ Fe)} \rightarrow \Delta rG\ \ ....(3)$$

This reaction is feasible only if the R.H.S equation (3) is negative. In the Ellingham diagram of the reaction 5.6 ΔG vs T plot moves upward and oxidation of C into CO_2 moves downward. Approximately in the vicinity of 1073K, C →CO curvefound underneath the Fe→FeO curve which indicates $\Delta G_{(C\rightarrow CO)}$ has lesser value than $\Delta G_{(Fe\rightarrow FeO)}$ which clearly suggests the feasibility of reduction process of FeO using coke at 1073 K. In a similar route Magnesium can reduce Al_2O_3.

Oxide ores of iron were reduced at variable temperatures in the Blast Furnace (See **Fig. 18.21**). The Hot air current provides a temperature of around 2170 K at the bottom part of the furnace and the temperature gradually cooled up to 1070 K at the top region of the Furnace. The hot air current charged with CO propelled to the upper region of the furnace where oxide ores (Fe_2O_3 and Fe_3O_4) get reduced to FeO relatively at a lower temperature as affirmed in the ΔG vs T plot with the intersection point in the range of 500-800 K.

$CaCO_3$ is decomposed to CaO which combines with silicate impurities which will be removed as slag ($CaSiO_3$). The Crude Iron recovered from the Blast furnace is called "Pig Iron" which contains 4% carbon content and several volatile and non-volatile impurities like P, S, Si, Mn etc. When Pig iron is combined with scrap iron and melt them with coke powder under the air blast provides Cast iron which contains reduced amount of carbon (3%). While

Wrought iron (also called Malleable iron) is one the purest form of commercially available iron which is prepared in a specially designed “Reverberatory furnace” which has a haematite lining that oxidizes carbon and other impurities.

Further addition of limestone acts as flux material that combines with oxidized compounds of S, Si, and P impurities to form slag which is subsequently removed to get pure Wrought iron. The chemical transformations that take place are listed below.

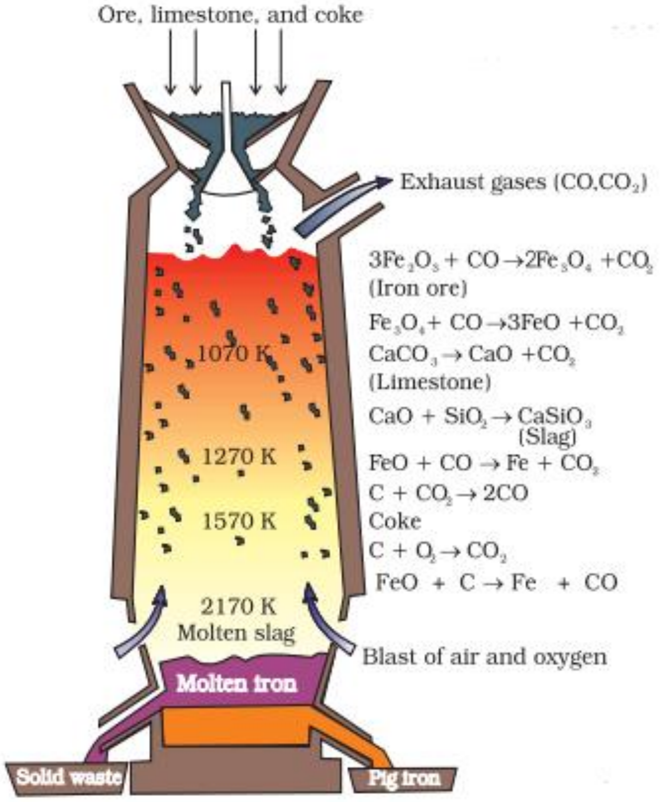


Fig. 18.21: *Blast Furnace*

$3Fe_2O_3$ [Iron ore]+ $CO \longrightarrow 2Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$
$CaCO_3$ [limestone] $\longrightarrow CaO + CO_2$
$CaO + SiO_2 \longrightarrow CaSiO_3$
[Slag]
$FeO + CO \longrightarrow Fe + CO_2$
C [Cocke]+ $CO_2 \longrightarrow 2CO$
$C + O_2 \longrightarrow CO_2$
$FeO + C \longrightarrow Fe + CO$
$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$

ii. Extraction of Copper from Cu_2O:

In the Ellingham curve (ΔG^{-} vs T), the line corresponding to the formation of Cu_2O appears at the topmost level indicating the reduction of it is very feasible using carbon at very low temperatures. But in nature, copper is usually found in the form of sulfide ores which are oxidized to copper oxides either through smelting or roasting methods. These oxides are heated in the Reverberatory furnace along with coke and silica. Coke reduced the oxides into crude copper while silica reacts with impurities like iron oxides to form removable slag leaving behind the copper matte which is a mixture of Cu_2S and FeS and other impurities.

Further Copper matte is loaded in a special Blast converter having silica lining in which leftover oxides/ sulfides are converted into molten metallic copper. On cooling it develops blisters owing to the dispersal of SO_2 gas from the molten copper hence it is called "Blister copper". The reactions involved in this process are shown below.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$Cu_2O + C \rightarrow 2\,Cu + CO$$
$$FeO + SiO \rightarrow \quad FeSiO_3\,(Slag)$$
$$2FeS + 3O_2 \rightarrow \quad 2FeO + 2SO_2$$
$$FeO + SiO_2 \rightarrow \quad FeSiO_3$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \quad \rightarrow 6Cu + SO_2$$

iii. Extraction of Zinc from ZnO:

It is evident from the Ellingham curve it is clear that the reduction of ZnO is carried out at far higher temperatures than the reduction of Cu_2O. The specially designed Brickettes made up of ZnO, Coke and Clay are used in the reduction process to get crude Zinc metal. The crude Zinc is refined by distillation process.

$$ZnO + C\ (coke) \rightarrow Zn + CO\ (at\ 1673K)$$

c. Drawbacks of Ellingham Diagram:

- It explains only the feasibility of chemical reaction but it does not provide any information about the reaction chemical kinetic.
- It always assumes the chemical reaction in equilibrium state.

18.3.2. Electrochemical Principles involved in Metallurgy:

We have seen how pyrometallurgy is based on thermodynamic concepts. In the reduction of metal ions in a solution or molten state, the same concepts work well. Here, they are either electrolyzed or reduced by the addition of a reducing element.

Electrolysis is employed in the reduction of molten metal salt. These techniques utilize electrochemical principles and can be understood using following equation.

$$\Delta G^{-} = -nFE^{-} \quad \text{……..(1)}$$

Here, E^{-} is the electrode potential of the redox couple produced in the system, and n is the number of electrons. The majority of reactive metals have electrode potentials that are significantly negative. This makes their reduction challenging. The less reactive metal will get out of the solution and the more reactive metal will remain in the solution if the difference between two values corresponds to a positive E and consequently a negative ΔG^{-} in equation **1**. For example;

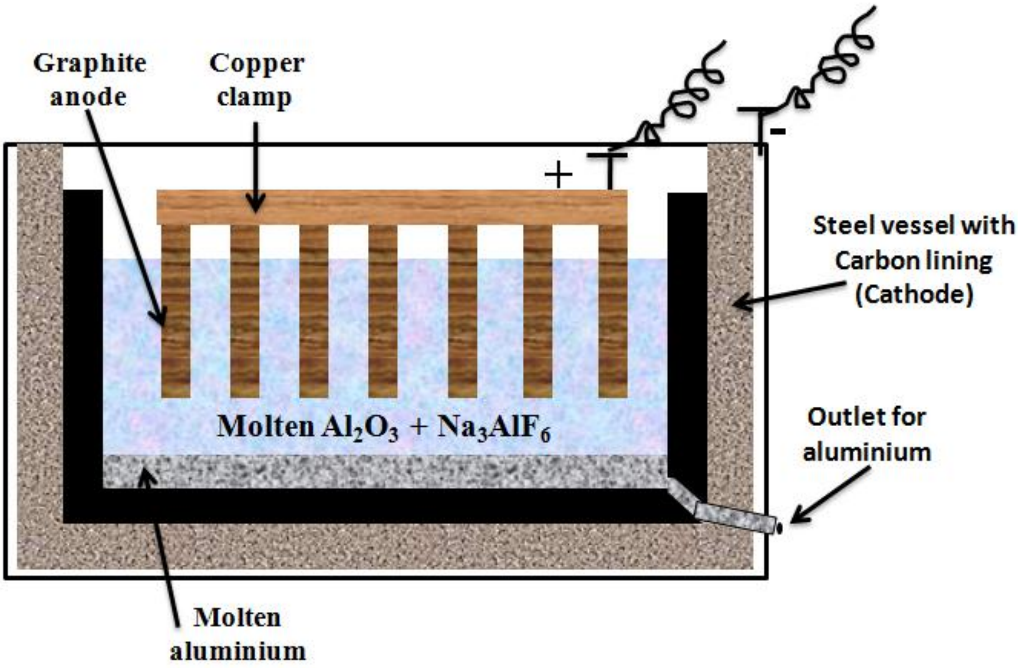
$$Cu^{2+}\ (aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}\ (aq)$$

The M^{n+} ions are released and deposited at the cathode, the negative electrode, in simple electrolysis. Regarding the reactivity of the metal created and the appropriate materials being utilized as electrodes, precautions must be taken. A flux may occasionally be applied to the molten material to increase conductivity.

When purified Al_2O_3 is combined with Na_3AlF_6 or CaF_2 in aluminium metallurgy to reduce the melting point and boost conductivity. Graphite serves as the anode and a steel tank with a carbon lining serves as the cathode in the electrolysis of a fused matrix. The overall reaction may be written as:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

This process of electrolysis is popularly known as ***Hall-Heroult*** process (see fig **18.22)**.



18.22: *Electrolytic cell for the extraction of Aluminum*

Thus, the molten mass is electrolyzed using carbon electrodes in an electrolytic cell. When the carbon of the anode combines with the oxygen released at the anode, CO and CO_2 are created. By doing this, each kg of aluminium created roughly 0.5 kg of carbon anode that was burned off.

These are the electrolytic reactions:

Cathode: Al^{3+} (melt) + $3e^-$ → Al(l)

Anode: C(s) + O^{2-} (melt) → CO(g) + $2e^-$

C(s) + $2O^{2-}$ (melt) → CO_2 (g) + $4e^-$

18.3.2. a. Copper Extraction from Cheap Ores and Scraps:

Lower-grade copper ores are processed using hydrometallurgy to extract copper. By utilizing acid or bacteria, it leached out. Cupric ion containing solution is treated using either hydrogen gas or scrap iron. The electrochemical reaction is shown below.

$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+ (aq)$.

18.3.2. b. Oxidative Extraction:

In addition to reductions, some extractions are performed using oxidation, especially for non-metals. Chlorine extraction from brine, which is common salt that is prevalent in seawater, is a straightforward example of oxidation-based extraction.

$2Cl^- (aq) + 2H_2O(l) \rightarrow 2OH^- (aq) + H_2(g) + Cl_2(g)$

This reaction which has a ΔG^{-} value around + 422 k.J. from which we get value of E- = -2.2 V using equation ΔG^{-} = - nE°F. Therefore, electrolysis will need an external e.m.f. of 2.2 V. However, in order to overcome additional impeding reactions in the solution, there must be extra potential. As a result, Chlorine gas is obtained with H_2 gas and aqueous NaOH solution as by-products. Molten NaCl may undergo electrolysis under these circumstances. But in that situation, Na metal rather than NaOH is created.

As was previously covered, the process of extracting gold and silver involves cyanide (CN^-) leaching of the metal. Ag to Ag^+ or Au to Au^+ oxidation is also taking place. Later, using the displacement method, the metals are retrieved using Zn as reducing agents.

$$4Au(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[Au(CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$$

18.4. Some Applications of Copper, Zinc and Aluminium:

Copper:

- Copper is a very good conductor of electricity and heat hence it is extensively used in making electrical and thermal equipment.
- Used in several alloys like Brass (Cu-60%, Zn-40%), Bronze (Cu-88%, Sn-12%), Gun metal (Cu-80-90%, Zn-<5%, Sn-10%) and Nickel silver (Cu-65%, Zn-17%, Ni-18%).

Zinc:

- Zinc is used in electrical batteries.
- Used in the galvanization of iron items.
- Zn is a constituent part of many important alloys like Brass (Zn-40%, Cu-60%) and German silver (Zn-25-35%, Cu-25-40% and Ni-40-50%).
- Zn dust is a very good reducing agent in synthetic chemistry.

Iron:

- Iron is exclusively used in the Construction field as a building material.
- Wrought iron is used in making wires, bolts, nuts, anchors, chains and agricultural equipment.
- Nickel steel, an alloy of iron, is used in the making of pendulum, automobile, and aviation designs.
- Another alloy of iron, Chrome steel is used in cutting and chorusing machinery.

Aluminium:

- Aluminium is used in the preparation of foils to wrap the food items.
- Used in the manufacturing of Paints and Lacquers.
- Used as a reducing agent in the extraction of Cr and Mn from their oxides.
- Being a very good conductor of electricity Al is used in Electrical instruments.
- Al is also used in the preparation of Light weighed alloys.

Intext Questions 18.4

1. According to the Ellingham diagram when will the reaction is feasible?

....

2. What material is used for the inner lining of the Reverberatory furnace?

……

3. What is the role of Flux material in the Electrochemical metallurgy?

……

4. Write the cathodic reaction in Electrochemical extraction of Aluminium?

……

5. Write the chemical composition of Gun metal.

……

What You Have Learnt

- Metals play an extremely useful role in day-to-day life.
- Most metals are found in nature in combined form.
- Only a few noble metals such as gold, silver, occur in nature in free state.
- The process of extraction of metals from their ores is called a metallurgical process.
- A naturally occurring material in which a metal or its compound occurs is called a mineral.
- A mineral from which a metal can be extracted economically is called an ore. Thus, all minerals do not serve the purpose of ores.
- Most active metals are highly electropositive and exist as Mn ions. Therefore, they are found in nature in association with some common anions, i.e., as salts like oxides, sulphides, carbonates, halides, silicates, etc.
- Some sulphides slowly undergo oxidation by air to form sulphates.
- India possesses rich mineral wealth with an abundance of iron, aluminium, and some amount of copper, tin, lead, silver, and gold.
- Various steps involved in the extraction of metal are:
- Crushing and pulverization
- Concentration or dressing of the ore
- Calcination or Roasting of the concentrated ore
- Reduction of the oxides to free metal.
- The metals thus obtained are then purified by employing some suitable method, viz. liquation, poling, distillation, electrolytic refining, Zone refining.
- Thermodynamic and electrochemical principles involved in advanced metallurgy. Applications of the Ellingham diagram. Applications of Cu, Fe, Zn and Cu.

Terminal Exercise

1. Name the metal oxides that are not reduced to metallic state by heating with carbon. Which reducing agent is used for these ores?
2. Which metalsulphide combines with its oxide to form metal? Give reactions.

3. Name four reducing agents other than carbon, used during smelting.
4. What is the difference between calcination and roasting?
5. Give the name and formula of at least one ore of the following metals:
   (i) copper (ii) zinc (iii) iron (iv) tin
6. What happens when
   (i) Calamine is calcined.
   (ii) Zinc blende is roasted.
   (iii)Silica is heated with limestone.
7. Describe the froth floatation method for the concentration of sulphide ore.
8. Explain the principles involved in Zone refining and Vapour phase refining methods with examples.
9. Give chemical equations involved in the self reduction method for the extraction of copper.
10. What is Ellingham Diagram? Explain the application of it.
11. Explain the principles of Electrochemistry used in extraction metals with suitable examples.
12. Write the important applications of Copper, Aluminium, Iron and Zinc.

Answers to Intext Questions

18.1

1. Mineral is a naturally occurring material in which a metal or its compound occurs. An ore is that mineral in which metal is present in large quantity and from which the metal can be extracted in pure and high quality, economically.
2. Gravity separation, magnetic separation, froth floatation, and chemical method.
3. Zinc

18.2

1. *Calcination:* It involves heating of the ore in a limited supply of air to a temperature that the ore does not melt.

Roasting: It involves heating of the ore in a free supply of air to a temperature that the ore does not melt.

Smelting: The extraction of metal in the fused state is termed smelting. The ore is reduced by carbon to the free metal.

Flux: It is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called slag.

Slag is a fusible chemical compound formed by the reaction of flux with gangue. Slag is not soluble in the molten metal and is thus separated.

2. Carbon in the form of coke.

3. Roasting; $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2(g)$

4. (i) $Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$

(ii) $ZnCO_3 \longrightarrow ZnO + CO_2$

18.3

1. Liquation
2. Copperandtin
3. Zinc

4. Copper,SilverandTin.
5. Metals like Ge, Si, Ga, B and In.
6. Ni(CO)$_4$

18.4

1. ΔG^{-} must be negative.
2. Haematite.
3. Flux reduces melting point and increases electrical conductance.
4. **Cathode:** Al^{3+} (melt) + $3e^{-} \rightarrow Al(l)$.
5. Cu-80-90%, Zn-<5%, Sn-10%

Chapter 19

HYDROGEN AND s-BLOCK ELEMENTS

Hydrogen, alkali metals (like sodium and potassium), and alkaline earth metals (like magnesium and calcium) are the essential parts of the world we live in. For example, hydrogen is used in making vanaspati. The yellow glow of streetlight is due to sodium. Sodium chloride, potassium chloride, and compounds of alkali metals are essential for life. Sodium hydroxide, sold under the name of caustic soda, is used in the manufacture of soap. Plaster of paris, a compound of calcium, is used as a building material as well as by doctors in setting bone fractures.

In this lesson, we shall study occurrence, physical and chemical properties, and uses of hydrogen and s-block elements (alkalimetals and alkaline earth metals).

Objectives

After reading this lesson, you will be able to:

- explain the unique position of hydrogen in the periodic table;
- compare and contrast the properties of different isotopes of hydrogen;
- recall the various physical and chemical properties and uses of hydrogen with chemical reactions;
- explain the structure of water molecule and ice;
- list the uses of heavy water;
- list the different methods of preparation of hydrogen peroxide;
- list oxidizing and reducing properties of hydrogen peroxide with at least two examples of each;
- list the uses of hydrogen peroxide;
- recall the names and formulae of some common ores of alkali and alkaline earth metals;
- recall the electronic configuration of alkali and alkaline earth metals;
- write reactions of alkali and alkaline earth metals with oxygen, hydrogen, halogens, and water;
- explain the trend of the basic nature of oxides and hydroxides.

19.1 Hydrogen

Hydrogen is the first element of the periodic table. Hydrogen has the simplest atomic structure and consists of a nucleus containing one proton with a charge +1 and one orbital electron. The electronic structure may be written as $1s^1$.

Occurrence of Hydrogen

Hydrogen is the widely available element in the universe and also in solar system. The planets like Jupiter and Saturn mostly consists of hydrogen but it is much less in the earth crust due to its light nature. It constitutes 15.4% of the earth's crust and the oceans.

19.1.1 Position in the Periodic Table

Where is hydrogen placed in periodic table?

Elements are placed in the periodic table according to their outermost electronic configuration. So, hydrogen ($1s^1$) may be placed with alkalimetals (ns^1). But hydrogen attains noble gas configuration of helium atom ($1s^2$) by gaining one electron. It forms the hydride ion H^- ($1s^2$) like halogens (ns^2np^5) by gaining one electron. On electrolysis of used alkali hydride, hydrogen is liberated at anode just as chlorine is liberated at anode during electrolysis of sodium chloride. Thus, hydrogen ought to be placed in group 17 along with halogens. Hydrogen also resembles group 14 elements, since both have a half-filled shell of electrons. So where should hydrogen be placed? This problem is solved by placing hydrogen neither with alkali metals nor with halogens. It has been given a unique position in the periodic table (see Periodic Table in lesson 4).

19.1.2 Isotopes of hydrogen

If atoms of the same element have different mass numbers, they are called isotopes. This difference in mass number arises because the nucleus contains a different number of neutrons.

Naturally occurring hydrogen contains three isotopes: protium ^1_1H or H, deuterium ^2_1H or D, and tritium ^3_1H or T. These three isotopes contain one proton and 0, 1, and 2 neutrons respectively in the nucleus (Fig 19.1). Protium is by far the most abundant. Naturally occurring hydrogen contains 99.986% of the H isotope, 0.014% of D, and 7×10^{-16} % of T, therefore the properties of hydrogen are essentially those of the lightest isotope. Tritium is radioactive and emits low energy particles ($t_{1/2}$ = 12.33 yrs).

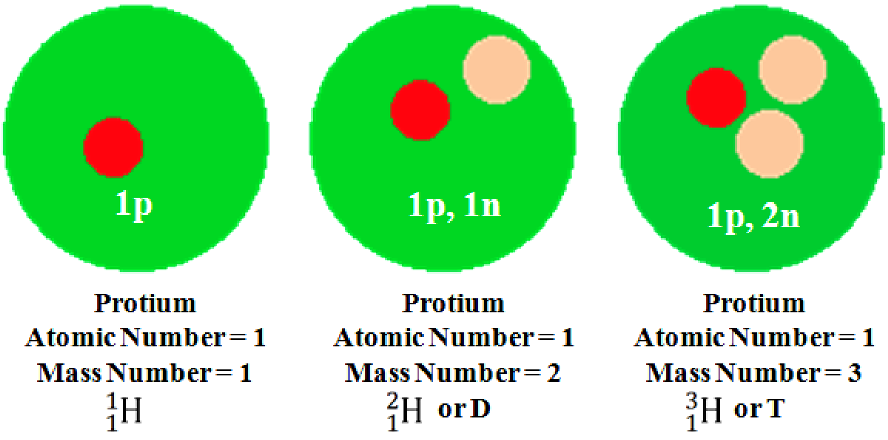


Fig19.1: Isotopes to hydrogen

Due to difference in mass of different isotopes, there arise a few differences in their properties. For example: ^1_1H ^2_1H ^3_1H

1. H_2 is more rapidly adsorbed on the metal surface than D_2.
2. H_2 reacts over 13 times faster with Cl_2 than does D_2.

Difference in properties that arises from the difference in mass is called isotope effect. Since the percentage difference in the mass of isotopes of hydrogen is very large. The difference in properties of isotopes of hydrogen is very large. The difference in properties of compounds containing these isotopes is also large.

Preparation of Dihydrogen

1. Laboratory preparation:

Zinc on reaction with dilute acids and with aqueous alkali produces hydrogen.

$$Zn + 2H^{+} \longrightarrow Zn^{+2} + H_2$$

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

2. Commercial preparation:

i) Acidified or alkaline water on electrolysis using platinum electrodes gives hydrogen.

$$2H_2O\ (l) \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_2(g) + O_2\ (g)$$

Pure hydrogen (99.95%) can be obtained from the electrolysis of warm barium hydroxide solution using nickel electrodes.

ii) While electrolyzing the brine solution in the manufacturing of Sodium hydroxide and Chlorine hydrogen will be liberated as a byproduct.

At cathode:

$$2Cl^{-}(aq) \longrightarrow Cl_2(g) + 2e^{-}$$

At cathode:

$$2H_2O\ (l) + 2e^{-} \longrightarrow H_2\ (g) + 2OH^{-}(aq)$$

Net reaction is

$$2Na^{+}\ (aq) + 2Cl^{-}(aq) + 2H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2Na^{+}(aq) + 2OH^{-}(aq)$$

iii) Also the reaction of steam at high temperature on hydrocarbons or coke in presence of a catalyst yields hydrogen.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{\text{270K}} nCO + (2n+1)\ H_2$$

The mixture of $CO+H_2$ is called SYNGAS or SYNTHETIC GAS as it is used in the synthesis of methanol and variety of hydrocarbons. This Syn gas is produced from sewage, saw-dust, scrap wood, news paper. The process of producing syngas from coal is called *Coal gasification.*

$$C(s) + H_2O \xrightarrow{\text{170K}} CO\ (g) + H_2\ (g)$$

19.1.3 Physical properties

Hydrogen is a diatomic gas, H_2. It is colourless and has no smell. It is the lightest of all the gases known. It is insoluble in water, acids, and most of the organic solvents. It is adsorbed when passed over platinum and palladium.

19.1.4 Chemical properties

1. Combustion: Hydrogen is combustible and burns in air with pale blue flame.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

2. Reducing property: Hydrogen reduces heated metal oxides to metals.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

$$CuO + H_2 \longrightarrow Cu + H_2O$$

3. Reaction with non-metals: Hydrogen combines with nitrogen, carbon, oxygen and chlorine under appropriate conditions to form ammonia, methane, water and hydrogen chloride respectively.

$$3H_2 + N_2 \longrightarrow 2NH_3$$

$$2H_2 + C \longrightarrow CH_4$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Reaction with metals: Hydrogen reacts with highly electropositive metals to from the corresponding hydrides.

$$2Na + H_2 \longrightarrow 2NaH$$

$$2Li + H_2 \longrightarrow 2LiH$$

19.1.5 Uses

Hydrogen is used:

1. for conversion of coal into synthetic petroleum.
2. in the manufacture of bulk organic chemicals, particularly methanol.
3. in the hydrogenation of oils. Vegetable oils change into vegetable ghee when hydrogen is passed through the oils at 443 K in the presence of nickel as a catalyst.
4. in the manufacture of ammonia, which is used in the production of fertilizers.
5. as primary fuel for heavy rockets.
6. for filling balloons.

Hydrogen as fuel

Hydrogen is a clean fuel; on combustion it releases only water along with large quantity of heat. Hydrogen can release more energy than petrol (about three times) and fewer pollutants (oxides of nitrogen since nitrogen present as impurity with hydrogen) on combustion. However the formation of oxides of nitrogen can be made neglezable by lowering the temperature so that the reaction between nitrogen and oxygen may not take place. Storage of hydrogen requires expensive insulated tanks made up of metal alloys like $NaNi_5$, $TI\text{-}TIH_2$, $Mg\text{-}MgH_2$.

Because of these limitations researchers are in search for alternative techniques to use dihydrogen in an efficient way. Main challenge in hydrogen economy is its transportation and storage of energy in the form of liquid or gaseous hydrogen. Here energy is transmitted in the form of dihydrogen and not as electric power. For the first time in India, a pilot project was launched in 2005 for running automobiles using hydrogen as fuel. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. Slowly the percentage of dihydrogen would be increased to reach the optimum level.

In recent days, it is also used in fuel cells for the generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the coming years, to use hydrogen as a common source of energy.

Intext Questions 19.1

1. Name the isotopes of hydrogen?

....

2. Name the isotope of hydrogen which is radioactive?

....

3. Why is hydrogen used for filling balloons?

....

4. Which gas is produced, when hydrogen combines with carbon?

....

19.2 Compounds of Hydrogen

19.2.1 Hydrides:

Hydrogen, under certain conditions, combines with almost all elements (except noble gases) to form binary compounds, called hydrides. Eg. MgH, B_2H.

The hydrides can be categorized into three:

1. Ionic or saline or saltlike hydrides
2. Covalent or molecular hydrides
3. Metallic or non-stoichiometric hydrides

1. Ionic or Saline Hydrides

These are hydrides formed with the s-block elements which are highly electropositive in nature. Significant covalent character is found in the lighter metal hydrides such as LiH, BeH_2, and MgH_2. These ionic hydrides are crystalline, non-volatile and non- Conducting in solid state. Ionic hydrides react vigorously with water produces dihydrogen gas.

$$NaH(s) + H_2O(aq) \longrightarrow NaOH(aq) + H_2(g)$$

2. Covalent or Molecular Hydride

Hydrogen forms molecular hydrides with p-block elements. Eg: CH_4, NH_3. H_2O and HF. According to the relative numbers of electrons and bonds in the Lewis structures, molecular hydrides can be classified into :

(i) electron-deficient, (ii) electron-precise, and (iii) electron-rich hydrides.

An *electron-deficient hydride* has few electrons to write its conventional Lewis structure. Eg: Diborane (B_2H_6). All elements of group 13 will form electron-deficient compounds. They act as Lewis acids i.e., electron acceptors.

Electron-precise hydrides have the required number of electrons to write its conventional Lewis structures. All elements of group 14 form such compounds (e.g. CH_4) which are tetrahedral in geometry.

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15-17 form such compounds. *Eg:* NH_3, has one lone pair, H_2O has two lone pairs and HF has 3 lone pairs.

These hydrides behave as Lewis bases i.e., electron donors. The presence of lone pairs on highly electronegative atoms like N. O and F in hydrides results in hydrogen bond formation between the molecules.

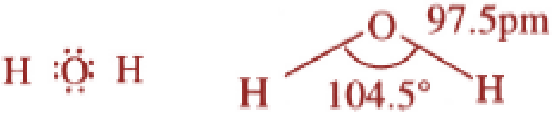
3. Metallic or Non-stoichiometric (or Interstitial) Hydrides

These hydrides are formed by most of the d-block and f-block elements except group 6, 7, 8 and 9. From group 6 only chromium forms CrH. Unlike saline hydrides, these hydrides are non- stoichiometric, and deficient in hydrogen. Eg: $LaH_{2.87}$, $YbH_{2.55}$ etc.

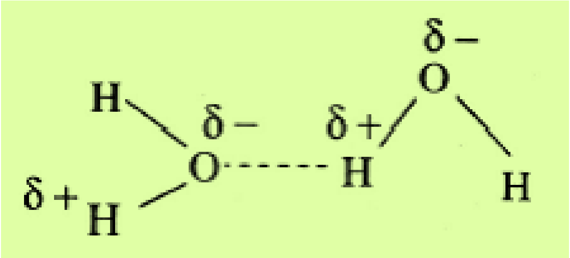
Except for hydrides of Ni, Pd, Ce and Ac, all other metallic hydrides have lattices different from those of the parent metals. The property of absorption of hydrogen by transition metals has wide application in catalytic reduction as well as hydrogenation reactions in the synthesis of variety of organic compounds. Some of the metals (e.g.. Pd. Pt) can put up a very large amount of hydrogen so this property has high potential for hydrogen storage and as a source of energy.

19.2.2 Water (H_2O)

This oxide of hydrogen is essential to all life. It occurs in the form of snow, as water in rivers, lakes, sea etc. and as vapour in the atmosphere. Water is a covalent compound made up of two hydrogen atoms linked with one oxygen atom through covalent bonds. Its Lewis structure and molecular structure are shown below.



Because of the large electronegativity of oxygen, water molecule is highly polar. It has partial negative charge (δ^-) on the oxygen atom and partial positive charge (+) on the hydrogen atom. An electrostatic attraction between H of one molecule with O of other molecule results in the formation of intermolecular hydrogen bonds.



The remarkable characteristic of water is that in solid form, it is less dense than liquid form. Consequently, an ice cube floats on water. Water molecules are joined together in an extensive three-dimensional network in which the oxygen atom is bonded to four hydrogen atoms, two by hydrogen bonds and two by normal covalent bonds, in a near tetrahedral hydrogen-bonded structure (Fig. 19.2), which has got open spaces. This is responsible for low density.

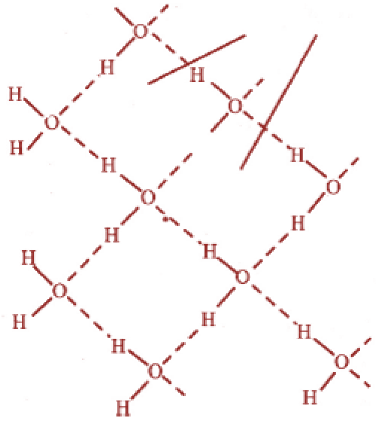


Fig.19.2: Tetrahedral arrangement of oxygen atoms in ice.

Chemical Properties of Water

(1) Amphoteric Nature:

Water can act as an acid as well as a base i.e., amphoteric in nature.

Eg; It acts as an acid with NH_3, and a base with H_2S.

$H_2O(l) + NH_3\ (aq) \longrightarrow OH^{-}(aq) + NH_4^{+}\ (aq)$

$H_2O(1) + H_2S(aq) \longrightarrow H_3O^{*}\ (aq) + HS^{-}\ (aq)$

The auto-protolysis of water takes place as follows:

$H_2O(l)\ +\ H_2O(l) \longrightarrow H_3O^{+}\ (aq) +\ OH^{-}\ (aq)$

(acid) (base) (conjugate acid) (conjugate acid)

acid-1 base-2 acid-2 base-1

(2) On reaction with electropositive metals releases hydrogen gas.

$2H_2O(1) + 2Na\ (s) \longrightarrow 2NaOH(aq) + H_2(g)$

Water is oxidised to O_2, during photosynthesis.

$6C0_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6\ (aq) + 60_2(g)$

On reaction with fluorine also it is releases O_2.

$2F_2(g) + 2H_2O(1) \longrightarrow 4H^{*}\ (aq) + 4F^{-}\ (aq) + O_2(g)$

(3) Hydrolysis Reaction:

Due to high dielectric constant, water dissolves many ionic compounds. Some covalent and ionic compounds are hydrolysed in water.

$P_4O_{10}\ (s) +6H_2O\ (1) \longrightarrow 4H_3PO_4\ (aq)$

$SiCL_4\ (1) +2H_2O\ (1) \longrightarrow SiO_2\ (s) + 4HCl\ (aq)$

$N^{3-}\ (s) + 3H_2O(1) \longrightarrow NH_3\ (g)+30H^{-}\ (aq)$

(4) Hydrates Formation:

From aqueous solutions many salts can be crystallised as hydrated salts. Here association of water is of different types

(i) *Coordinated water* e.g.: $[Cr\ (H_2O)_6]^{3+}\ 3C1^{-}$

(ii) *Interstitial water* e.g., $BaCl_2.2H_2O$

(iii) *Hydrogen-bonded water* e.g. $[Cu(H_2O)_4]^{2+}\ SO_4^{-2}.H_2O$ in $CuSO_4.5H_2O$

19.2.3 Heavy water and its applications

Water containing deuterium in place of ordinary hydrogen (protium) is termed as heavy water (D_2O). Heavy water is separated from water by electrolysis. The equilibrium constant for the dissociation of water containing protium is very high (1.0×10^{-14}) as compared to water containing deuterium (3.0×10^{-15}).

e.g.

$$H_2O \rightarrow H^+ + OH^-$$
$$D_2O \rightarrow D^+ + OD^-$$

O-H, bonds are broken more rapidly than OD bonds. Thus, when water is electrolyzed, H_2 is liberated much faster than D_2, and the remaining water thus becomes enriched in heavy water D_2O. In order to obtain one litre of almost pure D_2O, we have to electrolyze about 30000 litres of ordinary water.

Uses:

1. Heavy water is used as a moderator in nuclear reactors. In this process the high speed neutrons are passed through heavy water in order to slow down their speed.
2. It is used in the study of mechanism of chemical reactions involving hydrogen.
3. It is used as the starting material for the preparation of a number of deuterium compounds, for example:

$$CaC_2 + 2D_2O \longrightarrow C_2D_2 + Ca(OD)_2$$
$$SO_3 + D_2O \longrightarrow D_2SO_4$$

19.2.4 Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is an important compound of hydrogen. Its chemical formula is H_2O_2.

Methods of preparation:

Two methods of preparation of hydrogen peroxide are given below:

1. by the action of dilute mineral acids (H_2SO_4) on metallic peroxides (barium peroxide, sodium peroxide)

$$BaO_2\cdot 8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$$
$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

2. By the electrolysis of H_2SO_4 (50% W/W) followed by distillation

$$\text{At cathode:} \quad 2H^+ + 2e^{-1} \rightarrow H_2$$

$$\text{At anode:} \quad 2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^{-1}$$

The anodic solution which contains persulphate ions $(S_2O_8)^{2-}$ is distilled with sulphuric acid at reduced pressure yielding H_2O_2

$$S_2O_8^{2-} + 2H^+ + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

Properties:

Hydrogen peroxide is a colorless syrupy liquid and has sharp odour. It has a boiling point of 423K. It is miscible in all proportions with water, alcohol and ether. The oxidation state of oxygen in hydrogen peroxide is 1, a value, which lies between the oxidation state of oxygen in O_2 (zero) and water (-2). Therefore, hydrogen peroxide acts as an oxidizing agent as well as a reducing agent in acidic and alkaline media.

Oxidizing Properties:

(a) Oxidizing action in acid solution:

$$\text{(i) } PbS + 4H_2O_2 \rightarrow PbSO_4 + .4H_2O$$

$$\text{(ii) } 2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

(b) Oxidizing action in alkaline solution:

$$MnCl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + MnO_2$$

(c) Reducing action in acid solution:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$

(d) Reducing action in alkaline solution:

$$\text{(i) } 2KMnO_4 + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2KOH$$

$$\text{(ii) } Cl_2 + H_2O_2 + 2KOH \rightarrow 2KCl + 2H_2O + O_2$$

Storage:

Hydrogen peroxide decomposes to water on exposure to light.

$$2H_2O_2\,(l) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$

Even the presence of traces of alkali (present in glass containers), the above reaction is catalysed. So H_2O_2 has to be stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser.

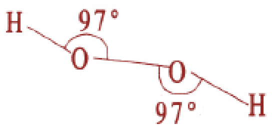
Uses:

Hydrogen peroxide is used:

1. for bleaching hair, leather and wool etc.
2. Used as an Antiseptic
3. as a germicide and disinfectant
4. as an explosive when mixed with alcohol.
5. in the preparation of foam rubber.
6. in pollution control *e.g.* treatment of drainage and sewage water for de-chlorination.

Structure:

The Lewis structure and molecular structure of hydrogen peroxide are shown below:



Intext Questions 19.2

1. Why does ice float on water?

....

2. What is heavy water? Write its important uses.

....

3. Give one method of preparation of hydrogen peroxide.

....

4. Give two uses of hydrogen peroxide.

....

5. How does hydrogen peroxide decolorize potassium permanganate?

....

19.3 s-Block Elements

The s-block elements have an outer electronic configuration ns^1 or ns^2 and are placed in the group 1 and 2 of the periodic table. Group 1 consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are collectively known as the alkali metals after the Arabic word *al-qis* meaning plant ashes. These ashes are particularly rich in carbonates of calcium, strontium, barium and radium. They are collectively known as alkaline earth metals.

19.3.1 The alkali metals

In this group all the elements are electropositive metals and there exists resemblance between the elements owing to their similar outer electron configuration. The occurrence and properties of alkali metals are discussed below:

Occurrence:

Sodium and potassium are abundant. Sodium is found as sodium chloride in the sea water and as sodium nitrate (Chile saltpeter) in the deserts of Chile. Potassium too, is found in sea water, and also as carnallite ($KCl.MgCI_2.6H_2O$). Lithium, rubidium and caesium occur in a few rare aluminosilicates. Francium is radioactive; its longest-lived isotope ^{223}Fr has a half-life of only 21 minutes.

19.3.1.1Electronic configuration

The alkali metals with their symbols, atomic numbers and electronic configurations are listed below in Table 19.1

Table19.1:Electronicconfigurationofalkalimetals

Element	Symbol	Atomic number	Electronic configuration
Lithium	Li	3	$ls^2,2s^1$
Sodium	Na	11	$ls^2, 2s^2p^6,3s^1$
Potassium	K	19	$ls^2,2S^2p^6,3s^2p^6,4s^1$
Rubidium	Rb	37	$ls^2,2s^2p^6,3s^2p^6d^{10},4s^2p^6,5s^1$
Cesium	Cs	55	$ls^2,2s^2p^6,3S^2p^6d^{10},4s^2p^6d^{10},5s^25p^6, 6s^1$

19.3.1.2 Physical properties of Alkali Metals

Alkali metals are placed in group 1 of periodic table. They readily form unipositive ions. As we go down the group the alkali metals show steady increase in size due to the addition of a new shell at each step. The increase in size of the atoms or ions, directly influences the physical and chemical properties of the alkali metals. Some physical properties are given in Table 19.2.

Table 19.2: Physical properties of alkali metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy ($kJmol^{-1}$)	Electro negativity	Density (gcm^{-3})	M.P. K	Electrode Potential (E^o volts)
Li	76	520.1	1.0	0.54	454	3.05
Na	102	495.7	0.9	0.97	371	2.71
K	138	418.6	0.8	0.86	336	2.83
Rb	152	402.9	0.8	1.53	312	2.89
Cs	167	375.6	0.7	1.90	302	2.93

The trends in physical properties are listed in Table 19.3.

Table 19.3: Trends in physical properties

No.	Characteristic	Trend
1.	Oxidation state	All elements show +1 oxidation state
2	Atomic/ionic Radii	Li < Na < K < Rb < Cs Atomic and ionic radii increases since number of shells increase as we go down the group.
3.	Ionization Energy	Li > Na > K > Rb > Cs As the size increases it becomes easier to remove an electron from the outer most shell.
4.	Electro negativity	Li > Na > K > Rb > Cs The electropositive character increases due to decrease in ionization enthalpy therefore electronegativity decreases.
5.	Metallic Character	Li < Na < K < Rb < Cs Metallic character increases as we go down the group due to increase in electropositive character.
6.	Density	Li< Na > K < Rb < Cs Generally density increases from Li to Cs as the atomic mass increases (exception K).
7.	Melting point& Boiling points	Li > Na > K > Rb > Cs Decreases down the group because of increasing size and weak intermetallic bond.
8.	Flame coloration	They show characteristic colors in the flame. The outer most electrons absorb energy and is excited to a higher energy level. This absorbed energy is remitted when the electron comes back to ground state. The difference in energy falls in the visible range of radiation hence the colors are seen. Li Na K Rb Cs Crimson red Yellow Pale violet Violet Violet

19.3.1.3 Chemical Properties

Alkali metals are the most reactive metals in the whole periodic table due to their ease in losing outermost electron, hence getting oxidized easily. As the ease of losing electrons increases, the reactivity increases down the group.

(i) Oxides: All alkali metals form oxides, which are basic in nature. Lithium forms only one type of oxide, lithium monoxide Li_2O. Sodium peroxide Na_2O_2 is formed when sodium is heated with oxygen. Other metals of this group also form superoxides MO_2 on reaction with oxygen.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

$$2Na(s) + O_2(g) \rightarrow N_2O_2(s)$$

$$K(s) + O_2(g) \rightarrow KO_2(s)$$

The formation of a particular oxide is determined by the size of the metal ion. Tiny lithium ion is notable to come in contact with a sufficient number of peroxo ions. However, the ions of potassium, rubidium, caesium are large enough to come in close contact with peroxo ions and form stable structures as superoxides.

(ii) Reactivity towards water: Although lithium has the most negative Eo, its reaction with water is considerably less vigorous than that of sodium which has the least negative Eo among the alkali metals (Table 19.2). The low reactivity of lithium is due to small size and high ionization enthalpy. All the metals of the group react with water explosively to form hydroxide and liberate hydrogen.

$$2M + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2$$

Basic character of oxides and hydroxides: The basic character of oxides and hydroxides of alkali metals increases with the increase in size of metal ion. So, lithium oxide and hydroxide are least basic whereas, caesium oxide and hydroxide are most basic in nature.

(iii) Hydrides: The alkali metals react with hydrogen at about 637K to form hydrides (MH), where M stands for alkali metals.

$$2M + H_2 \longrightarrow 2MH$$

(iv) Halides: Alkali metals react with halogens to form halides:

$$2M + X_2 \longrightarrow 2MX \text{ (X=F, Cl, Br, I)}$$

(v) Reducing nature: Alkali metals are strong reducing agents. The reducing property increase with decrease in ionization energy values down the group. Lithium has the strong reducing power; this exception is due to large heat of hydration of lithium ion

(iv) Solution in Liquid ammonia: Alkali metals can dissolve in liquid ammonia gives deep blue colour solution which has conducting nature.

$$M + (x+y)\ NH_3 \longrightarrow [M(NH_3)_x]^+ + [e\ (NH_3)_y]^-$$

The blue colour of the solution is due to the presence of ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and If the solution is kept for long metal amide is formed as product.

$$M^+_{(am)} + e^- + NH_3\ (1) \longrightarrow MNH_{2(am)} + \tfrac{1}{2}H_2(g) \text{ (Here 'am' denotes solution in ammonia.)}$$

In concentrated solution, the blue colour changes to bronze colour on warming and become diamagnetic.

Uses:

1. Lithium is the lightest metal. Alloy of Lithium is used in aircraft parts, armour plates.
2. Lithium deuteride is used as fusion fuel in thermonuclear reactions.
3. Lithium batteries are packed with lot of energy, used in devices like cell phones, computers.
4. Liquid Sodium is used as coolant in nuclear reactors
5. Sodium compounds are used in paper, textile, petroleum and chemical industries.
6. Potassium has a vital role in biological system. It maintains blood pressure and acidity levels in our body.
7. Potassium hydroxide is used to make detergents.
8. Cesium is used in photoelectric cells due to its quick electron emission.

General characteristics of the compounds of the alkali metals:

Compounds of the alkali metals are generally ionic in nature. Following are some of the general characteristics of some of their compounds.

(i) Oxides and Hydroxides

On combustion in excess of air, lithium forms Lithium oxide, Li_2O (and some peroxide Li_2O_2), sodium forms the peroxide, Na_2O_2, (and some superoxide NaO_2,) potassium, rubidium and caesium form the superoxides, MO_2. The stability of the peroxide or superoxide increases with increases in the size of the metal ion is due to the stabilisation of large anions by larger cations through lattice energy effects.

These oxides are easily hydrolysed by water to form the hydroxides according to the following reactions:

$$M_2O + H_2O \longrightarrow 2M^+ + 2OH^-$$
$$M_2O_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2$$
$$2MO_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The oxides and the peroxides are colourless in pure form. But superoxides are yellow or orange in colour and are also paramagnetic in nature. Sodium peroxide is widely used as an oxidising agent in inorganic chemistry.

The alkali metal hydroxides are the strongest of all bases and dissolve freely in water with evolution of excess heat due to intense hydration.

(ii) Halides

The alkali metal halides MX (X=F, Cl, Br, I) are colourless crystalline solids. They are prepared by the reaction of the suitable oxide, hydroxide or carbonate with hydrohalic acid (HX). All of these halides have high negative enthalpies of formation; $\Delta_f H$ always becomes less negative from fluoride to iodide.

The melting and boiling points of alkali metal halides have the trend follows:

fluoride > chloride > bromide > iodide.

All these halides are soluble in water. LiF is less soluble in water is due to its high lattice enthalpy and the low solubility of Cs l is on account of its smaller hydration enthalpy of its two ions.

(iii) Salts of Oxo-Acids

Oxo-acids are those in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom e.g., carbonic acid $H_2CO_3^-$ $[OC(OH)_2]$; sulphuric acid, H_2SO_4–$[O_4S(OH)_2]$.

The alkali metals form salts with all the oxo-acids. They are generally soluble in water. Alkali metal carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) also are highly stable to heat. As the Electropositive nature increases down the group, the stability of the carbonates and bicarbonates increases. Lithium carbonate is less stable due to its very small size so, polarises a large CO_3^{-2} ion and dissociate into more stable Li_2O and CO_2.

Anomalous behavior of Lithium:

The anomalous behavior of Lithium is due to

(1) Very small size of Lithium atom and its ion

(2) Increased polarizing power (i.e., charge/ the: radius ratio), results in increased Covalent character of lithium compounds which is responsible for their solubility in organic solvents.

Some of the abnormal properties of Lithium are given below

1. Lithium is much harder while other alkali metals are soft.
2. Lithium is least reactive but the strongest reducing agent among all the alkali metals.
3. Lithium forms monoxide with Oxygen, unlike other alkali metals.
4. LiCl is deliquescent and crystallises as a hydrate, $LiCl.2H_2O$ whereas other alkali metal chlorides do not form hydrates.
5. Lithium hydrogen carbonate is not obtained in the solid form while all other elements form solid hydrogen carbonates.
6. Lithium unlike other alkali metals forms no ethynide on reaction with ethyne.
7. Lithium nitrate when heated gives lithium oxide, Li_2O, whereas other alkali metal nitrates decompose to give the corresponding nitrite.

$$4LINO_3 \longrightarrow 2Li_2O_2 + 4\ NO_2 + O_2$$

$$2\ NaNO_3 \longrightarrow 2NaNO_3 + O_2$$

8. LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Diagonal relationship between Lithium and Magnesium:

The equal size of lithium and magnesium results in the formation of diagonal relationship. Atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii: Li^+ = 76 pm, Mg^{+2} = 72 pm. The main points of similarity are:

1. Both lithium and magnesium are quite hard and lighter than other elements in their respective groups.
2. Both reacts with water and form oxides and hydroxides are much less soluble and their hydroxides decompose on heating.
3. Both form ionic nitride, LI_3N and Mg_3N_2, when heated with atmospheric nitrogen.
4. Both Li and Mg combine with Oxygen to give monoxides Li_2O, MgO.
5. The carbonates of lithium and magnesium decompose easily on heating to form the corresponding oxides with the evolution of CO_2.

6. Both do not form Solid bicarbonates.
7. Both LiCl and $MgCl_2$ are soluble in ethanol because of covalent character.
8. Both LiCl and $MgCl_2$ are deliquescent and crystallise from aqueous solution as hydrates, $LiCl2H_2O$ and $MgCl_2$, $8H_2O$.

Some Important compounds of SODIUM:

Here are some of the industrially important compounds of sodium are described:

i. Sodium Carbonate ($Na_2CO_3.10H_2O$): Sodium carbonate also called Washing Soda, is prepared by the Solvay process. In this process ammonium carbonate (produced by the passage of CO_2 gas into Ammonia solution) reacts with concentrated brine solution.

$$NH_4\,HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$$
$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Properties: Sodium carbonate is readily dissolves in water. It exists as decahydrate. On heating, it loses water, becomes completely anhydrous called Soda Ash.

Uses: It is used in the manufacturing of detergents, soaps, and paper. Also in the manufacturing of water glass, borax and many other sodium compounds. It is used as a water softener. Also In the laboratory as a reagent in qualitative and quantitative analysis.

ii. Sodium bicarbonate ($NaHCO_3$): It is also called Baking Soda. It is prepared by the reaction of concentrated sodium carbonate solution with CO_2.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\,NaHCO_3$$

Sodium bicarbonate reduces acidity in stomach. It can be used as a mild anti septic also used in fire extinguishers to liberate CO_2 due to formation of soapy foam.

iii. Sodium Chloride (NaCl): Most abundant source of sodium chloride is found in sea water and in land lakes in the form of rock salt. From these sources NaCl is obtained by evaporation by solar heat and wind. Pure NaCl is obtained by dissolving crude NaCl in minimum amount of water and filtered to remove insoluble impurities. The obtained solution is then saturated with HCl. Ordinary NaCl is slightly hygroscopic due to presence of Ca and Mg chlorides. It is used as common salt (essential constituent of our diet), food preservative. It is also used to de-ice roads and sidewalks.

iv. Sodium hydroxide (NaOH): It is also called Caustic soda. NaOH is prepared by the Castner-Kellner method. In this method, brine solution is electrolyzed to sodium amalgam (mercury being as cathode and carbon as anode) which on treatment with water gives NaOH. Sodium hydroxide used in the manufacturing of soap, paper and artificial silk. It is used in the textile industries for mercerizing cotton fabrics. Also as a laboratory reagent.

Intext Questions 19.3

1. Arrange the alkali metals in order of increasing ionization enthalpy.

....

2. Which of the alkali metals forms only monoxide?

....

3. Write down the chemical equation for the reaction of sodium with water.

....

4. What type of bond exists in the hydrides of alkali metals?

....

5. Name the element which forms (i) peroxide, (ii) superoxide.

....

6. Castner –Kellner method is used for the preparation of which compound

....

19.4 The Alkaline Earth Metals

You have seen a gradual increase in size of the alkali metals as we moved down the Group 1 of the periodic table. Identical observations may be made in the case of alkaline earth metals placed in Group 2 of the periodic table. Some physical properties of the alkaline earth metals are given in Table 19.4. An alkaline earth metal atom is smaller in size compared to its adjacent alkali metal. This is due to the added proton in the nucleus, which exerts a pull on the electrons in an atom resulting in squeezing of the atom. This reduction in size shows higher control of the nucleus on the electrons in the shells.

Table 19.4: Physical properties of the alkaline earth metals

Symbol	Ionic Radius (pm)	FirstIonization enthalpy (kJmol^{-1})	Electro negativity	Density (gcm^{-3})	M.PK	Electrode Potential (E^{o})volts
Be	89	899	1.5	1.85	1562	1.70
Mg	136	737	1.2	1.74	924	2.38
Ca	174	590	1.0	1.55	1124	2.76
Sr	191	549	1.0	2.63	1062	2.89
Ba	198	503	0.9	3.59	1002	2.90

The ease of losing electrons makes the alkaline earth metals good reducing agents. But this property is less prominent as compared to the corresponding alkali metals.

19.4.1 Occurrence

The alkaline earth metals are too reactive to occurnative. Magnesium is the second most abundant metallic element in the sea, and it also occurs as carnallite ($KCl.MgCl_2.6H_2O$) in earth crust. Calcium occurs as calcium carbonate (marble, chalk etc) and with magnesium as dolomite ($CaCO_3.MgCO_3$). Other ores of calcium are anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$). Strontium and barium are rare and are found as carbonates and sulphates. Beryllium too is rare and is found as beryl ($Be_3Al_2(SiO_3)_6$).

19.4.2 Electronic Configuration

The electronic configurations of the alkaline earth metals are listed in Table 19.5.

Table19.5: Electronic configuration

Element	Symbol	Atomic number	Electronicconfiguration
Beryllium	Be	4	$1s^2,2s^2$
Magnesium	Mg	12	$1s^2,2s^2p^6,3s^2$
Calcium	Ca	20	$1s^2,2s^2p6,3s^2p^6,4s^2$
Strontium	Sr	38	$ls^2,2s^2p^6,3S^2p^6d^{10},4s^2p^6,5s^2$
Barium	Ba	56	$1s^2,2s^2p^6,3s^2p^6d^{10},4s^2p^6d^{10},5s^25p^6,6s^2$

19.4.3 Physical properties of alkaline earth metals

Alkaline earth metals are less electropositive than alkali metals. The electropositive character of alkaline earth metals increases down the group. They achieve an inert gas configuration by the loss of two electrons. Some physical properties and their trends are given in Table 19.6.

Table 19.6: Trends in physical properties

No.	Characteristic	Trend		
1.	Oxidation state	All elements show +2 oxidation state		
2.	Atomic / ionic radii	Be < Mg < Ca < Sr < Ba Size of alkaline earth metals increases from top to bottom due to increase in the number of shells.		
3.	Ionization enthalpy	Be > Mg > Ca > Sr > Ba As the size increases it becomes easier to remove an electron from the outer most shell.		
4.	Electro negativity	Be > Mg > Ca > Sr > Ba As the electropositive character increases from top to bottom due to decrease in ionization energy, electro negativity decreases from top to bottom.		
5.	Metallic character	Be < Mg < Ca < Sr < Ba Metallic character increases as we go down the group due to increase in electropositive character.		
6.	Density	Generally density increases from top to bottom as the atomic mass increases.		
7.	Melting point & Boiling point	They show higher values of melting and boiling points as compared to alkali metals because of the smaller size and stronger metallic bonds. There is no regular trend down the group. It depends upon packing.		
8.	Flame coloration	Except Be and Mg (due to small size and higher ionization enthalpy) all other alkaline earth metals impart characteristic colours to the Bunsen flame.		
		Ca	**Sr**	**Ba**

		Brick red	Crimson red	Sea green

19.4.4 Chemical Properties of Alkaline Earth Metals

The alkaline earth metals are reactive metals, though less reactive than alkali metals. There activity increases from top to bottom in a group due to increase in electropositive character.

(i) Reactivity and E^o values: The near constancy of the $E^O(M^{2+}/M)$ values for group 2 metals (Table 19.4) is somewhat similar to that for group 1 metals. Therefore, these metals are electropositive and are strong reducing agents. The less negative value for be arises from, the large hydration energy associated with the small size of Be^{2+} being countered by relatively large value of the enthalpy of atomization of beryllium.

(ii) Oxides: The alkaline earth metals burn in oxygen forming the ionic oxides of the type MO where M stands for alkaline earth metals except Sr, Ba, and Ra which for peroxides. Peroxides are formed with increasing ease and increasing stability as the metal ions become larger.

$$2Mg + O_2 \rightarrow 2MgO \qquad 2Ca + O_2 \rightarrow 2CaO$$

$$2Be + O_2 \rightarrow 2BeO \qquad Ba + O_2 \rightarrow 2BaO$$

Basic character of the oxides increases gradually from BeO to BaO. Beryllium oxide is amphoteric, MgO is weakly basic while CaO is more basic.

(iii) **Hydrides:** The alkaline earth metals combine with hydrogen to form hydrides of general formula MH_2

$$M + H_2 \rightarrow MH_2 (M = Mg, Ca, Sr, Ba)$$

(iv) **Reaction with water:** Usually the alkaline earth metals react with water to liberate hydrogen. Be does not react with water or steam even at red heat and does not get oxidized in air below 837K.

$$Mg + H_2O \rightarrow MgO + H_2$$

Ca, Sr, and Ba react with cold water with increasing vigour.

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

(v) Halides: All the alkaline earth metals combine directly with the halogens at appropriate temperature forming halides, MX_2 where M stands for alkaline earth metals.

$$M + X_2 \rightarrow MX_2$$

(vi) Reaction with acids: Alkaline earth metals on reaction with acids liberate H_2 gas**.**

$$M + 2HCl \longrightarrow MCl_2 + H_2$$

(vii) Reaction with Liquid ammonia: Like alkali metals, alkaline earth metals also form deep blue black colour on reaction with liquid ammonia, forms ammoniated ions.

$$M + (x+y)\ NH_3 \longrightarrow [M(NH_3)x]^{+2} + 2[e(NH_3)y]$$

Uses:

1. Beryllium is used in the manufacture of alloys. Cu-Be alloys are used in the preparation of high strength springs.
2. Mg form alloys with Al, Zn, Mn and Sn. Mg-Al alloys are used in construction of aircrafts.
3. Milk of magnesia is used to treat antacid.

4. Magnesium carbonate is used in tooth paste.
5. Ca is used in the extraction of metals from their oxide where reduction with carbon is difficult.
6. Radium salts are used in radiotherapy like in the treatment of cancer.

General characteristics of compounds of the alkaline earth metals:

The compounds of alkaline earth metals are ionic in nature but less ionic than corresponding compounds of alkali metals.

The general characteristics of some of the compounds of alkaline earth metals are described below.

(i) *Oxides and Hydroxides:* The alkaline earth metals on reaction with oxygen form the monoxide (MO). Oxides of alkaline earth elements are ionic in nature and form hydroxides on reaction with water, except for BeO which is amphoteric in nature.

$$MO + H_2O \rightarrow M(OH)_2$$

The basic character of these hydroxides increase with increasing atomic number from $Mg(OH)_2$ to $Ba(OH)_2$. These hydroxides are less basic than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with both acid and alkali.

$$Be(OH)_2 + 2OH^- \longrightarrow \underset{\text{Beryllate ion}}{[Be(OH)_4]^{2-}}$$

$$Be(OH)_2 + 2HCl + 2H_2O \longrightarrow [Be(OH)_4]Cl_2$$

(ii) *Halides:* Except for beryllium halides, all other halides of alkaline earth metals are ionic in nature. Beryllium halides are essentially covalent and soluble in organic solvents.

(iii) *Salts of Oxoacids*: Some of salts of oxoacids are:

Carbonates: Carbonates of alkaline earth metals are insoluble in water and can be precipitated by addition of a sodium or ammonium carbonate solution. The solubility of carbonates in water decreases as the atomic number increases These carbonates decompose on heating to give carbon dioxide and the oxide. Beryllium carbonate is unstable and can be kept only in the atmosphere of CO_2.

(iv) *Sulphates*: The sulphates of the alkaline earth metals are all white solids and are stable to heat. Sulphates of Be and Mg are readily soluble in water because of their more hydration enthalpy and the solubility decreases from $CaSO_4$ to $BaSO_4$.

(v) *Nitrates*: The nitrates of alkaline earth are formed by the dissolution of carbonates in dilute nitric acid. Among these nitrates Barium Nitrate does not crystalline with molecules of water and Magnesium nitrate crystallizes with six molecules of water. This shows a decreasing tendency to form hydrates with increasing size. All of them decompose on heating to give the respective oxide.

Anomalous beryllium behaviour of beryllium

Beryllium shows anomalous behaviour as compared rest of the alkali earth metals.

1. It shows diagonal relationship to aluminium
2. It has exceptionally small atomic and ionic size so it forms largely covalent compounds.
3. Due to absence of *d*-orbital in its valency shell, its co ordination number is 4. For the rest of the members has coordination number 6 by making use of *d*-orbitals.

4. Beryllium oxide and hydroxide are amphoteric in nature whereas oxides and hydroxides of other alkaline earth metals are basic.

Diagonal Relationship between Beryllium and Aluminium

(i) These two elements have same electro negativity and the polarising power.

(ii) $BeCl_2$ and $AlCl_3$ act as a Lewis acids and can be used as Friedel – Crafts catalyst

(iii) Both Be and Al are resistant to the action of acids because of the presence of protective oxide film on their surface.

(iv) Both Be, Al chlodrides have chlorine bridged structures in vapour phase.

(v) Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{-2}, AlF_6^{-3}.

Some important compounds of calcium

Industrially important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulphate, calcium carbonate and cement.

Calcium Oxide or Quick Lime, CaO:

Calcium oxide is a white amorphous solid. On exposure to air, it absorbs moisture and carbon dioxide. It is prepared by heating limestone ($CaCO_3$) at 1070-1270 K.

$$CaCO_3 \xrightarrow{heat} CaO+CO_2$$

The carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion. The addition of water to lime is called slaking of Lime. Slaking of quick lime with soda gives Sodalime.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$CaO + CO_2 \longrightarrow CaCO_3$$

A mixture of 1 part of slacked line, 3 parts of sand and water is known as lime–mortar slacked line. When mixed sand harden due to the formation of calcium silicate.

$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$

Mortar becomes hard with time due to several chemical reactions. Mortar mixed with cement is called “cement mortar”. This is stronger than mortar.

Uses:

(i) It is a food additive used as an acidity regulator.

(ii) It is the primary constituent in the manufacturing of cement.

(iii) It is used in the purification of sugar and in preparing bleaching powder & sodium carbonate.

Calcium Hydroxide (Slaked lime), $Ca(OH)_2$,

It is a white amorphous powder. It is sparingly soluble in water. The aqueous solution of it is known as lime water and a suspension of slaked lime in water is known as milk of lime. Calcium hydroxide is prepared by adding water to quick lime, CaO.

$$CaO + H_2O \longrightarrow Ca\,(OH)_2$$

When carbon dioxide is passed through lime water it turns milky due to the formation of calcium carbonate. On passing excess of carbon dioxide, the precipitate dissolves to form calcium bicarbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

Calcium hydroxide also reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_2 + 2C1_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + 2H_2O$$

Uses:

(i) $Ca(OH)_2$ is used in the paper industry during kraft process which converts wood into pulp.
(ii) $Ca(OH)_2$ is used as flocculant or clarifying agent in sewage treatment process.
(iii) It is used in root canal treatment to fill human teeth cavities.
(iv) It also used in leather industry to separate hair or fur from the animal hide.
(v) Also used in the process of sugar and sugar beed.

Calcium Carbonate, $CaCO_3$

Calcium carbonate available in nature in several forms like chalk, marble, pumice stone etc. It is a white fluffy powder, insoluble in water. When heated to 1200 K, it decomposes to liberate CO_2 gas. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$
$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

On reaction with dilute acids, it releases carbon dioxide.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

Uses:

(i) It is important constituent in the building material like marble, cement and in the manufacture of quick lime.
(ii) Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.
(iii) It is also used as an antacid, mild abrasive in tooth paste.
(iv) In food industry, it is used in chewing gum, pastries, bread stuffs, crisps and cookies.
(v) It is used in the manufacturing of face powders, cosmetic foundations.
(vi) Lime stone is used as a flux in metallurgies.

Calcium Sulphate (Plaster of Paris), $CaSO_4\ ½\ H_2O$

It is a hemihydrate of *$CaSO_4$*. It is also called Plaster of Paris. It is prepared by heating gypsum ($CaSO_4\ 2H_2O$) at 393 K. Above 393K anhydrous calcium sulphate is formed. This is known as 'dead burnt plaster'.

$$2(CaSO_4.2H_2O) \longrightarrow 2(CaSO_4).H_2O+3H_2O$$

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

i. It is used to make cast in bone manufacturing.
ii. It is employed in dentistry to fill the gap in teeth.
iii. It is used in the making of moulds, statues and busts.
iv. The largest use of Plaster of Paris is in the construction field.

Cement: Cement is an important building material. The construction sector plays a very important role in the Indian economy. It is also called Portland cement because it resembles with the natural limestone quarried in the Isle of Portland, England.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated, fused together to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($CaSO_4$, $2H_2O$) to form cement.

Cement when mixed with water, setting of cement takes place to give a hard mass. This is due to the heat liberated during the hydration of constituents molecules and their rearrangement. The purpose of adding gypsum is only to slow down the process of setting of the cement so that it gets sufficiently hardened.

Intext Questions 19.4

1. Arrange the alkaline earth metals in order of increasing reactivity.

....

2. Name an amphoteric oxide of alkaline earth metals.

....

3. What is the Formulae of Lime stone.

....

4. Major use of plaster of paris in which field?

....

What You Have Learnt

- Hydrogen can either be placed with alkali metals or with halogens.
- Hydrogen exists in three isotopic forms namely hydrogen, deuterium and tritium.
- Hydrogen is a combustible gas and has reducing property.
- There are two important oxides of hydrogen: water and hydrogen peroxide.
- Cage-like structure of ice makes it float on water.
- Water containing deuterium in place of ordinary hydrogen is known as heavy water.
- Heavy water can be separated from ordinary water by electrolysis or distillation.
- Heavy water is used as moderator in nuclear reactors.
- Hydrogen peroxide acts both as oxidizing and reducing agent.
- The alkali and alkaline earth metals show regular variation in various properties along a group and period.
- Alkali metals react with hydrogen, water and halogens to form hydrides, hydroxides and halides respectively.
- Basic nature of oxides and hydroxides of group 1 and group 2 elements

Terminal Exercise

1. Write three general characteristics of the s-block elements which distinguish them from the elements of other blocks.
2. The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
3. What happens when?
    (a) Sodium metal is dropped in water.
    (b) Sodium metal is heated in free supply of air.
    (c) Sodium peroxide dissolves in water.
4. Explain why hydrogen is best placed separately in the periodic table of elements.
5. Describe the industrial applications of hydrogen.
6. Discuss the importance of heavy water in nuclear reactor and how is it prepared from normal water?
7. Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen?.
8. Why is iceless dense than water and what kind of attractive forces must be over come to melt ice?
9. Show by proper chemical reactions how hydrogen peroxide can function both as an oxidizing and a reducing agent?
10. Compare the properties of alkali metals and alkaline earth metals with respect to:
(a) Atomic radii (b) ionization energy (c) melting points (d) reducing behavior

Answers to Intext Questions

19.1

1. Three isotopes of hydrogen are (a) protium,(b) deuterium and (c) tritium
2. Tritium.
3. It is lightest of all the gases known.
4. Methane (CH_4).

19.2

1. Ice is less dense as compared to water. It has open spaces in the hydrogen bonded structure.
2. D_2O; Moderator is nuclear reactors.
3. $BaO_2.8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$
4. (a) as a bleaching agent. (b) Germicide and disinfectant.
5. H_2O_2 reduces $KMnO_4$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$$

Mn(+7) is reduced to Mn(+2)

19.3

1. Cs < Rb < K < Na < Li 2. Lithium
3. $2Na + 2H_2O_2 \longrightarrow NaOH + H_2$
4. Ionic. 5. (i) Sodium (ii) potassium 6. Sodium Hydroxide

19.4

1. Be < Mg < Ca < Sr < Ba 2. BeO 3. $CaCO_3$ 4. Construction field.

19.5 Hard & Soft Water

Water which does not give table lather readily with soap solution is called hard water. The hardness of water is due to the presence of calcium and magnesium bicarbonates, chlorides and sulphates in it. Iron salts also cause hardness.

Soap is sodium salt of higher fatty acid like palmitic acid, oleic acid or stearic acid. If soap solution readily gives lather with the given samples of water then that water is called soft water.

When soap is added to hard water, it reacts with calcium and magnesium ions in it to form the insoluble calcium magnesium soaps

$$2\ \text{Na Soap(aq)} + \frac{Ca^{2+}_{(aq)}}{Mg^{2+}_{(aq)}} \rightarrow \frac{Ca}{Mg}\text{Soap} \downarrow + Na^{+}_{(aq)}$$

Hence soap is wasted as mentioned above.

Temporary Hardness

Presence of bicarbonates of calcium and magnesium are said to cause temporary hardness to water. Removal of temporary Hardness of water

a) Boiling: Temporary hardness can be removed by boiling hard water. On boiling hard water, bicarbonates of calcium and magnesium decompose to form respective insoluble carbonates.

$$Mg(HCO_3)_{2(aq)} \xrightarrow{\text{boiling}} MgCO_{3(s)} \downarrow + H_2O_{(l)} + CO_{2(g)}$$

$$Ca(HCO_3)_{2(aq)} \xrightarrow{\text{boiling}} CaCO_{3(s)} \downarrow + H_2O_{(l)} + CO_{2(g)}$$

b) Clarke’sprocess: Requisite quantity of milk of lime is added to the water sample to remove temporary hardness.

$$Ca(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2CaCO_{3(s)} \downarrow + 2H_2O_{(l)}$$

$$Mg(HCO_3)_{2(aq)} + 2\,Ca(OH)_{2(aq)} \longrightarrow 2CaCO_{3(s)} \downarrow + Mg(OH)_{2(s)} \downarrow + 2H_2O_{(l)}$$

A word of caution is necessary here. In case, any excess of milk of lime is added, the water sample is rid off temporary hardness but acquires permanent hardness.

Permanent Hardness of Water:

Presence of chlorides and sulphates of calcium and magnesium as dissolved salts causes permanent hardness to water. This type of hardness cannot be removed by boiling because these salts are not decomposed by boiling water.

a) Gan’s permutit process (Base Exchange process):

Permutit is artificial zeolite. Chemically it is sodium aluminium orthosilicate. $Na_2Al_2Si_2O_8 \text{ x } H_2O$ Sodium carbonate, alumina and silica are fused together to obtain permutit. In a suitable container, permutit is packed and hard water is allowed to percolate through it.

Calcium and magnesium ions which cause hardness in water are replaced by sodium ions which do not cause hardness. Thus, water is softened and the soft water is taken out through the outlet.

b) Calgon Process:

Calgon is sodium hexa metaphospate ($Na_6P_6O_{18}$). This does not precipitate the calcium or magnesium salts but removes Ca^{2+} and Mg^{2+} ions from water either by adsorption or by forming a complex salt. Either way, hardness of water is removed.

c) Ion exchanged method:

Recently, suitable ion exchange resins have been developed to remove all mineral salts from water. Thus, “de-ionised water” is obtained which can be used for laboratory work and Industry. The deionization of water is carried out in two steps as mentioned below.

i) Water is passed through a tank containing cation exchangers in which consists of giant organic molecules having –COOH groups.

$$2RCOOH + Ca^{2+} \longrightarrow (RCOO)_2Ca + 2H^+(aq)$$

Resin from hard water retained in the resin

The Ca^{2+}, Mg^{2+} and any other cation in the sample of water are replaced by the H^+ ions from the resin.

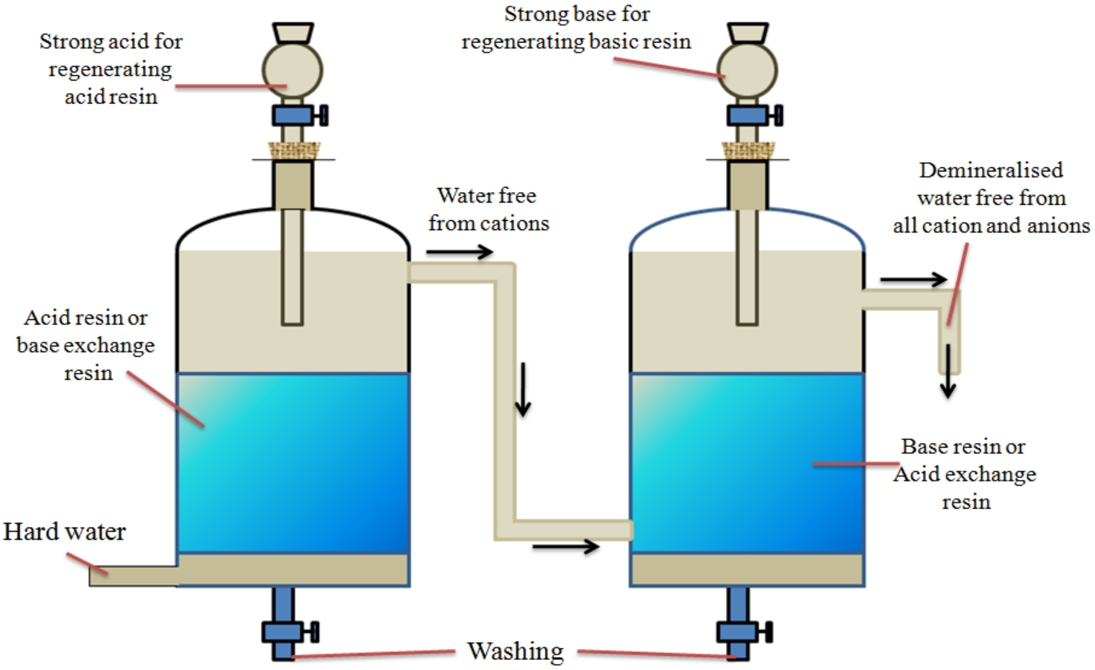


Fig.19.2.1. an Ion exchange method

ii) Then, water is passed through a tank containing an ion exchange resin where anion in the water is replaced by OH ions from the resin. An ion exchange resins are giant organic molecules with basic groups (OH^-) attached to them.

$$(RNH_3)OH + Cl^- \longrightarrow (RNH_3)Cl + OH^-$$

$$2(RNH_3)OH + SO^{2-}_4 \longrightarrow (RNH_3)_2SO_4 + 2OH$$

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

From step I Released   From step II Released

De ionised water can be used in place of distilled water. Cation exchange resins can be “revived” or “regenerated” by passing a moderately concentrated solution of sulphuric acid through it. The anion exchange resin can be “revived” by treating with moderately concentrated solution of caustic of caustic soda or sodium carbonate.

Disadvantages of hard water: Hard water, when used in boilers in industries causes formation scales in boiler. This eats away the metal layer and also causes wastage of heat energy. Hence only soft water is used in industries. Besides, hard water causes wastage of soap.

Measurement of Hardness of water: Hardness of water is due to the presence of soluble salts of calcium or magnesium. Quantity of these salts in a certain volume or weight of water measures the extent of hardness or degree of hardness.

Degree of hardness of water: The degree of hardness is refined as the number of parts by weight of calcium carbonate (equivalent to various calcium and magnesium salts) presents in a million parts (ppm) by weight of water.

19.5 Intext Questions:

1. What is meant by hard water?

……

2. Which salts cause hardness to water?

……

3. Write the chemical equation when soap is dissolved in water.

……

4. How do we remove the temporary hardness of water?

……

What you have learnt:

1. Description about soft water and hard water.
2. Temporary hardness.
3. Different methods for removal of hardness.
4. Different disadvantages due to hard water.
5. Measuring the hardness of water.

Terminal Exercise:

1. How to remove temporary hardness?
2. Explain about Clark’s Method?
3. How to remove hardness water by permutit method?
4. Explain about ion exchange method?

19.5 Answers to intext questions:

1. Water which does not give lather with soap is called hard water.

2. Hardness of water is due to the presence of calcium & magnesium bicarbonates, chlorides and sulphate.

3. $$2\text{Na Soap (aq)} + \frac{Ca+2(aq)}{Mg+2(aq)} \longrightarrow \frac{Ca}{Mg}\text{ soap} + Na^{+}$$

4. Boiling Water

19.6 Biological importance of metal

19.6.1 Biological importance of Na and K

1. There are 27 metals and non-metals in living systems out of them Na, Ka, Mg and Ca are required in major quantities.
2. The presence of Na^+ and K^+ ions inside and outside the cell produce an electrical potential across the cell membrane.
3. The presence of Na^+ ions is associated with the movement of glucose into the cells. The excess Na^+ ions entering the cell are expelled in the pumping out process.
4. The potassium ions are essential for the metabolism of glucose inside the cell and in the synthesis of proteins and the activation of certain enzymes.

19.6.2 Biological importance of Mg and Ca Role of Mg+2 ions

1) Mg^{+2} are concentrated in animal cells
2) Enzymes like 'phosphohydrolyses' and 'phosphotransferases' contain Mg^{+2} ions. These enzymes participate in ATP reactions and release energy in the process.
3) Mg^{+2} is constituent of chlorophyll

Role of Ca+2 in biology

1) Ca^{+2} is present in bones and teeth as apatite $Ca_3(PO_4)_2$. Enamel on teeth is flour apatite.
2) It is necessary for blood clotting.
3) Ca^{+2} ions are necessary to maintain heart beating.
4) Ca^{+2} ions are necessary for muscle contraction.

Chapter 20

GENERAL CHARACTERISTICS OF THE *p*-BLOCK ELEMENTS

The *p*-block of the periodic table consists of the elements of groups 13,14, 15, 16, 17 and 18. These elements are characterized by the filling up of electrons in the outermost *p*-orbitals of their atoms. Some of these elements and their compounds play an important role in our daily life.

For example:

- *Nitrogen is used in the manufacture of ammonia, nitric acid and fertilizers. Trinitrotoluene (TNT), nitroglycerine, etc., are compounds of nitrogen, which are used as explosives.*
- *Oxygen present in air is essential for life and combustion processes.*
- *Carbohydrates, proteins, vitamins, enzymes, etc., which contain chain of carbon atoms, are responsible for the growth and development of living organisms.*

The usual trends (vertical as well as horizontal) in various properties observed in the *s*-block are observed in this block, too. As we move from top to bottom through a vertical column (group) some similarities are observed in the properties. However, this vertical similarity is less marked in the p-block than that observed in the s-block, especially in groups 13 and 15; vertical similarity is increasingly shown by the later groups. As far as the horizontal trend is concerned, the properties vary in a regular fashion as we move from left to right across a row (period).

In this lesson we shall study some important physical properties *w.r.t.* the of electronic configuration of the atom. Finally, we shall relate the periodicity in atomic properties to the observed chemical behaviour of their compounds, with special reference to their oxides, hydrides and halides.

Objectives

After reading this lesson you will be able to:

- describe the general mode of occurrence of these elements in nature;
- recall the electronic configurations of the p-block elements;

- explain the variations in atomic and physical properties such as
  i. atomic and ionic sizes;
  ii. ionization enthalpy;
  iii. electro negativity;
  iv. electron-gain enthalpy;
  v. metallic and non-metallic behaviours along the period and in a group of the periodic table;
- correlate the properties of the elements and their compounds with their positions in the periodic table;
- explain the anomalous properties of the first element in each group of this block and
- explain inert pair effect.

20.1 Occurrence of the p-block Elements in Nature

The p-block elements do not follow any set pattern of mode of occurrence in nature. Some of them occur free as well as in the combined state in nature. For example, elements such as oxygen, nitrogen, carbon, sulphur occur in both the forms. Noble gases occur in free state only. All other elements usually occur in the combined state. The distribution of these elements in nature is also far from any uniform pattern. Some of them are quite abundant, e.g., oxygen, silicon, aluminium, nitrogen etc. On the other hand the heavier members in each group of the block are generally much less abundant. The important minerals associated with elements will be considered whenever it is necessary at the appropriate places in the text.

20.2 Electronic Configuration

Among the elements of *p*-block, the *p*-orbitals are successively filled in a systematic manner in each row. Corresponding to the filling up of 2*p*, 3*p*, 4*p*, 5*p* and 6*p* orbitals five rows of *p*-block elements are there. The outer electronic configuration of the atoms of these elements is ns^2np^6.

20.3 Atomic Size

The atomic radius of the of *p*-block elements generally decreases on moving across a period from left to right in the periodic table. It is because the addition of electrons takes place in the same valence shell and are subjected to an increased pull of the nuclear charge at each step. The variation in atomic size along a period is shown in Table 20.1.

Table 20.1 : Variation in Atomic Size in a row from Boron to Fluorine

Element	Boron	Carbon	Nitrogen	Oxygen	Fluorine
Outer electronic configuration	$2s^2\ 2p^1$	$2s^2\ 2p^2$	$2s^2\ 2p^3$	$2s^2\ 2p^4$	$\mathbf{2s^2\ 2p^5}$
Nuclear charge	+5	+6	+7	+8	**+9**
Effective nuclear charge	+2.60	+3.25	+3.90	+4.55	**+5.20**
Atomic size (pm)	**88**	**77**	**70**	**66**	**64**

On moving down a group, the atomic radius of the elements increases as the atomic number increases. This is due to the increase in the number of shells as we move from one element to the next down the group. The increase in nuclear charge is more than compensated by the additional shell. The variation in atomic size on moving down a group is shown in Table 20.2.

Table 20.2 : Variation in atomic size down a group

Elements of Group 13	Outer electron configuration	Nuclear charge	Effective nuclear charge	Atomic size (pn)
Boron	$2s^2\ 2p^1$	+5	+2.60	88
Aluminium	$3s^2\ 3p^1$	+13	+ 11.60	118
Gallium	$4s^2\ 4p^1$	+31	+29.60	124
Indium	$5s^2\ 5p^1$	+49	+47.60	152
Thallium	$6s^2\ 6p^1$	+81	+ 79.60	178

20.4 Ionization Enthalpy

It is the amount of energy required to remove the most loosely bound electron from the outermost shell of a neutral gaseous atom. It is measured in $kJ\ mol^{-1}$ and is known as first ionization enthalpy.

The first ionization enthalpy of the p-block elements generally increases on moving from left to right along a period. It is because as we move from left to right along a period, the atomic size decreases. In a small atom, the electrons are held tightly. The larger the atom, the less strongly the electrons are held by the nucleus. The ionization enthalpy, therefore, increases with decrease in atomic size. However, there are certain exceptions, e.g., the first ionization enthalpy of a group 16 element is lower than that of a group 15 element. It is because in case of a group 15 element, the electron is to be removed from the half-filled *p*-orbitals. A comparison of first ionization energies of some elements is given in Table 20.3.

Table 20.3: Comparison of first ionization enthalpies ($kJ\ mol^{-1}$)

B	C	N	0	F	Ne
801	1086	1403	1310	1681	2080

Al	Si	P	S	Cl	Ar
577	796	1062	999	1255	1521

In general the first ionization enthalpy decreases in a regular way on descending a group. It is because on descending a group, the atomic size increases. As a result the electrons are less tightly held by the nucleus and therefore, first ionization enthalpy decreases.

Intext Questions 20.1

1. Which of the following atoms is expected to have smaller size?

(i) $_9F$ and $_{17}Cl$ (ii) $_6C$ and $_{14}Si$ (iii) $_5B$ and $_6C$ (iv) $_6C$ and $_7N$

....

2. Which atom in the following pairs of atoms is expected to have higher ionization enthalpy?

(i) ${}_{4}$Be and ${}_{5}$B (ii) ${}_{16}$S and ${}_{17}$Cl (iii) ${}_{2}$He and ${}_{10}$Ne (iv) ${}_{8}$O and ${}_{16}$S

....

3. Arrange the following atoms in order of increasing ionization enthalpy: ${}_{2}$He, ${}_{4}$Be, ${}_{7}$N, ${}_{11}$Na

....

4. How does the ionization enthalpy vary in general in a group and in a period of the *p-block* elements?

....

20.5 Electron Gain Enthalpy

When an electron is added to a neutral gaseous atom, heat energy is either released or absorbed. The amount of heat energy released or absorbed when an extra electron is added to a neutral gaseous atom is termed as electron gain enthalpy, i.e., energy change for the process :

$$X\,(g) + e^- \longrightarrow X\,(g)$$

Generally for most of the atoms, the electron gain enthalpy is negative, i.e., energy is released when an electron is added to a neutral gaseous atom. But for some atoms, the electron gain enthalpy is a positive quantity, i.e., energy is absorbed during the addition of an electron.

Electron affinity generally becomes more negative on moving from left to right along a period. It is because on moving across a period, the atomic size decreases. As a result the force of attraction exerted by the nucleus on the electron increases. Consequently the atom has a greater tendency to gain an electron. Hence, electron gain enthalpy becomes more negative.

On moving down a group, the electron gain enthalpy becomes less negative. This is due to the increase in atomic size and thus, less attraction for the electrons; the atom will have less tendency to gain an electron. Hence, electron gain enthalpy becomes less negative. But in the halogen group, the electron gain enthalpy of chlorine is more negative than that of fluorine. It is because the size of the F atom is very small which makes the addition of electron less favourable due to inter electronic repulsion. Similar situation exists for the first element of each group.

Table 20.4 : Electron gain enthalpies of some p-block elements in kJ mol1

B	C	N	O	F	Al	Si	P	S	Cl
0.30	1.25	+0.20	1.48	3.6	0.52	1.90	0.80	2.0	3.8

20.6 Electronegativity

Electronegativity is defined as a measure of the ability of an atom to attract the shared electron pair in a covalent bond to itself.

Electronegativity increases along the period and decreases down the group.

Fluorine is the most electronegative of all the elements. The second most electronegative element is oxygen followed by nitrogen in the third position.

20.7 Metallic and Non-metallic Behaviour

The elements can be broadly classified into metals and non-metals. Metals are electropositive in character i.e., they readily form positive ions by the loss of electrons whereas non-metals are electronegative in character i.e., they readily form negative ions by the gain of electrons. The metallic and non-metallic character of *p*-block elements varies as follows:

Along the period the metallic character decreases, whereas non-metallic character increases. It is because on moving across the period, the atomic size decreases due to the increased nuclear charge and hence, ionization energy increases.

On moving down the group the metallic character increases, whereas non-metallic character, decreases. It is because on moving down a group, the atomic size increases. As a result the ionization energy decreases and tendency to lose electrons increases. Therefore, metallic character increases and non-metallic character decreases.

20.8 Anomalous behaviour of the first Element in Each Group of the p-Block

The elements comprising s-block and p-block are called main groups or representative elements. Since the atomic radii decrease across a period, the p-block atoms are smaller than their nearest s or d block atoms; thus F atom has the smallest radius. Associated with small atom the 2*p* orbitals are very compact and influence the bonds formed. Inter electronic repulsions are thus more significant in 2*p* than in *np* orbitals (where $n > 2$). This results in the N − N, O−O and F−F bonds being comparatively weaker than the P−P, S−S and Cl−Cl bonds, respectively.

The small size of the atoms of N, O and F results in their high electonegativity values. This is reflected in the formation of relatively strong hydrogen bonds in X−H .... Y, where X and Y may be N, O or F.

Carbon, nitrogen and oxygen differ from other elements of their respective groups due to their unique ability to form $p\pi$ - $p\pi$ multiple bonds. For example C = C, C≡C, N = N, O = O, etc. The later members such as Si, P, S, etc., do not form $p\pi$ - $p\pi$ bonds because the atomic orbitals (3*p*) are too large to achieve effective overlapping.

The valence shell capacity of the p-block elements in the second period limits the coordination number to a maximum of 4. However, in compounds of the heavier members the higher coordination numbers are attainable. Thus BH_4^- and BF_4; contrast with $[AlF_6]^{3-}$; CF_4 contrasts with $[Si\ F_6]^{2-}$ and NH_4^+ ; contrasts with $[PCl_6]^-$. In the heavier members of each group d-orbitals are available for bonding and their participation may be envisaged in the attainment of the higher coordination number.

20.9 Inert Pair Effect

Among the elements of p-block, in groups 13,14 and 15, there is a general trend that the higher oxidation states become less stable in-going down the group. Thus although boron and aluminium are universally trivalent, gallium, indium and thallium exhibit + 1 state as well. In fact + 1 state of thallium is very stable. Similar situations are noticed in groups 14 and 15. Though carbon is universally tetravalent, it is possible to prepare divalent germanium, and lead compounds. The stable state of +3 in antimony and bismuth in group 15 is another example.

Outer electron configurations of group 13, 14 and 15 elements are ns^2np^1, ns^2np^2 and ns^2np^3, respectively. They are thus expected to show the higher oxidation state of +3, +4 and +5 respectively. But the preference of heavier elements of these groups to show + 1, +2 and +3 states, respectively indicate that two electrons do not participate in bonding. The reluctance of s-electrons to take part in chemical bonding is known as ***inert pair effect***.

The so called "inert pair effect" is therefore, ascribed to two factors.

1. The increase in the promotion energy from the ground state ($ns^2\ np^1$) to the valence state ($ns^1\ np^2$).
2. Poorer overlap of the orbitals of the large atoms and hence poorer bond energy.

The net result is the lesser stability of higher oxidation state with the increasing atomic number in these groups. Once the involved energies are taken into consideration, the so called "inert pair effect" term loses its significance.

Intext Questions 20.2

1. Why does fluorine have electron gain enthalpy lower than chlorine?

....

2. Which atom in the following pair of atoms has greater electron gain enthalpy?

(i) F, CI (ii) Br, I (iii) I, Xe (iv) O, F (v) O, S

....

3. Give two reasons for the fact that the first element in each group of *p-block* exhibits unique behaviour.

....

4. Explain why oxygen exists as a gas whereas sulphur exists as a solid.

....

5. Mention two reasons which are responsible for the so called "inert pair effect".

....

6. What is the consequence of "inert pair effect" on the oxidation states of Tl and Pb?

....

20.10 General Trends in the Chemistry of the p-Block Elements

The p-block elements except noble gases react with hydrogen, oxygen and halogens to form various hydrides, oxides and halides respectively. A more or less regular trend is observed to the properties of these compounds on moving down any particular group. The noble gases have almost zero electron afinity and have very high ionization enthalpies.

Therefore, under normal conditions, the atoms of noble gases have little tendency to gain or lose electrons.

20.10.1 Hydrides

The hydrides of the p-block elements are listed in table 20.5. They are covalent molecules and their bond angles are consistent with VSEPR theory. The angles decrease from 109.5° in CH_4 to 107° in NH_3 and 104° in H_2O.

These hydrides are volatile in nature. Generally their acid strength increases from left to right and from top to bottom.

Table 20.5 : Hydrides of p-block elements

Group				
13	**14**	**15**	**16**	**17**
B_2H_6	CH_4	NH_3	H_2O	HF
$(AIH_3)_X$	SiH_4	PH_3	H_2S	HCl
Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr
InH_3	SnH_4	SbH_3	H_2Te	HI
TIH_3	PbH_4	BiH_3	H_2Po	

20.10.2 Oxides

p-Block elements form a number of oxides on reacting with oxygen. The oxides E_2O_n (n = 3, 5 or 7) are the highest oxides formed by the elements in the groups 13, 15 or 17 respectively. The oxides EO_n (n = 2, 3 or 4) are formed by the elements in groups 14, 16 or 18 respectively. Thus, nitrogen forms NO, NO_2, N_2O_3 and N_2O_5; phosphorus forms P_4O_6 and P_4O_{10}, xenon forms XeO_3 and XeO_4.

- In any particular group, the basic nature of the oxides (oxidation state of the element remaining same) increases with increase in atomic number.
- In a particular period the acidity increases with increase in the oxidation state of the element.

20.10.3 Halides

A review of the properties of halides of *p-block* elements reveals that most of them are covalent halides. In a group the covalent character of halides decreases down the group.

Where an element exhibits more than one oxidation state, the covalent character of a halide increases with the increase in the oxidation state of the element forming halides. For example, whereas $PbCl_2$ is an ionic halide, $PbCl_4$ is covalent. Similarly the covalent character of halides of a particular element increases from fluoride to chloride to bromide.

Covalent halides are generally gases, liquids or solids with low melting points. These halides usually hydrolyse to give the oxoacid of the element.

For example $SiCl_4$ reacts vigorously with water

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

In general the chlorides, bromides and iodides are found to be more stable with lower oxidation state of the element, whereas fluorides are formed in the higher oxidation states. The halides are usually formed by the direct union of the element with the halogen. For example

$$C(S) + Cl_2(g) \longrightarrow CCl_4(l)$$

$$2As(S) + Cl_2(g) \longrightarrow AsCl_3(s)$$

Intext Question 20.3

1. Which of the following oxides is the most acidic?

   (i) Al_2O_3 (ii) CO_2 (iii) SO_2

……………………………………………………………………………………………………

2. Which of the following hydrides of main group elements is the most acidic?

   (i) H_2Se (ii) H_2O iii) HCl (iv) HI

……………………………………………………………………………………………………

3. Arrange the following in increasing order of covalent character.

   $SiCl_4$, CCl_4, $SnCl_4$, $GeCl_4$

……………………………………………………………………………………………………

4. What happens when $SiCl_4$ reacts with water. Write complete chemical equation for the reaction

……………………………………………………………………………………………………

5. How do the bond angles vary among the following hydrides

   NH_3, PH_3 , AsH_3, SbH_3

……………………………………………………………………………………………………

6. Give equations for the formation of the following from the elements:

   (i) Al_2O_3 (ii) $SiCl_4$ (iii) CCl_4

……………………………………………………………………………………………………

7. Which is more covalent in each of the following pairs?

   (i) $AlCl_3$ and BCl_3 (ii) $PbCl_2$ and $PbCl_4$

……………………………………………………………………………………………………

What You Have Learnt

- The elements of groups 13, 14, 15, 16, 17 and 18 constitute the p-block of the periodic table.
- Some of the elements of the p-block are widely and abundantly found in nature, viz., oxygen, silicon, aluminium, etc.
- Many physical and chemical properties of the p-block main group elements show periodic variation with atomic number.
- The ionization enthalpy is the energy required to remove the outermost electron from a neutral gaseous atom.

- The electron gain enthalpy is the energy change when a neutral atom in a gaseous state accepts an electron.
- Electronegativity is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself.
- The top element in each group shows a unique behaviour.
- The reluctance of s-electrons to take part in bond formation is known as "inert pair effect"
- p-Block elements form a number of oxides on reacting with oxygen.
- Most of the elements of the p-block form covalent halides.
- General characteristics of the p-block hydrides, halides and oxides.

Terminal Exercise

1. Which groups of the 'periodic table' constitute p-block?
2. How does the magnitude of ionization energy of an atom vary along the group in the periodic table?
3. How does electronegativity change along a row of elements in the periodic table?
4. Explain 'Metallic character decreases along a period but increases on moving down a group'.
5. Discuss the trends in the chemistry of p-block elements with respect to:
    (i) acidic and basic nature of the oxides;
    (ii) ionic and covalent nature of the hydrides.
6. What is the cause of anomalous behaviour of the top element in each group of the p-block elements.
7. What is 'inert pair effect'? Is there any inert pair present or is it a misnomer?
8. Comment on the nature (ionic/covalent) of the hydrides of the p-block elements
9. How does the covalent character of halides of an element change with oxidation state of the element?
10. Which is likely to form higher halides with an element exhibiting variable oxidation state, F_2 or Cl_2?

Answers to Intext Questions

20.1

1. (i) 9F (ii) 6C (iii) 6C (iv) 7N
2. 4Be (ii) 17Cl (iii) 2He (iv) 8O
3. Na < Be < N < He
4. In a group, it decreases down the group and it usually increases along a period.

20.2

1. The unexpectedly low value of electron gain enthalpy for F as compared to that of Cl atom may be attributed to the extremely small size of F atom vis-a-vis Cl atom. The addition of an electron produces a negative ion which has a high electron density and leads to increased interelectronic repulsions.
2. (i) Cl (ii) Br (iii) I (iv) F (v) S
3. (i) Small size (ii) absence of d-orbital

4. Because oxygen can form multiple bonds (O = O).
5. (i) Lower bond energy in the compounds of heavier atoms and

(ii) the higher energy involved in promotion from the ground state (s^2p^1) to the valence state

(s^1p^2).

6. Lower oxidation states become more stable.

For Tl, + 1 and for Pb, +2.

20.3

1. SO_2
2. HI
3. $SnCl_4 < GeCl_4 < SiCl_4 < CCl_4$
4. $SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$
5. The bond angle decreases from 107° to almost 90°.
6. (i) $4Al(s) + 3O_2(g) \longrightarrow 2AlO_3(s)$

   (ii) $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(l)$

   (iii) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(l)$
7. (i) BCl_3 (ii) $PbCl_4$

Chapter 21

p-BLOCK ELEMENTS AND THEIR COMPOUNDS - I

You have already studied the general characteristics of the p-block elements in the previous lesson. Now, we shall discuss some of the important elements and their compounds. Groups 13, 14 and 15 of the periodic table will be considered in this lesson and groups 16, 17 and 18 in the next lesson.

Objectives

After reading this lesson, you will be able to

- describe the methods of preparation of boric acid, borax, diborane and boron trifluoride;
- explain the structure of diborane, boric acid and boron trifluoride;
- list the uses of borax, boric acid and boron trifluoride;
- list examples of double salts;
- describe the preparation and uses of aluminium trichloride and potash alum;
- explain the structure of aluminium trichloride;
- list the allotropes of crystalline carbon;
- compare the structures of diamond and graphite;
- explain the structure and properties of carbon monoxide, carbon dioxide and silicon dioxide;
- compare hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride;
- describe preparation and uses of silicon carbide;
- explain the processes for manufacture of ammonia and nitric acid;
- list the properties and uses of ammonia and nitric acid;
- explain nitrogen fixation: natural and industrial and
- list a few nitrogenous, phosphatic and mixed fertilizers with their importance.

21.1 Boron and Aluminium

Boron and aluminium are the first two members of Group13 of the periodic table. Though the outer most electronic configurations of boron and aluminium are similar yet there is a big difference between the properties of their compounds. This will become clear when we study the compounds of boron and aluminium.

21.1.1 Boric Acid

Preparation: Boric acid (also called ortho boric acid) H_3BO_3, $[B(OH)_3]$ is prepared by the action of sulphuric acid on concentrated solution of borax ($Na_2B_4O_7.10H_2O$). Boric acid separates as white flaky crystals.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

Properties and Structure: Boric acid is a white crystalline solid. It is soluble in water. It behaves as a weak Lewis acid rather than a protonic acid because it combines with hydroxyl ions (OH) of water to liberate hydronium (H_3O^+).

Thus

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

When heated, it decomposes to meta boric acid and finally to boric anhydride (or boric oxide) at red heat

$$2B(OH)_3 \xrightarrow[H_2O]{375K} 2BO(OH) \xrightarrow[-H_2O]{\text{Red heat}} B_2O_3\,(\uparrow)\ \text{(Boric oxide)}$$

In boric acid, $B(OH)_3$ units are linked by hydrogen bonds to give two dimensional sheets (Fig. 21.1). The sheets are held together by weak vander Waals forces which are responsible for the cleavage of solid structure into flakes.

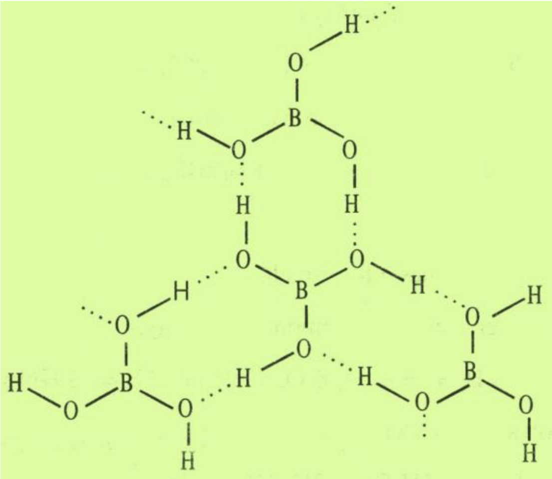


Fig.21.1: Structure of boric acid; the dotted lines represent hydrogen bond

Uses: Boric acid is used:

(i) as an antiseptic,

(ii) as a food preservative, and

(iii) in making enamels, pottery glazes and glass.

21.1.2 Borax, $Na_2B_4O_7.10H_2O$

In crude form borax occurs as tincal in dried up lakes of India. It is also prepared from the mineral colemanite, $Ca_2B_6O_{11}$ by the action of concentrated solution of sodium carbonate.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

Borax is crystallised from the filtrate. Borax is a white crystalline solid of the formula $Na_2B_4O_7.10H_2O$.

On heating it loses water of crystallisation. It is used:

(i) as an alkaline buffer in dyeing and bleaching processes

(ii) as a preservative
(iii) in the manufacture of optical and borosilicate glasses
(iv) as a flux, and
(v) in making glazes for pottery and tiles.

21.1.3 Diborane, B_2H_6

Diborane is the most important hydride of boron.

Preparation:

It is prepared by the following methods:

(i) By the action of lithium aluminium hydride on boron trichloride

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(ii) By the action of lithium hydride on boron tri fluoride

$$8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$$

Properties:

- Diborane is a toxic gas and has a foul smell.
- It burns in oxygen to give enormous amount of energy.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O;\ H = 1976\ \text{kJ/mol}$$

- It is readily hydrolysed by water

$$B_2H_6 + 6H_2O_2 \longrightarrow H_3BO_3 + 6H_2$$

Structure: The molecular structure of diborane is shown below. The two boron atoms and the four terminal hydrogen atoms lie in one plane, the two bridging hydrogen atoms lie symmetrically above and below the plane. If we consider the bonding situation in B_2H_6, there are eight BH bonds but only twelve valence electrons. Obviously there are not enough electrons to fill all the available orbitals to form eight normal covalent (two-centre) bonds. Thus bonding in diborane is described in terms of two multicentre bonds, i.e., 3c-2e or three centre two electron BHB bonds and four normal B-H bonds.

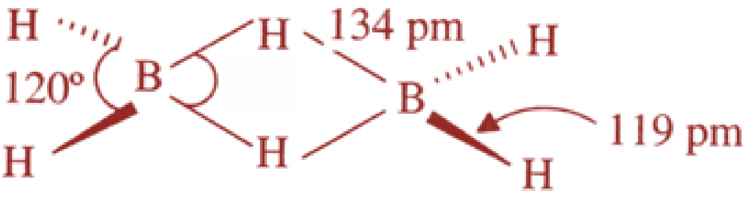


Fig.21.2: Structure of diborane, B_2H_6

21.1.4 Boron Trifluoride

Boron forms halides BX_3 (X = F, Cl, Br, I). All these halides with exception of fluoride, are formed by the action of appropriate halogen on boric oxide at high temperature. Boron trifluoride is formed by the action of hydro fluoric acid on boron oxide. Thus

$$B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$$

BF_3 hydrolyses according to the following equation

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4$$

BF_3 acts as an electron acceptor (Lewis acid) since B does not have an octet of electrons in its valence shell; in fact it has a sextet. It forms complexes with nitrogen and oxygen donors, e.g. NH_3 and ether, thus completing the octet of boron.

$$F_3B \leftarrow NH_3 \text{ and } F_3B \leftarrow OEt_2$$

Boron tri fluoride is used as a catalyst in Friedel-Crafts reaction such as alkylation and acylation and in polymerization reactions.

The structure of boron trifluoride is shown in Fig 21.3:

BF bond in BF3 has a multiple bond character since its structure is are so nance hybrid of three resonating structures.

Note that in the resonating structures boron completes its octet.

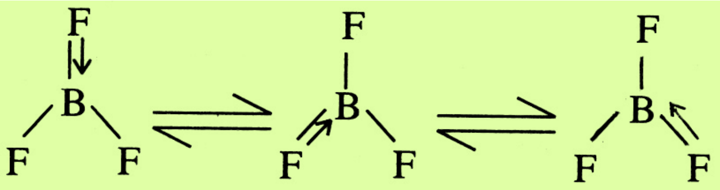


Fig21.3:Resonatingstructuresofborontrifluoride

21.1.5 Aluminium trichloride

Aluminium trichloride exists as a dimer as Al_2Cl_6 at room temperature and as a monomer at high temperatures and is made by passing hydrogen chloride or chlorine over heated aluminium under anhydrous condition.

$$2Al + 6HCl \longrightarrow Al_2Cl_6 + 3H_2$$

$$2Al + 3Cl_2 \longrightarrow Al_2Cl_6$$

When pure, it is a white solid which sublimes at 453K. Aluminum has only three valence electrons. When these are used to form three covalent bonds, the atom has only six electrons in its valence shell. Since it is electron deficient it, therefore, exists as a dimer. The aluminium atoms complete their octets by dative bonding from two chlorine atoms. The arrangement of chlorine atoms about each aluminium atom is roughly tetrahedral. The structure of the dimer is shown in Fig.21.4.

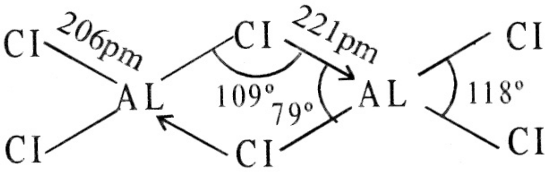


Fig.21.4: Structure of $AlCl_3$

When treated with water it gives hydrated aluminium ions and Cl ion

$$Al_2Cl_6 + 6H_2O \rightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$$

Anhydrous aluminium chloride is used as a catalyst in Friedel-Crafts reaction because of its Lewis acid character.

21.1.6 Double Salts: Alums and Potash Alum

When two salts capable of indendent existence are mixed and the solution of the mixture is allowed to crystallise, crystals comprising both the salts are characteristically formed. However, in solution all the ions exist freely. Such substances are called double salts. For example, when a solution containing potassium sulphate and aluminium sulphate is allowed to crystallise, transparent octahedral crystals of Potash Alum $K^+ Al^{3+} (SO_4)^{2-}.12H_2O$ are obtained. The solid contains $[K(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$ and SO_4^{2-} ions and it is a double salt since it gives the tests of its constituent ions in solutions. The double sulphate with similar composition and properties are called alums.

It is possible to replace the trivalent aluminium cation by trivalent metal ion of the similar ionic size, e.g. Ti^{3+}, Cr^{3+}, Fe^{3+} and CO^{3+}. It is also possible to prepare a series of alums in which potassium ion is replaced by ammonium ion, NH_4^+.

The alums are isomorphous, a few typical ones are given below:

Ammonium alum	$(NH_4)\ Al\ (SO_4)_2.\ 12H_2O$
Chrome alum	$K\ Cr\ (SO_4)_2.\ l2H_2O$
Ammonium chrome alum	$(NH_4)\ Cr\ (SO_4)_2.\ 12H_2O$
Ferric alum	$K\ Fe\ (SO_4)_2.\ 12H_2O$

Potash alum, $K\ Al(SO_4)_2.\ l2H_2O$, is by far the most important of all the alums. It is used as a mordant in dyeing industry and also in purifying water. (Often it is formulated as $K_2SO_4.Al_2(SO_4)_3\ .24H_2O$.

IntextQuestions21.1

1. Write the formula of the following: (i) Boric acid (ii) Borax

....

2. Write one reaction for the preparation of diborane.

....

3. What is the general formula of alums?

....

4. Write the formula of anhydrous solid aluminium trichloride and its structure.

....

5. Mention one use each of

(i) borax ....

(ii) boric acid ....

(iii) boron trifluoride ....

21.2 Carbon and Silicon

Carbon and silicon belong to Group 14 of the periodic table. Both elements show significant differences in their chemistry. There are thousands of hydrocarbons (alkanes and other compounds of carbon and hydrogen) but only a few silanes (compounds of silicon and hydrogen are known). It is because carbon has the unique ability to form compounds in which the carbon atoms are bonded to each other in chains or rings. This property is called catenation which is due to the fact that C-C bond is much stronger than Si-Si bond.

21.2.1 Allotropic Forms of Carbon

Diamond and Graphite: Structures and Properties

Diamond and graphite, both are crystalline forms of carbon. But they are structurally different. Due to the difference in the arrangement of carbon atoms, they show different properties. In diamond, each carbon atom is sp^3 hybridized and is linked to four other carbon atoms by strong covalent bonds in a tetrahedral fashion. It gives rise to a three-dimensional arrangement (Fig. 21.5). On the other hand, in graphite, the carbon atoms are arranged in layers. In each layer a particular carbon atom is sp^2 hybdridized and is linked to three other carbon atoms in a hexagonal arrangement. The fourth electron is free and does not participate in bonding. The different layers are held together by weak vander Waals forces (Fig 21.6).

Chemically speaking diamond is unreactive and bums in oxygen only if heated above 800°C, forming carbon dioxide. It reacts with fluorine (but not with chlorine) at 973K giving carbon tetrafluoride. Alkalies and acids have no action on diamond. It is the hardest natural substance.

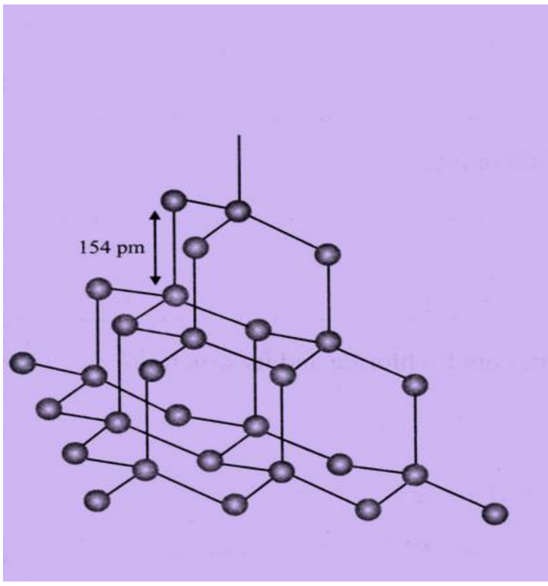


Fig.21.5: Structure of diamond

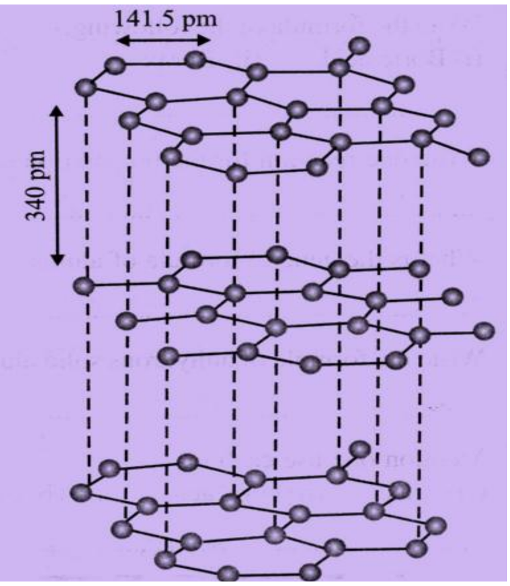


Fig.21.6: Structure of graphite

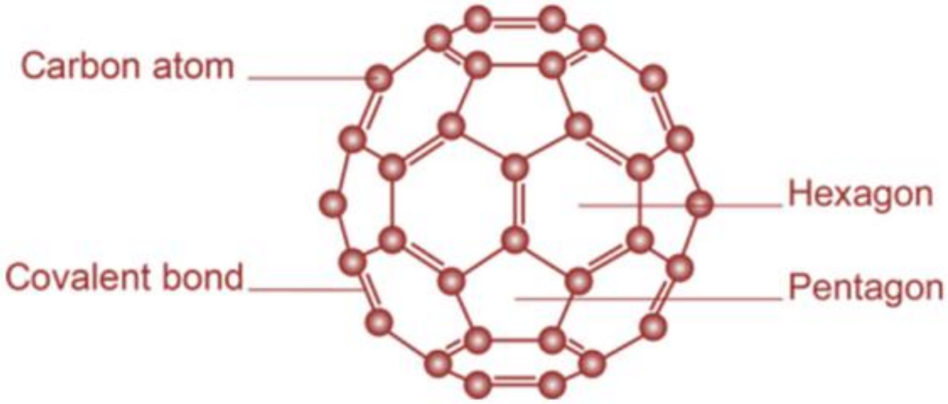
Graphite, on the other hand, is reactive. It burns in air at 873K to form CO_2. It is not attacked by dilute acids but concentrated sulphuric acid reacts with graphite to give graphite bisulphate in solution. It does not react with chlorine also.

Diamond is used for cutting and grinding hard substances such as rocks, glass, etc., and in die for drawing wire for watch springs and lamp filaments. Beside all these, diamond is widely used in jewellery.

Graphite is used as electrodes, as lubricant, for making crucibles, for casting of metals, for lead pencils and as a constituent of heat resistant paints.

Fullerenes

Fullerene, a newly discovered allotrope of carbon is called “Buckminster Fullerene” after the name of American architect Buckminster Fuller. The most common Fullerene molecule has 60 carbon atoms and the carbon atoms are linked to create the shape of a hollow soccer ball. The outer surface of fullerenes can be altered by chemical reactions.



21.2.2 Oxides of Carbon and Silicon

Structure

Carbon forms two oxides, viz., carbon monoxide and carbon dioxide. The bonding in carbon monoxide may be represented as, three electron pairs shared between the two atoms. The three electron pairs consist of one sp hybridized σ bond and two π bonds.

$:C\,\vdots\vdots\,O:$ $\qquad$ $:C\overset{\leftarrow}{\equiv}O:$

The structure of carbon dioxide on the other hand is linear O = C = O. There are two bonds and two bonds in the molecule CO_2. The carbon atom uses *sp* hybrid orbitals to form bonds with oxygen atoms. The remaining two *2p* orbitals of carbon overlap with *2p* orbitals one each from the two O atoms to form the π bonds

$$O = C = O$$

Silicon also forms two oxides: SiO and SiO_2: Not much is known about silicon monoxide as its existence is only known at high temperatures. Silica (SiO_2) is widely found as sand and quartz.

SiO_2 is a high melting solid and it exists in twelve different forms, each of which, has different structure. The main forms are quartz and cristobalite, each of which has a different structure at different temperatures. In all these forms silicon is tetrahedrally surrounded by four oxygen atoms and each oxygen is attached to two silicon atoms. The sp^3 orbitals of Si overlap with 2*p* orbitals of O atoms. Each corner of tetrahedron is shared by other tetrahedra. This gives an infinite structure a macromolecule.

Properties

Carbon monoxide is a neutral oxide. It is a colourless, odourless and a poisonous gas and burns with a blue flame. It is toxic because it forms a complex with the haemoglobin in the blood which prevents the haemoglobin from carrying oxygen around the body. This leads to oxygen deficiency resulting in unconsciousness or death. Carbon monoxide is an important industrial fuel and is also a strong reducing agent.

Carbon dioxide is an acidic oxide. It is a colourless and odourless gas and can be liquified under pressure at low temperature. Solid carbon dioxide is called dry ice.

SiO_2 is an acidic oxide and is unreactive in all its forms. It shows very limited reactions. It dissolves slowly in aqueous alkalies and more rapidly infused alkalies or fused carbonates forming silicates. Silica also reacts with fluorine and HF to form silicon tetra fluoride.

$$\begin{aligned} SiO_2 + 2NaOH &\longrightarrow Na_2SiO_3 + H_2O \\ SiO_2 + 2F_2 &\longrightarrow SiF_4 + O_2 \\ SiO_2 + 4HF &\longrightarrow SiF_4 + 2H_2O \end{aligned}$$

21.2.3 Halides of Carbon and Silicon

Carbon and silicon form tetrahalides like CCl_4 and $SiCl_4$, respectively. In the tetrahalides of these elements there are four covalent bonds, with a tetrahedral arrangement; the central atom is sp^3 hybridized. Carbon tetrachloride can be rightly called as tetrachloro methane and silicon tetrachloride as tetrachloro silane.

Carbon tetrachloride is prepared by the action of chlorine on carbon disulphide in the presence of a catalyst (usually $MnCl_2$)

$$CS_2 + 3Cl_2 \xrightarrow{MnCl_2} CCl_4 + S_2Cl_2$$

Silicon tetrachloride, $SiCl_4$, is formed by heating amorphous silicon in a current of dry chlorine.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

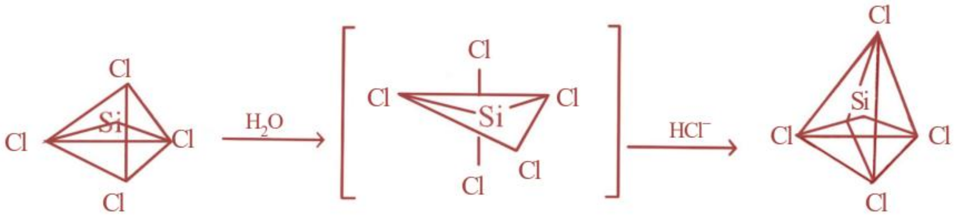
It can also be obtained by passing dry chlorine over an intimate mixture of silica and carbon strongly heated in a crucible. Thus

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

Carbon tetra chloride is not hydrolysed by water where as silicon tetrachloride is readily hydrolysed.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

The difference in the behaviour of CCl_4 and $SiCl_4$ towards water can be explained as follows. A lone pair of electrons from the O atom of H_2O molecule is donated to the empty 3*d*-orbital on Si. Subsequently one of the hydrogen atoms of water molecule combines with a chlorine atom of $SiCl_4$. This process goes on till all the chlorine atoms are replaced by OH groups.



Since there is no d orbital in carbon in CCl_4, does not hydrolyse.

Silicon forms complex ion like SiF_6^{2-} but carbon does not form similer ions like CF_6^{2-}. It is because unlike carbon there are empty 3*d* orbitals in silicon. The availability of *d* orbitals is responsible for the ability of silicon and not carbon to form complex ion SiF_6^{2-}.

21.2.4 Silicon Carbide, SiC

Silicon carbide (SiC) is commonly known as *carborundum*. It is extremely hard and chemically a very stable material. It is made by heating silica with excess of carbon in an electric furnace

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

In silicon carbide, there are three dimensional arrays of Si and C atoms, each atom of Si or C is tetrahedrally surrounded by four of the other type. Thus, this structure is very much similar to that of diamond. Silicon carbide or carborundum is widely used as an abrasive.

Intext Questions21.2

1. Write two properties of diamond which are not exhibited by graphite.

....

2. What is the state of hybridization of carbon in (i) diamond (ii) graphite?

....

3. What is the nature of bond in carborundum?

....

4. Write the state of hybridization of carbon in CCl_4

....

5. Which one is affected by water and why: CCl_4 or $SiCl_4$?

....

6. Which is an acidic oxide, CO or CO_2?

....

7. What happens when SiO_2 is attacked by F_2?

....

21.3 Nitrogen and Phosphorus

Nitrogen and phosphorus belong to Group 15 of the periodic table. They form a number of industrially important compounds like ammonia, nitric acid and fertilizers. Let us study about them.

21.3.1Ammonia

Ammonia is prepared in the laboratory by heating an ammonium salt with a base:

$$2NH_4^+ + OH^- \rightarrow 2NH_3 + H_2O$$

$$2NH_4^+ + CaO \rightarrow Ca^{2+} + 2NH_3 + H_2O$$

It may also be prepared by treating a nitride with water.

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

It is manufactured industrially by passing nitrogen and hydrogen over an iron catalyst at 750K and under a pressure of about 200 atmospheres (Haber'sprocess).

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H = -46\ kJ\ mol^{-1}$$

In the actual process the hydrogen required is obtained from water gas and the nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (l:3 by volume) is compressed to 200-300 atm and then passed in to the catalytic tubes packed with the catalyst. The catalyst in made by fusing Fe_3O_4 with KOH and Al_2O_3. The temperature of the catalytic tubes is maintained at 673-773K by heating them electrically. The issuing gas containing about 10percent ammonia is cooled and the liquid ammonia condenses. The unconverted mixture of hydrogen and nitrogen is returned to the inlet and passed again over the catalyst. A typical plant might be arranged as shown in Fig.21.7

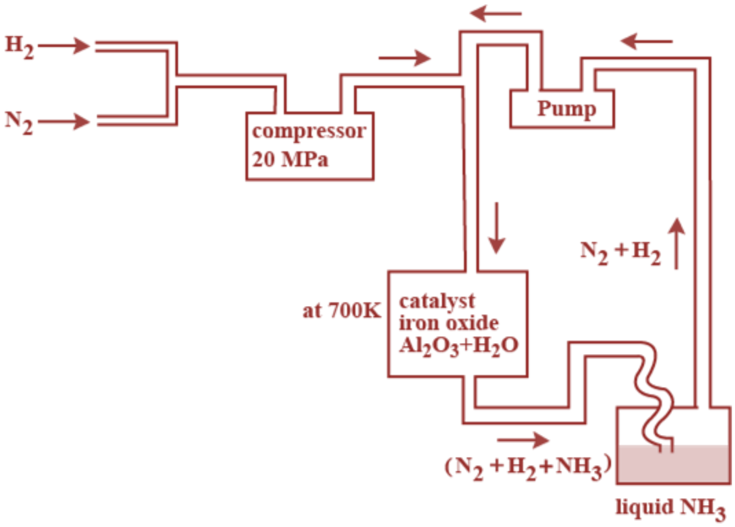


Fig.21.7:The Haber process for the manufacture of ammonia

Properties

Ammonia is a colourless and pungent smelling gas. It is readily liquified at a pressure of about nine atmospheres at ordinary temperatures.The liquid boils at 239.6K and freezes at 96K. Liquid ammonia resembles water in being highly associated because of its polar nature and strong hydrogen bonding.

Ammonia is extremely soluble in water. The hydrated ammonia molecule, $NH_3.H_2O$, is loosely called ammonium hydroxide, NH_4OH, which is a weak base, the ionization reaction being

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$

The undissociated molecule, NH_4OH, is essentially a non-existent entity. It can only exist as NH_4^+ and OH^- ions.

Chemical reactions

(i) Action of heat: When heated above 500°C it begins to decompose into its elements. The decomposition is accelerated by metallic catalysts

$$2NH_3 \rightarrow N_2 + 3H_2$$

(ii) With oxygen: Ammonia does not burn in air but freely burns in pure oxygen with a yellowish flame giving nitrogen and steam.

$$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O$$

In the presence of a catalyst, e.g. hot platinum, ammonia burns in air to give nitric oxide

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

(iii) As a reducing agent. If ammonia is passed over those heated metallic oxides which are reducible by hydrogen, e.g. CuO, PbO, etc., it is oxidised to nitrogen and water:

$$3PbO + 2NH_3 \rightarrow 3Pb + N_2 + 3H_2O$$

(iv) With acids. It is easily absorbed by acids to form ammonium salts, e.g.:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The reaction can occur even if the acid is a gas, e.g.:

$$NH_3 + HCl \rightarrow NH_4Cl \,(\text{i.e. } NH_4^+Cl^-)$$

(v) With chlorine: Ammonia reacts with chlorine, the products varying according to conditions:

$$\left.\begin{aligned} &2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl \\ &6HCl + 6NH_3 \rightarrow 6NH_4Cl \end{aligned}\right\} \text{(with excess of ammonia)} \qquad \ldots (1)$$

$$\left.\begin{aligned} &NH_3 + 3Cl_2 \rightarrow \underset{\text{nitrogen trichloride}}{NCl_3} + 3HCl \\ &HCl + NH_3 \rightarrow NH_4Cl \end{aligned}\right\} \begin{array}{l}\text{(when chlorine is in}\\ \text{large excess)}\end{array} \qquad \ldots (2)$$

(vi) With metal salts: With some metal salts, aqueous ammonia reacts to form metal hydroxides which are precipitated.

For example, ammonia solution precipitates copper (II) hydroxide when treated with a copper salt,

$$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$$

In excess of ammonia, the precipitate of Cu(OH)2 dissolves to form tetra amrnine complex

$$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_3 \rightarrow \underset{\text{tetraammine copper (II) sulphate}}{[Cu(NH_3)_4]^{2+}\,SO_4^{2-}} + 2H_2O$$

Similar complexes are formed with many metallic salts and complex ions such as $[Ag(NH_3)_2]^+$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$

Uses: Ammonia is used for a number of purposes, some important uses are:

- In the manufacture of ammonium sulphate for use as a fertilizer.
- In the manufacture of nitric acid (Ostwald process)
- In the manufacture of sodium carbonate by Solvay process.
- Liquid ammonia is used in refrigerators.
- Ammonia solution is used as a domestic cleaner: as a grease remover and in laundry

Structure: Ammonia molecule is trigonal pyramid with the nitrogen at the apex. The nitrogen atom is sp^3 hybridized in which a lone pair of electrons occupies one of the tetrahedral positions. The angle H-N-H becomes 107° instead of 109° (in CH_4) due to lone pair - bond pair repulsion (Fig.21.8).

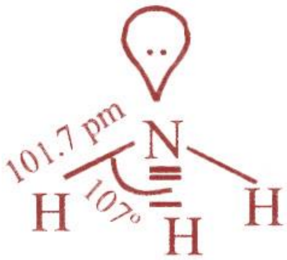


Fig.21.8: *Structure of ammonia*

21.3.2 Oxoacids of Nitrogen

There are several oxoacids of nitrogen such as nitrous acid, HNO_2, hyponitrous acid, $H_2N_2O_2$ and nitric acid, HNO_3. of this nitric acid is the most important and will be considered here in detail.

Nitric Acid, HNO_3

Preparation

In the laboratory, nitric acid can be prepared by heating $NaNO_3$ or KNO_3 with concentrated H_2SO_4 in a glass retort and condensing the vapours corning out of the retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

In industry it is manufactured by the catalytic oxidation of ammonia which involves the following reactions (Ostwald process):

$$4NH_3 + 5O_2 \xrightarrow[Pt]{1173K} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The aqueous nitric acid can be concentrated by distillation followed by dehydration with conc. H_2SO_4.

Properties

Physical: It is a colourless liquid of density $1.50gcm^{-3}$ at 248K. The acid is freely miscible with water forming a constant boiling mixture containing 98% of acid, b.p. 393K.

Chemical:

a) In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions.

$$H_2O + HNO_3 \longrightarrow H_3O^+ + NO_3^-$$

b) It is neutralised by appropriate alkalies to yield nitrates.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

c) On heating it gives NO2

$$4HNO_3 \longrightarrow 4NO_2 + O_2 + 2H_2O$$

d) It is a good oxidizing agent and oxidizes non metals, metals and organic compounds, some examples of which are given below:

$$\text{(i)}\quad C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$$

$$\text{(ii)}\quad S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$\text{(iii)}\quad P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

$$\text{(iv)}\quad I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$\text{(v)}\quad Cu + \underset{\text{cone.}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Cu + \underset{\text{dil.}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$\text{(vi)}\quad 4Zn + \underset{\text{dil.}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$\text{(vii)}\quad Mg + \underset{\text{dil.}}{2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2$$

(viii) Aluminium loses its normal reactivity i.e. becomes passive after being dipped in conc.HNO_3. This is due to the formation of a thin protective layer of aluminium oxide on its surface which prevents further action.

$$\text{(ix)}\quad \underset{\textbf{glycerine}}{C_3H_5(OH)_3} + 3HNO_3 \xrightarrow{\text{conc. } H_2SO_4} \underset{\textbf{trinitroglycerine (explosive)}}{C_3H_5(NO_2)_3} + 3H_2O$$

glycerine trinitroglycerine(explosive)

Structure: In the gaseous state HNO_3 exists as a planar molecule with the structure: (Fig.21.9)

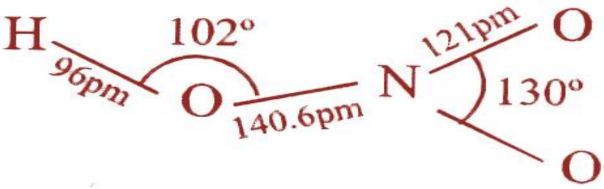


Fig . 21.9: Structure of nitricacid molecule

Uses: Nitric acid is used in the manufacture of nitrates which are used as fertilizers, and explosives, trinitroglycerine and trinitrotoluene(TNT)

- It is used as an oxidizing agent in laboratory, *e.g.* Fe(II) gets oxidized to Fe(III)
- Conc. HNO_3 is a constituent of aquaregia (HNO_3 : HCl = 1:3)
- HNO_3 (100%) is a constituent of rocket propellant

IntextQuestions21.3

1. Does 'NH_4OH' exist as a molecule?

....

2. What is the bond angle in NH_3 molecule?

....

3. What is the state of hybridization of N in NH_3?

....

4. Name three elements which are essential to plant growth.

....

What You Have Learnt

- Method of preparation of boric acid. The acidic nature and structure of boric acid.
- Method of preparation and uses of borax.

- Methods of preparation and uses of boron trifluoride and diborane.
- The Lewis character and use of boron trifluoride.
- Preparation of aluminium trichloride and its structure
- Method of preparation of alums and uses
- The comparison of diamond and graphite
- The structure and properties of carbon monoxide, carbon dioxide and silicon dioxide.
- Comparison of the hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride.
- Preparation and uses of silicon carbide (carborundum)
- The methods of preparation, properties and uses of ammonia and nitric acid.

Terminal Questions

1. Why is boric acid not a protonic acid?
2. Discuss the structure of boric acid.
3. Draw the Lewis structure of CO and CO2 molecules.
4. Why does BF3 act as a Lewis acid?
5. What is catenation? Why does carbon show catenation but silicon does not?
6. Compare the structure of CO2 and SiO2.
7. Describe briefly the Haber process for the manufacture of ammonia.
8. Why is graphite a conductor of electricity but diamond is not?

Answers to Intext Questions

21.1

1. (i) $B(OH)_3$ (ii) $Na_2B_4O_7.10H_2O$

2. $4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$

3. $NM(SO_4)_2.12H_2O$

Where N = mono valent large cation like K^+ or NH^+ and

M = tri valent cation like Al^{3+}, Fe^{3+}, Cr^{3+}

4. Al_2Cl_6

5. **(i)** as a flux, for glazing pottery and tiles: in the manufacture of optical and borosilicate glasses. **(ii)** as an antiseptic, as a food preservative, for making enamels **(iii)** as a catalyst in Friedel-Crafts reaction.

21.2

1. Hardness and conducting nature.

Diamond: hard, non conducting;

Graphite: soft, conducting.

2. sp^3 in diamond and sp^2 in graphite.

3. Covalent

4. sp^3

5. $SiCl_4$, as silicon can accept electron pair in its d-orbitals from water molecule.

6. CO_2

7. $SiO_2 + 2F_2 \longrightarrow SiF_4 + O2$

21.3

1. No. Nitrogen cannot increase its covalency beyond 4.
2. 107°. 3. sp3 4. N, P and K

21.1.5.a Aluminium: Uses and Reactions

- The important minerals of Aluminium are Bauxite ($Al_2O_3.2H_2O$) Cryolite (Na_3AlF_6).
- Bauxite is the most important mineral used for the extraction of Aluminium.
- Bauxite contains impurities such as Fe_2O_3 (red Bauxite) and SiO_2 (White Bauxite)

Reactions of Al with acids and alkalies:

Al is an amphoteric metal. It reacts with acids and alkalies.

I. Reaction with acids:

Dilute (or) concentrated acids dissolve Al and gives H

$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3H_2\uparrow$$

$$2\,Al + 3H_2SO_4 \longrightarrow Al_2\,(SO_4)_3 + 3H_2\uparrow$$

Very dilute HNO_3 is reduced to NH_4NO_3 by Al

$$8\,Al + 30\,HNO_3 \longrightarrow 8\,Al\,(NO_3)_3 + 3\,NH_4\,NO_3 + 9\,H_2O$$

Conc. HNO_3 makes Al passive due to the formation of a thin film of oxide layer on the metal surface.

II Reactions with alkalies:

Al reacts with alkalies and gives aluminate (or) meta aluminate and liberates H_2

$$2\,Al + 2\,NaOH + 2\,H_2O \longrightarrow 2\,NaAlO_2 + 3\,H_2\uparrow$$

$$2\,Al + 6\,NaOH \longrightarrow 2\,Na_3AlO_3 + 3\,H_2\uparrow$$

Uses:

1. It is used for making electrical cables.
2. It is used in making trays, picture frames etc.
3. It is used as a deoxidizer in metallurgies.
4. The mixture of Al powder and Ammonium nitrate is called ammonal. It is used in explosives.

Alloys of aluminium:

S.No.	Alloy	Composition		Use
1.	Magnalium	1-15% Mg	85-99% Al	Cheap balances, Utensils in the laboratory
2.	Aluminiumbronze	10-12% **Al**	88-90% **Cu**	Cheap Jewellery, Photo Frames, Making coins.
3.	Duralumin	95% **Al** 0.5% **Mg**	4% **Cu** 0.5% **Mn**	Making airship
4.	Y-alloy	92.5% **Al** 2% **Ni**	4% **Cu** 1.5% **Mg**	Making parts of aeroplanes

21.1.5.a Intext Questions:

1. Write any two uses of Aluminium.
2. Write any two alloys of Aluminium.

21.1.5.a Answers Intext Questions:

1. i) It is used in making trays and photo frames. ii) It is used for making electrical cables.
2. Magnalium, Y-alloy

21.2.1.a Similarities between Carbon and Silicon:

1. Both carbon and silicon have similar outer shell configuration i.e. ns2np2
2. Valency of the two elements is four.
3. Both are non-metals. Their oxides are acidic in nature.
4. Both C and Si exhibit catenation property.
5. Both exhibit allotropy.

Both C and Si forms similar type of compounds.

S. No.	Compound	C-Compound	Si-Compound
1.	Dioxides	CO	SiO
2	Acids	H_2CO_3 ; (COOH)2	H_2SiO_3 ; (SiOOH)2
3.	Hydrides	CH_4 ; C_2H_6	SiH_4 ; Si_2H_6
4.	Chlorides	CCl_4 ; $CHCl_3$	$SiCl_4$; $SiHCl_3$

Table 21.2.1.a

Differences between C and Si:

1. C is an important element in plants and animals where as silicon is important in minerals.
2. The melting and boiling points of carbon are very high when compared to silicon.
3. The allotrope of carbon (graphite) is a good conductor of electricity while silicon is semi conductor.
4. Carbon forms large number of compounds due to its high catenation power where as silicon exhibits less catenation and forms only a limited number of compounds.
5. Both carbon and silicon forms tetrachlorides which are covalent in nature. CCl_4 is not hydrolyzed but $SiCl_4$ can be easily hydrolyzed.

Uses of oxides of carbon:

The uses of carbon oxides like carbonmonoxide (CO), Carbonoxide (CO_2) and carbon Suboxide(C_3O_2) are

Uses of CO and CO_2

S. No.	Carbonmonoxide	Carbondioxide
1.	CO is an important component fuels like producer gas, Water gas and coal gas.	Solid CO_2 is called dry ice. It is used as a refrigerant.
2.	CO is a good reducing agent.	It is used as a coolant in the lab.
3.	CO is used as a good ligand ligand in metallurgy of Ni by Mond's process.	It is used in the Manufacture of urea and in neutralising alkalies.
4.		It is used as fire extinguisher.

C_2O_3 reacts with H_2O and gives malonic acid, $CH_2(COOH)_2$

Important compounds of silicon:

Silicon Dioxide:

It is known to exist in crystalline and amorphous forms.

Eg:- Quartz, tri dymite and crystobalite are crystalline varieties.

Extremely pure silica is called quartz or Rock crystal. When mixed with amorphous silica it is known as flint. Amorphous form is present in plants and animals. Silica is prepared in the laboratory as follows.

1. By burning silicon in air or oxygen.

$$Si + O_2 \longrightarrow SiO_2$$

Properties:

1. SiO_2 does not dissolve in water.
2. It does not react with HCl, HBr and HI. It reacts with HF to form silicon tetra fluoride.

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2H_2O$$

3. It is an acidic oxide. It reacts with alkalies to form silicates.

$$SiO_2 + 2KOH \longrightarrow K_2SiO_3 + H_2O$$

4. It reacts with metal oxides at high temperature to form metal silicates.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

$$SiO_2 + Na_2O \longrightarrow Na_2SiO_3$$

5. When silica is heated with coke in an electric furnace to form silicon carbide. It is called carborundum.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

6. When silica is heated to 1600^0C it changes to quartz glass. It is used in light experiments.

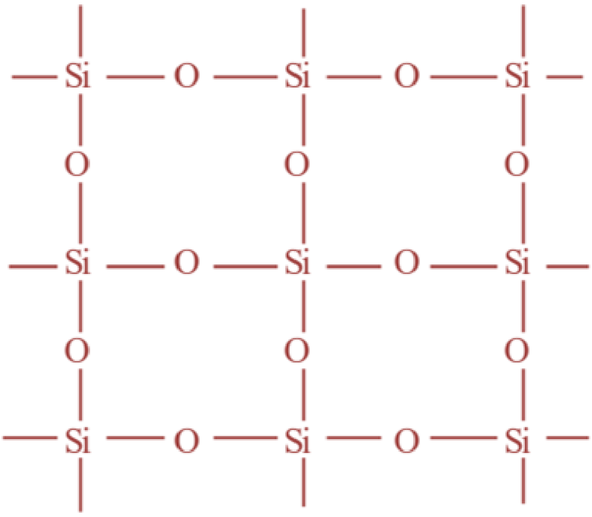
Uses:

1. Silica, as sand is used in construction of buildings.
2. SiO_2 is an acid flux in metallurgies.
3. Colored quartz is used as gems.
4. Transparent quartz for lenses and optical instruments.

Structure:

It has three dimensional structure. Each silicon atom is linked to four oxygen atoms by covalent bonds and they are arranged tetrahedrally around silicon.

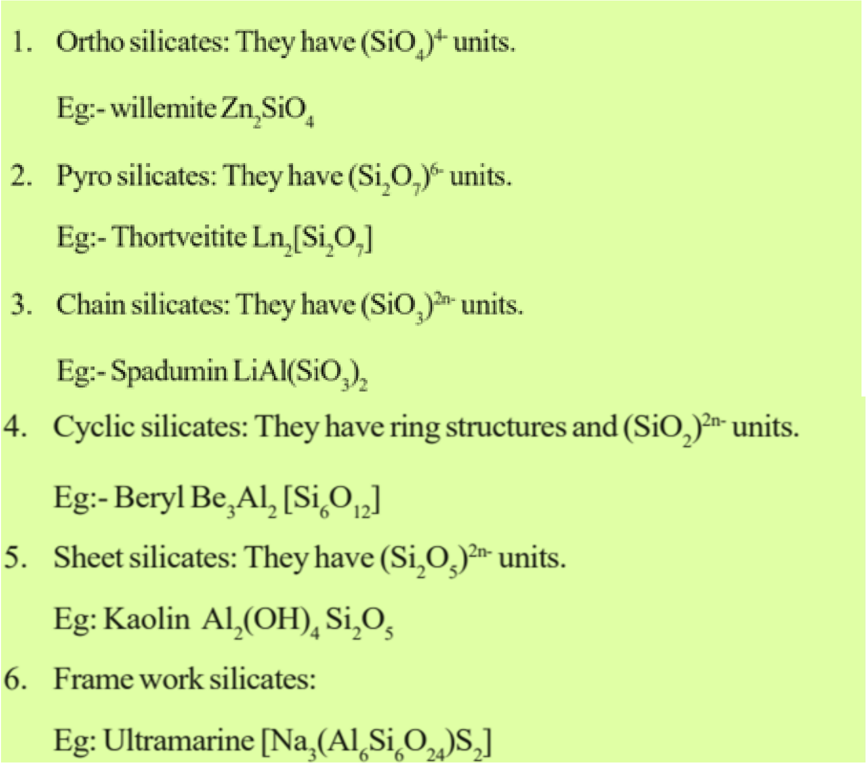
It exists in the solid state due to its giant molecular structure.



Silicates:

Many building materials are silicates.

For eg:- Granites, slates, bricks, cement, ceramics and glass. The Si-O bonds in silicates are very strong. Silicates are divided into six types.



1. Ortho silicates: They have $(SiO_4)^{4-}$ units.

   Eg:- willemite Zn_2SiO_4

2. Pyro silicates: They have $(Si_2O_7)^{6-}$ units.

   Eg:- Thortveitite $Ln_2[Si_2O_7]$

3. Chain silicates: They have $(SiO_3)^{2n-}$ units.

   Eg:- Spadumin $LiAl(SiO_3)_2$

4. Cyclic silicates: They have ring structures and $(SiO_2)^{2n-}$ units.

   Eg:- Beryl $Be_3Al_2\,[Si_6O_{12}]$

5. Sheet silicates: They have $(Si_2O_5)^{2n-}$ units.

   Eg: Kaolin $Al_2(OH)_4\,Si_2O_5$

6. Frame work silicates:

   Eg: Ultramarine $[Na_3(Al_6Si_6O_{24})S_2]$

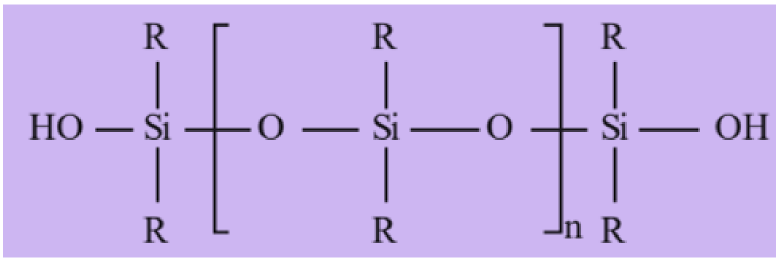
Uses:

1. Clay minerals are used for absorbing chemicals.
2. Mica are used for electrical insulation.
3. Variety of silicates are used for ornaments and Jewellery.
4. Cement, ceramics and glass are all used to man.

5. Asbestos is used for thermal insulation.

Silicones: Poly organo silicon compounds are called silicones. They may belong chain linear compounds (or) cyclic and branched chain compounds. They are prepared from carbon silicon halides.

$$2R\text{-}Cl + Si \xrightarrow[300^0C]{Cu} R_2SiCl_2$$



$$HO-\overset{R}{\underset{R}{Si}}-\left[O-\overset{R}{\underset{R}{Si}}-O\right]_n-\overset{R}{\underset{R}{Si}}-OH$$

Uses:

1. Rubbers preparation
2. To prepare water proof clothes and papers
3. To prepare grease, lubricants in aeroplanes
4. They are used as insulator for electrical motors.
5. They are used in paints and enamels because they can with stand high temperatures.

Zeolites:

Replacement of one or two silicon atoms in $[Si_2O_8]$ form zeolites. They are three dimensional structures without metal ions. They act as ion exchangers and as molecular sieves. H_2O molecules, NH_3, CO_2 and ethanol can be trapped in the zeolite cavities of different sizes. They trap Ca^{2+}, Mg^{+2} ions from hard water and replace them by Na^+ ions to give soft water.

21.3.3.a Oxyacids of Phosphorous

After reading the lesson, you will be able to know

* The preparation and structures of oxyacids of Phosphorous.

Phosphorous forms two series of oxoacids, phosphorous series of acids and Phosphoric series acids. The suffixes '-ous' and '-ic' refer to the lower (+I or +II) oxidation states and higher (+V) oxidation state) oxidation states of the principal element Phosphorous.

Phosphorous series of acids:

The Phosphorous series of acid are less commonly known. All these acids contain P-H bonds and Phosphorous is present in +III oxidation state.

Hypo Phosphorous acid (H_3PO_2)

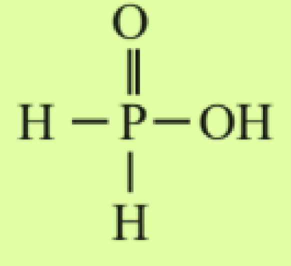
It is prepared in the laboratory by the interaction of yellow or white phosphorous and dilute solution of $Ba(OH)_2$ on heating.

$$6\,H_2O + 2P_4 + 3Ba(OH)_2 \longrightarrow \underset{\text{Barium hypo phosphoric}}{3\,Ba\,(H_2PO_2)_2} + \underset{\text{Phosphine}}{2\,PH_3\uparrow}$$

From this barium salt, H_3PO_2 is obtained.

Hypo phosphorous acid H_3PO_2 is a monobasic acid very strong reducing agent and it is oxidized to H_3PO_3

Structure of hypophosphorous acid is represented is follow:



H_3PO_2 is monobasic acid

Meta phosphorous acid$(HPO)_2$

Metaphosphorous acid is veryless known. Its basicity is one. Its structure is not known. Normally this exists as cyclic compound due to polymerization. The structure of its monomer is drawn by analogy with meta phosphoric acid HPO_3.

HO–P=O HPO_2

Ortho phosphorous acid(H_3PO_3)

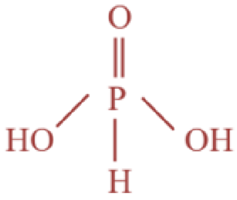
Ortho phosphorous acid is prepared by dissolving phosphorous (III) oxide P_4O_6 in cold H_2O

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3 \text{ or } P(OH)_3$$

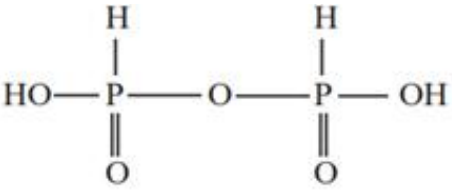
a. H_3PO_3 contains two acidic hydrogens. i.e. its basicity is two. It gives two series of salts. They are primary phosphates (containing $H_2PO_3^-$) or dihydrogen phoshates. Secondary phosphates (containing HPO_3^{-2}) or mono hydrogen phosphites.

b. Phosphorous acid and ortho phosphates are very strong reducing agents in basic solutions. Hg^{+2}, Ag^+ or Cu^{+2} salts are reduced to Hg, Ag or Cu respectively. It is oxidized to H_3PO_4.

Structure of ortho phosphorous acid



Pyrophoshorous acid is also known as $H_4P_2O_5$
Its structure can be written as



Various acids series of acids

a. Ortho phosphoric acid H_3PO_4
b. Meta phosphoric acid HPO_3
c. Pyro phosphoric acid $H_4P_2O_7$
d. Hypo phosphoric acid $H_4P_2O_6$
e. Peroxy phosphoric acid H_3PO_5

in all these acids phosphorous is tetrahedrally surrounded and is four coordinate wherever possible.

a. Ortho phosphoric acid H_3PO_4

1. It is prepared by dissolving P_4O_{10} in water. $P_4O_{10} + 6H_2O \longrightarrow 4\,H_3PO_4$
2. It is weak tribasic acid and has no oxidizing or reducing properties. It gives three series of salts. These are dihydrogen phosphates (example NaH_2PO_4); mono hydrogen phosphates (example Na_2HPO_4) and normal phosphates (example Na_3PO_4)
3. The solid acid absorbs water and forms a colorless, syrupy liquid (syrupy phosphoric acid)
4. On heating, it loses water in a step wise order and forms Pyro phosphoric acid

$$H_3PO_4 \xrightarrow[-H_2O]{520K} \underset{\text{Pyro Phosporic acid}}{H_4P_2O_7} \xrightarrow[-H_2O]{870K} \underset{\text{meta phosphoric acid}}{HPO_3}$$

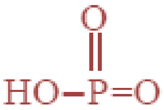
And then Meta phosphoric acid.

b. Metaphosphoric acid(HPO_3)

It is formed by heating pyrophosphoric acid or ortho phosphoric acid to 870K. It is a glassy transparent solid. Hence it is called as glacial phosphoric acid.

It is a mono basic acid. Its salts are known as metaphosphates. There is no evidence for the existence of free monophosphate ions (PO_3^-) or of the dimetaphosphate $(P_2O_6)_2^-$ or $(PO_3)_2$

But tri and tetra metaphosphates form a family of ring compounds. The structure of metaphosphoric acid is represented as



$$HO-\overset{\overset{\displaystyle O}{\|}}{P}=O$$

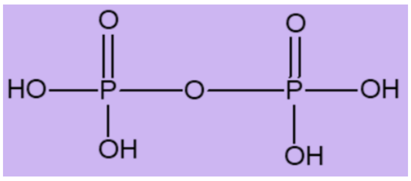
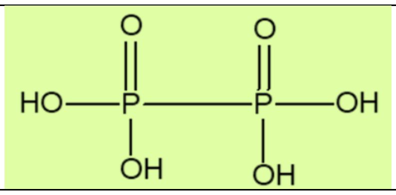
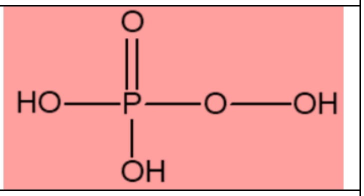
c. Pyrophosphoric acid ($H_4P_2O_7$)

Pyrophosphoric acid is formed by heating an equimolecular mixing of the ortho and meta phosphoric acids at 373K

It is tetra basic acid but gives only two series of salts.

Example: $Na_2P_2O_7$ $Na_4P_2O_7$

Pyrophosphates give positive answer to the molybdate test i.e. they give ammoniumphosphomolybdate $(NH_4)_3PO_{12}(MoO_3)$.

The structure are written as:		
		
Pyrophosphoric acid $H_4P_2O_7$	Hypo phosphoric acid $H_4P_2O_6$	Peroxy phosphoric acid H_3PO_5

Some important characteristics of oxyacids of Phosphorous

i. In all these oxoacids, phosphorous is tetrahedrally surrounded by atoms.
ii. In all these oxyacids, at least one -OH group is linked to the phosphorous atoms. The hydrogen atoms in –OH groups are ionizable and are responsible for the acidic nature.
iii. The phosphorous series of acids may have P - H bonds in addition to P-OH bonds.

iv. The P - H bonds are responsible for the reducing properties of the acids.
v. Phosphoric series of acids do not have P - H bonds

21.3.3.a Intext questions:

1. What are the acids in phosphorous series of acids?

....

2. Which of the acids of phosphorous does not show monomeric state but cyclic structure?

....

Terminal exercise:

1. Write an essay on the preparation and properties of
    - a. Ortho phosphoric acid   b. Meta phosphoric acid.
    - c. pyro phosphoric acid   d. Hypo phosphoric acid
2. Write at least one method of preparation for each of the phosphorous series of acids and write their corresponding structures.
3. Write a method of preparation for each and write neatly the structures of any two of the following acids.
    - a. Hypo phosphorous acid   b. Hypo phosphoric acid
    - c. Meta phosphorous acid   d. Meta phosphoric acid

21.3.3.a Answers to Intext question:

1. Hypophosphorous acid, Pyrophosphorous acid and metaphosphorous acid
2. Metaphosphorous acid

What you have learnt:

1. Preparation, properties and structure of acids in phosphorous acid series
2. Preparation, properties and structure of acids in phosphoric acid series.

Chapter 22

p-BLOCK ELEMENTS AND THEIR COMPOUNDS - II

You have already studied the chemistry of the elements of Groups 13, 14 and 15. In this lesson we shall deal with the chemistry of the elements of Groups 16, 17 and 18.

Objectives

After reading this lesson you will be able to:

- classify oxides into acidic, basic and amphoteric types;
- describe the manufacture of sulphuric acid;
- recall the preparation, properties and uses of ozone;
- recall the characteristics of hydrogen halides (HF, HCl);
- list the oxides and oxoacids of chlorine;
- compare the acidic behaviour of oxoacids of chlorine;
- write the general molecular formulae of interhalogen compounds;
- discuss the structures of interhalogen compounds;
- list a few chlorofluoro carbons and explain their uses and their effect on environment;
- explain the unreactive nature of noble gases;
- recall the preparation of xenon fluorides and oxides, and
- illustrate the structures of XeF_2, XeF_4, XeF_6, XeO_3 and XeO_4.

22.1 Oxygen and Sulphur

Oxygen and sulphur are the first two members of the 16th group of the periodic table. In this section you will learn about some compounds of oxygen and sulphur including environmentally important ozone and industrially important sulphuric acid.

22.1.1. Classification of Oxides

The binary compounds of oxygen with other elements (metals or non-metals) are called oxides. An understanding of the nature of an oxide provides a clue to the nature of the element which forms the oxide. Depending upon the acid-base behaviour of the oxides, they can be classified into the following categories.

1. Acidic oxides **2. Basic oxides** **3. Amphoteric oxides** **4. Neutral oxides**

1. Acidic Oxides: Acidic oxides are generally formed by non-metallic elements and some metals in higher oxidation states. Examples of some acidic oxides are CO_2, SO_2, N_2O_5, P_4O_{14}, C1$_2$O$_7$, Mn_2O_7, etc. These oxides combine with water to form acids where as with alkalies they form salt and water.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

However, certain acidic oxides do not form acids on reacting with water. But they react with alkalies to form salt and water, e.g., SiO_2

$$SiO_2 + 2\,NaOH \longrightarrow \underset{\textbf{Sodium silicate}}{Na_2SiO_3} + H_2O$$

2. Basic oxides: Metals combine with oxygen to form basic oxides. The basic oxides react with acids to form salt and water.

$$FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

The oxides of the metals of Groups1 and 2 react with water to form hydroxides known as **alkalies**.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

3. Amphoteric oxides: Almost all metallic oxides are basic oxides. But some metallic oxides show the characteristics of both acidic as well as basic oxides, i.e., they react with both acids as well as bases to form salt and water. Such oxides are called *amphotericoxides.* The oxides of zinc, aluminium, lead and tin are amphoteric in nature.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2NaOH \longrightarrow \underset{\textbf{Sodium zincate}}{Na_2ZnO_2} + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow \underset{\textbf{Sodium aluminate}}{2NaAlO_2} + H_2O$$

4. Neutral oxides: These oxides are neither acidic nor basic. Examples are carbon monoxide, (CO), nitric oxide (NO), nitrous oxide (N_2O), etc.

Intext Questions 22.1

1. Give one example each of basic oxide, acidic oxide and amphoteric oxide.

....

2. Classify the following oxides in to acidic, basic or amphoteric oxides: K_2O, SiO_2, SO_2, FeO, Al_2O_3, ZnO, CrO_3.

....

3. Give chemical equations to illustrate the amphoteric behavior of ZnO.

....

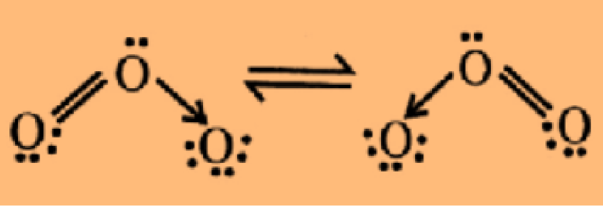
4. Name the compound formed when the oxide of an element of Group1or 2 reacts with acid?

....

22.2 Ozone

Ozone is an allotrope of oxygen. You must have learnt through the media that ozone layer depletion in the upper atmosphere is causing a great environmental concern. We will now study the preparation, properties, importance and uses of ozone.

Structure of Ozone: Ozone forms a V-shaped molecule. The central O atom uses sp^2 hybrid orbitals for bonding. The structure of ozone can be explained as a resonance hybrid of the following two structures, (oxygen – oxygen bond length 128 pm and bond angle 117°)



Properties of Ozone

(a) **Physical:** Ozone is a pale blue gas which turns into blue liquid at 161K. At 80K it freezes to a violet black solid. It is ten times as soluble in water as oxygen.

(b) **Chemical:** The chief characteristic of ozone is that it is unstable and that it gives energy loaded nascent oxygen. Its reactions are closely paralleled to the reactions of hydrogen peroxide.

1. Catalytic decomposition: Ozone in aqueous solution decomposes on standing. Above 373K ozone decomposes very rapidly. Even at ordinary temperature it decomposes in the presence of chlorine, bromine, nitrogen pentoxide and other acidic oxides and oxides of transition metals.

$$2O_3 \rightarrow 3O_2$$

***2. Oxidizing properties*:** In the presence of reducing agents ozone furnishes active atom of oxygen according to the equation.

$$O_3 \rightarrow O_2 + O$$

In most of the reactions, oxygen gas is liberated as the reduction product from ozone.

(i) It oxidizes black lead sulphide to white lead sulphate.

$$4O_3 + PbS \rightarrow PbSO_4 + 4O_2$$

(ii) Ozone oxidizes acidified ferrous sulphate to ferric sulphate

$$O_3 + 2FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2$$

(iii) Ozone oxidizes moist sulphur to sulphuric acid and phosphorus to phosphoric acid.

$$3O_3 + S + H_2O \rightarrow H_2SO_4 + 3O_2$$

$$5O_3 + 2P + 3H_2O \rightarrow 2H_3PO_4 + 5O_2$$

(iv) *Ozone tails mercury:* Normally mercury does not stick to glass but if exposed to ozone it loses its convex meniscus and leaves a ‘tail’ or trail of minute droplets on a glass surface. This is supposed to be due to the formation of stray molecules of mercurous oxide which affect the surface only.

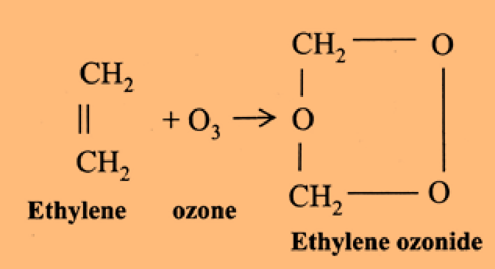
$$O_3 + 2Hg \rightarrow Hg_2O + O_2$$

The ‘tailing’ effect can be removed by washing with dilute acid.

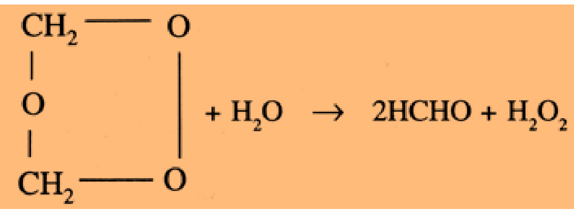
(v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.

$$O_3 + 3SnCl_2 + 6HCl \rightarrow 3SnCl_4 + 3H_2O$$

3. *Ozonides:* All unsaturated organic compounds combine with ozone to form unstable compounds called ozonides, e.g.



The ozonides are hydrolysed by water to give aldehydes or ketones or both.



This technique is called *ozonolysis* and is widely used to locate the position of double bond in organic compounds.

Uses of Ozone

Some of its applications are given below:

1. *Water purification:* Small ozone-air plants function as part of the water purification setup. Ozone is a powerful germicide and it can purify a water spray effectively; it does not produce the unwanted by-products that other sterilizing agents do.

2. *Air purification:* Ozone is also used to purify air in tunnels, wells and crowded subways and cinema halls.

3. *Refining oils:* Vegetable oil and ghee go rancid when stored for a long time. This is caused by bacterial growth in the small water content present in them. If ozone is bubbled through oil, all such growing organisms are destroyed and we get purified oil.

4. *Dry bleach:* Ozone is also used to bleach waxes, flour, sugar and starch. Hydrogen peroxide, which produces water and other agents which act only in solution, cannot be used in these cases.

5. *In Industry and in the Laboratory:* It is widely used in certain organic preparation. Its use in ozonolysis has already been mentioned.

Intext Questions 22.2

1. What are ozonides? What happens when an ozonide is hydrolysed?

....

2. Write the reactions which occur when ozone reacts with

(i) ferrous sulphate (ii) stannous chloride

....

3. Which is more soluble in water, oxygen or ozone?

....

4. Draw the structure of ozone molecule, O_3.

....

5. What is meant by "tailing of mercury"? How is it removed?

....

22.3 Sulphuric Acid

The most important compound of sulphur is sulphuric acid. Sulphuric acid or the 'oil of Vitriol' was known to the alchemists and their predecessors. Before the coming of Chamber process in the last century, it was obtained by heating hydrated sulphates.

Manufacture: The two main processes used for the manufacture of sulphuric acid are:

(1) Lead Chamber process **(2)** the Contact process.

Now a days sulphuric acid is mostly manufactured by Contact process.

Manufacture of sulphuric acid by Contact Process involves the following steps:

(i) Sulphur dioxide gas is produced by burning sulphur in air or by roasting of pyrites.

$$S + O \rightarrow SO_2$$

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(ii) Sulphur dioxide produced is then freed from dust and other impurities such as arsenic compounds.

(iii) The purified sulphurdioxide in then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to720K.

$$2SO_2 + O_2 \xrightarrow[720K]{V_2O_5} 2SO_3$$

The plant is operated at a pressure of 2 atmospheres and temperature of 720K.

(iv) The sulphur trioxide gas in then absorbed in conc.H_2SO_4 to form oleum ($H_2S_2O_7$). If SO_3 is directly dissolved in water, a highly corrosive mist of sulphuric acid is formed.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

(v) Oleum is then diluted with water to obtain sulphuric acid of desired strength.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulphuric acid obtained from the contact process is about 96-98% pure.

Properties of Sulphuric acid

(i) Physical properties: Pure sulphuric acid is a thick colourless oily liquid. Its melting point is 283.5K. Concentrated sulphuric acid dissolves in water with the liberation of a large amount of heat. While preparing dilute H2SO4, water must not be added to conc.H2SO4. Dilute sulphuric acid is prepared by adding Conc.H2SO4 slowly and with constant stirring to water. If water is added to the acid, the heat produced is so large that it could throw out drops of sulphuric acid and burn you.

Chemical properties: The most important properties of sulphuric acid are its oxidizing and dehydrating properties.

(i) Oxidizing properties: Hot concentrated sulphuric acid acts as an oxidizing agent and oxidizes metals, non-metals and compounds.

Oxidation of metals

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

$$Zn + 2H_2SO_4 \longrightarrow ZnSO_4 + 2H_2$$

Oxidation of non-metals

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

Oxidation of compounds

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

$$8HI + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$

$$3H_2S + H_2SO_4 \longrightarrow 4S + 4H_2O$$

Dehydrating properties: Conc. H_2SO_4 is a strong dehydrating agent. It removes water of crystallization from copper sulphate (which is blue in colour) and turns it to white colour.

$$\underset{\textbf{blue}}{CuSO_4.5H_2O} \xrightarrow[-5H_2O]{\text{conc. } H_2SO_4} \underset{\textbf{white}}{CuSO_4}$$

It also removes water from carbohydrates leaving behind, black mass of carbon.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

Uses of Sulphuric Acid

Sulphuric acid is known as the king of chemicals. It is practically used in every industry. It is used in the manufacture of fertilizers, paints and pigments, detergents, plastics and fibres, etc.

Intext Questions 22.3

1. Write a reaction to show the

(i) oxidizing property of sulphuric acid

(ii) dehydrating property of sulphuric acid

………

2. In the manufacture of sulphuric acid by Contact process, SO_3 is dissolved in conc.H_2SO_4 and not in water. Why?

………

3. Write the reaction that takes place in the presence of a catalyst in the contact process.

………

22.4 Fluorine and Chlorine

Fluorine and chlorine are the first two members of Group 17. Fluorine is the most electro negative element. In this section we shall briefly learn about fluorine and chlorine and study in some detail about the hydrogen halides, oxides and oxoacids of chlorine and interhalogen compounds.

Fluorine is extremely difficult to prepare owing to its highly reactive nature. It is the strongest chemical oxidizing agent hence cannot be prepared by oxidation of fluoride ions. It is prepared by the electrolysis of potassium hydrogen fluoride (KHF_2) in anhydrous hydrogen fluoride. Hydrogen fluoride undergoes electrolytic dissociation.

$$2HF \rightarrow F_2 + H_2$$

The fluorine obtained is contaminated with hydrogen fluoride which may be removed by passing the gas over solid NaF.

Fluorine is a pale-yellow gas which fumes in air.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2.$$

Fluorine is highly reactive. It combines with various metals and non-metals to form fluorides. With hydrogen halides it acts as an oxidizing agent, e.g.

$$2HX + F_2 \rightarrow 2HF + X_2 \ (X = Cl, Br \text{ or } I)$$

Fluorine is widely used in the preparation of fluorinated hydrocarbons which in turn find various uses in industry.

Chlorine is usually prepared by the oxidation of chlorides by strong oxidizing agents, such as MnO_2, $KMnO_4$.

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

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

On a large scale chlorine is obtained as a byproduct in the electrolysis of sodium chloride. Chlorine is a greenish yellow gas and can be liquefied by pressure alone at room temperature; it is quite reactive and forms chlorides of metals and nonmetals when reacted with them. It also oxidizes ammonia to nitrogen

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

Large quantities of chlorine are used in bleaching industry and in the manufacture of plastics, synthetic rubbers, antiseptics and insecticides.

22.4.1 Hydrogen Halides and Hydrohalic Acids

The hydrogen halides under consideration are HF, HCl, HBr and HI. The bond distance H-X increases with the size of halogen atom. The bond also becomes more covalent and less ionic. Since the bond length increases, the hydrogen halide in aqueous solution loses hydrogen ion more easily with increasing size of halogen, and the acid strength increases in the order **HF < HCl < HBr < HI**

The aqueous solutions of hydrogen halides are, in general, known as hydrohalic acids or simply halogen acids. (Hydrofluoric, hydrochloric, hydrobromic, and hydroiodic acids)

Preparation of Hydrogen Halides

Industrially HF is made by heating CaF_2 with strong H_2SO_4.

Hydrogen chloride is made by heating a mixture of NaCl and conc.H_2SO_4 at 423K

$$NaCl + H_2SO_4 \xrightarrow{423K} HCl + NaHSO_4$$

$$NaCl + NaHSO_4 \xrightarrow{823K} HCl + Na_2SO_4$$

High purity HCl is made by the direct combination of the elements (H_2 and Cl_2)

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Phosphoric acid is used to make HI

$$H_3PO_4 + NaI \longrightarrow HI + NaH_2PO_4$$

HBr is made by a similar method. Also we use red phosphorus for making HBr and HI

$$2P + 3Br_2 \longrightarrow 2PBr_3$$
$$PBr_3 + 6H_2O \longrightarrow 6HBr + 2H_3PO_3$$
$$2P + 3I_3 \longrightarrow 2PI_3$$
$$2PI_3 + 6H_2O \longrightarrow 6HI + 2H_3PO_3$$

Properties of the Halogen Halides

HF is a liquid at room temperature (b.p. 293K), where as HCl, HBr and HI are gases. The boiling point of HF is unexpectedly high as compared to HCl (189K), HBr (206K) and HI (238K). This is due to the formation of hydrogen bonds between the F atom of one molecule and the H atom of another molecule (Fig.22.2).

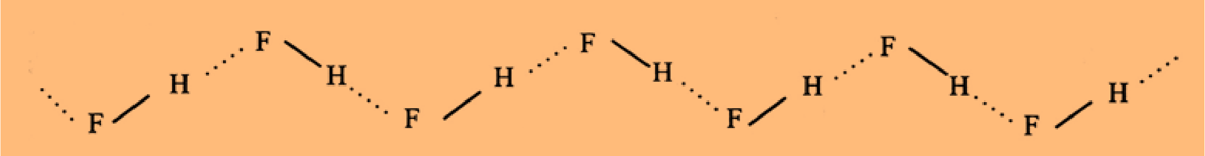


Fig.22.2: *Intermolecular Hydrogen bonding in HF molecule*

In the gaseous state, the hydrogen halides are essentially covalent. In the aqueous solutions they ionize to form ions but HF ionizes to a very small extent.

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

The bond dissociation energy of the hydrogen halides follow the order **HF>HCl>HBr>HI**. The stability of hydrogen halides to thermal decomposition therefore decreases in the order **HF>HCl>HBr>HI.** The acid strength of the acids increases in the order **HF<HCl<HBr<HI.** The aqueous solution known as hydrofluoric acid, hydrochloric acid, hydrobromicacid and hydroiodic acid possess the usual property of acids, e.g. they react with bases to form salts and water and with metals to form salts and hydrogen.

Uses of Hydrogen Halides

Hydrogen fluoride is used to prepare certain fluorides mainly fluorocarbons or freons. It is also used in etching glass and in removing and from casting. Hydrogen chloride is primarily used for preparing chlorides. Large quantities of hydrochloric acid are used in the manufacture of aniline dyes and for cleaning iron before galvanization. Hydrogen bromide and hydrogen iodide are used to prepare bromide and iodide salts. Hydrogen iodide is also used as a reducing agent in organic chemistry.

22.4.2 Oxides and Oxoacids of Halogens

There are several compounds containing halogen and oxygen. Oxygen is less electronegative than fluorine, hence the compounds of oxygen with fluorine are known as oxygen fluorides (e.g.OF_2). Other halogens are less electronegative than oxygen. Thus they are known as halogen oxides. Only the oxides of chlorine are important and they are described here.

Oxides of chlorine: The main oxides are listed below:

Chlorine monoxide - Cl_2O
Chlorine dioxide - ClO_2
Chlorine hexoxide - Cl_2O_6
Chlorine heptoxide - Cl_2O_7

Chlorine monoxide, Cl_2O, is prepared by passing chlorine over freshly prepared mercury (II) oxide

$$2\,Cl_2 + 2\,HgO \longrightarrow Cl_2O + HgO.\,HgCl_2$$

It is a pale yellow gas which decomposes violently on heating and dissolves in water forming Hypo chlorous acid.

$$Cl_2O + H_2O \longrightarrow 2HOCl$$

It is a powerful oxidizing agent.

Chlorinedioxide, ClO_2, is prepared by the action of concentrated sulphuric acid on potassium chlorate

$$KClO_3 + H_2SO_4 \longrightarrow \underset{\textbf{chloric acid}}{HClO_3} + KHSO_4$$

$$3HClO_3 \longrightarrow \underset{\textbf{perchloric acid}}{HClO_4} + 2ClO_2 + H_2O$$

It is an orange gas and explosive in nature.

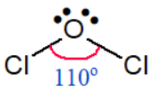
Chlorine hexoxide, Cl_2O_6, is prepared by the action of ozone on chlorine at low temperature. It is a red liquid and dissolves in alkalies producing chlorate and perchlorate

$$Cl_2O_6 + 2OH^- \longrightarrow ClO_3^- + ClO_4^- + H_2O$$

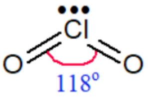
Chlorine heptoxide, Cl_2O_7 is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263K.

$$P_4O_{10} + 4HClO_4 \longrightarrow 4HPO_3 + 2Cl_2O_7$$

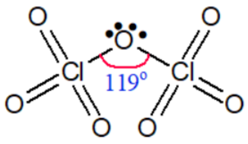
It is a colour less oil which explodes on heating or striking. The structures of chlorine oxides are as follows:



Cl_2O



ClO_2



Cl_2O_7

Oxoacids of chlorine

Chlorine forms four oxoacids. Those are:

Hypochlorous acid (HOCl), Chlorous acid (HOClO),
Chloric acid ($HOClO_2$) Perchloric acid ($HOClO_3$)

Hypochlorous acid, HOCl is known only in solution. It is prepared by shaking chlorine water.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

Its salt NaOCl is used as a bleaching agent.

Chlorous acid, HOClO is also known in solution, certain chlorite salts of alkali and alkaline earth metals are known in solid state, e.g., $NaClO_2.3H_2O$. The acid is prepared by the action of barium chlorite with sulphuric acid.

$$\underset{\textbf{barium chlorite}}{Ba\,(ClO_2)_2} + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$$

Chloric acid, $HOClO_2$ is prepared by the action of barium chlorate with sulphuric acid.

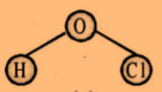
$$\underset{\textbf{barium chlorate}}{Ba\,(ClO_3)_2} + H_2SO_4 \longrightarrow HClO_2 + BaSO_4$$

Perchloric acid, $HOClO_3$, is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure.

$$\underset{\textbf{potassium perchlorate}}{2KClO_4} + H_2SO_4 \longrightarrow 2HClO_4 + K_2SO_4$$

It is a colourless oily liquid and combines vigorously with water forming hydronium perchlorate (**$H_3O^+\ ClO^-_4$**). It is one of the strong acids. It is also an oxidizing agent.The oxoacids of chlorine are listed in the following table showing their structures.

Table22.1: Oxoacids of chlorine

Name	**Hypochlorous acid (a)**	**Chlorous acid (b)**	**Chloric acid (c)**	**Perchloric acid (d)**
Formula of oxoacid	HOCl	HOClO	$HOClO_2$	$HOClO_3$
Oxidation state of chlorine	+1	+3	+5	+7
Structure	 (a)	 (b)	 (c)	 (d)

The acid strength of the oxoacids of chlorine increases as the number of O-atoms present in the acid increases. It is because oxygen is more electronegative than chlorine. As the number of O-atoms bonded to the Cl atom increases, more electrons will be pulled away more strongly from the O-H bond. As a result the O-H bond will be weakened. Thus $HOClO_3$ require the least energy to break the O-H bond and form H+. Thus, HOCl is a very weak acid where as $HOClO_3$ is the strongest acid, thus the acid strength increases in the order.

$$\mathbf{HOCl < HOClO < HOClO_2 < HOClO_3}$$

22.4.3 Chlorofluoro carbons(CFC)

Chlorofluoro carbons are the compounds of carbon where chlorine and fluorine are substituted for hydrogen in saturated hydrocarbons e.g. CCl_2F_2, $CFCl_3$, $C_2F_4Cl_2$ etc. These compounds have very high capacity to retain heat. It is believed that the capacity to retain heat is about 10,000 times more than that of carbon-dioxide. Thus these molecules are capable of cooling other systems by taking away their heat.

Chlorofluorocarbons are also termed as freons. About 5 thousand metric tons of CFC's are still being produced in our country annually. In addition to their usage as aerosols, solvents, foam blowing agents and refrigerants, they are also known to cause environmental hazard. CFCs react with protective ozone layer in the stratosphere, thus causing perforation through which radiations from outer sphere enter our atmosphere and cause damage to our life systems. The destruction of ozone layer is termed as *ozone depletion* and it is creating a ozone hole.

22.4.4 Inter halogen Compounds

The halogens form a series of mixed binary compounds called the interhalogens. These compounds are of the type XX′, XX'_3, XX'_5, and XX_7'. The compounds of the type XX´ are known for all combinations. Compounds of XX'_3, and XX'_5 types are known for some, and of XX'_7 type only IF_7 is known.

Preparation

The interhalogen compounds canbe prepared by direct reaction between the halogens. They can also be prepared by the action of a halogen on a lower interhalogen.

$$Cl_2 + F_2 \text{ (equal volumes)} \xrightarrow{473K} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess } F_2\text{)} \xrightarrow{573K} 2ClF_3$$

$$I_2 + 5F_2 \xrightarrow{293K} 2IF_5$$

$$I_2 + 7F_2 \xrightarrow{523-573K} 2IF_7$$

Intext Questions 22.4

1. Name the most electronegative halogen.

....

2. Name the halogen that can react with an inert gas.

....

3. Write a chemical reaction used for the laboratory preparation of chlorine.

....

4. Arrange the hydroacids of halogens in the decreasing order of their strength.

....

5. What group of carbon compounds is supposed to cause ozone depletion?

....

22.5 Compounds of Noble Gases

The group 18 of the periodic table consists of six elements-helium, neon, argon, krypton, xenon and radon. These elements are termed as 'noble gases'. The name noble gas implies that they tend to be unreactive and are reluctant to react just like noble metals. Except helium which has 2 electrons and forms a complete shell $1s^2$, the other elements of the group have a closed octet of electrons in their outer shell $ns^2\ np^6$. This electronic configuration is very stable and the ionization energies of the atoms of these elements are very high. Therefore, the atoms of noble gases have a little tendency to gain or lose electrons. Hence these elements exhibit lack of chemical reactivity.

The first compound of noble gases was made by Neil Bartlettin 1962 by the reaction of xenon with PtF6. Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar donot form any compounds where as Kr does form KrF_2, Radon is a radioactive element and all its isotopes have very short half lives.

Xenon Compounds

Xenon reacts with fluorine to form binary fluorides, XeF_2, XeF_4 and XeF_6. The product formed depends on the temperature and xenon-fluorine ratio. Thus XeF_2, XeF_4 and XeF_6 are all white solids. They readily sublime at 298K. They differ in their reactions with water.

$$\underset{(2:1\ \text{ratio})}{Xe + F_2} \xrightarrow{873K, 1bar} XeF_2(s)$$

$$\underset{(1:5\ \text{ratio})}{Xe + 2F_2} \xrightarrow{873K, 7bar} XeF_4(s)$$

$$\underset{(1:20\ \text{ratio})}{Xe + 3F_2} \xrightarrow{573K, 60\,bar} XeF_6\,(s)$$

XeF_2 dissolves in water and undergoes slow hydrolysis in water.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

XeF_4 and XeF_6 react with water violently to give xenontrioxide and hydrogen fluoride.

$$6\,XeF_4 + 12H_2O \longrightarrow 4\,Xe + 2XeO_3 + 24\,HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeF6 on partial hydrolysis gives, xenon oxofluorides.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

The xenon fluorides react with strong Lewis acids to form complexes.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ + [PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ + [SbF_6]^-$$

XeF_6 may also act as a fluoride accepter from fluoride ion donors to form fluoroxenate anions.

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^- \ (M = Na, K, Rb, Cs)$$

XeO_3 can be prepared by hydrolysis of XeF_6

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeO_4 can be prepared by the reaction of barium peroxenate with conc. sulphuric acid

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

Structure of Xenon compounds

The structures and shapes of the common xenon fluorides and oxides are shown below. The shapes of these molecules can be explained in terms of VSEPR theory which you have already learnt in chemical bonding.

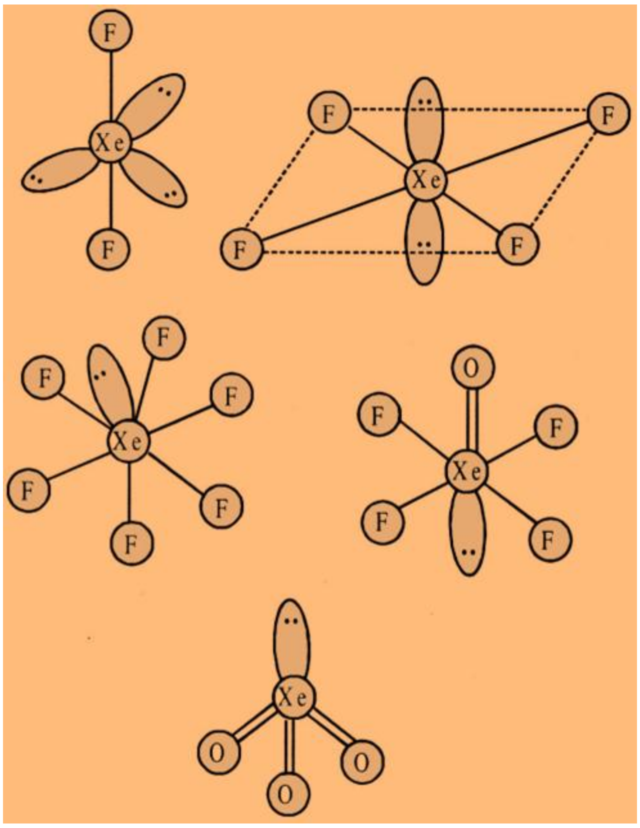


Fig.22.3:*ThestructuresofXeF$_2$, XeF$_4$, XeF$_6$, XeO$_3$ and XeOF$_4$*

What You Have Learnt

- ❖ While sulphur exists as S8 molecules oxygen exists as O_2 molecules. Both these elements form divalent anion show ever sulphur also shows +4 and +6 oxidation state. Oxygen and sulphur are non-metals of group number 16.
- ❖ The binary compounds of oxygen with other elements are known as oxides. The oxides can be classified as: acidic oxides, basic oxides and amphoteric oxides.
- ❖ Ozone, an allotrope of oxygen is prepared by Siemen’s ozonizer.
- ❖ Sulphuric acid displays strong acid character and possesses oxidizing and dehydrating properties.
- ❖ Chlorine forms a number of oxo acids: HOCl, $HClO_2$, $HClO_3$ and $HClO_4$.
- ❖ The binary compounds of halogens with one another are called interhalogen compounds.

- Halogens are placed in group number 17 of the periodic table. All members of the group are very reactive. They show variable oxidation states. Halogens react with otherhalogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids.
- Fluoro chloro carbons are called freons which decompose ozone and are therefore environmentally hazardous.
- Helium, neon, argon, krypton, xenon and radon are the members of Group number 18 and are collectively called noble gases.
- Xenon is known to react with fluorine to form XeF_2, XeF_4 and XeF_6.

Terminal Exercise

1. Which one of the following oxides can react with an acid as well as with an alkali: SO_2, CaO, ZnO, MgO?
2. Write two oxides which donot react with either acids or alkalies. Which type of oxides are they?
3. Isozone an allotrope of oxygen? Which is more soluble in water oxygen or ozone?
4. What is the state of hybridization of the central oxygen atom in O_3 molecule?
5. Why does ozone tail mercury?
6. Which property of ozone makes it useful for bleaching?
7. Write the conditions which are required to convert SO_2 to SO_3 in the manufacture of sulphuric acid by contact process.
8. What is oleum?
9. Why is sulphuric acid known as king of chemicals?
10. Fluorine never acts as a central atom in any interhalogen compounds. Why?
11. Draw the structure of BrF.
12. Arrange the hydrogen halides in order of their acid strength in aqueous solution.
13. Why is F_2O not known as fluorine oxide? Instead it is known as oxygen fluoride, OF_2.
14. Which is the strongest acid among the oxoacids of chlorine and why?
15. What happens when XeF_4 reacts with SbF_5? Write the complete equation for the reaction.

Answers to Intext Questions

22.1

1. Basic oxide: CaO; acidic oxide: SO_2; amphoteric oxide: ZnO.
2. Acidic oxide: SiO_2, SO_2, CrO_3

   Basic oxide : K_2O, FeO

   Amphoteric oxide: Al_2O_3, ZnO
3. $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

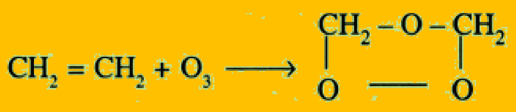
   $ZnO + 2NaOH \longrightarrow Na_2Zn\,O_2 + H_2O$
4. An oxide of group 1, K_2O and of Gr 2 BaO

   $K_2O + 2HCl \longrightarrow 2KCl + H_2O$

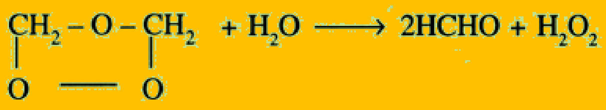
   $BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$

22.2

1. When ethene combines with O_3, an ozonide is formed, thus



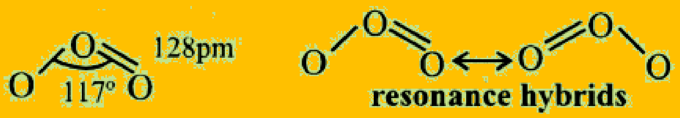
On hydrolysis it gives HCHO,



2. (i) $2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + H_2O + O_2$

   (ii) $3SnCl_2 + O_3 + 6HCl \longrightarrow 3\,SnCl_4 + 3H_2O$

3. Ozone is 10 times more soluble than O_2.



4.

5. Mercury loses its convex meniscus and leaves a "tail" or a trail of minute droplets on a glass surface when exposed to ozone. This is due to the formation of mercurous oxide. The tailing effect can be removed by washing the *mercury* with a dilute acid.

22.3

1. (i) Oxidizing property of conc. H_2SO_4

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

   (ii) Dehydrating property: It removes water from sugar

$$C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11H_2O$$

2. A corrosive mist of sulphuric acid is formed.

3. $2SO_2 + O_2 \xrightarrow[720K]{V_2O_5} 2SO_3$

22.4

1. Fluorine
2. Fluorine
3. $2\,NaCl + 3H_2SO_4 + MnO_2 \longrightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2$
4. HI > HBr > HCl > HF
5. Chlorofluorocarbons (or freons)

22.1.a Manufacture of sulphuric acid:

Sulphuric acid is the most important acid used in the chemical industry. It was called as “oil vitriol”. Because of its wide applications, H_2SO_4 is referred as “the king of chemicals”. It is manufactured by the contact process.

Contact process:

The three main aspects of the contact process are:

I. Sulphur dioxide production:

Sulphur dioxide required for the process is obtained by burning either S or iron pyrites in oxygen.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

II. Sulphur trioxide formation:

Sulphur dioxide is oxidized catalytically with atmospheric oxygen to sulphurtrioxide SO_3

$$2SO_2 + O_2 \xrightarrow[\Delta]{\text{Catalyst}} 2SO_3$$

III. Sulphur trioxide is absorbed in H_2SO_4

The pure SO3 formed is absorbed in 98% conc.Sulphuric acid to get oleum or pyrosulphuric acid $H_2S_2O_7$. Oleum is diluted with water to obtain sulphuric acid of desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Le Chatelier’s principle:

In presence of a Catalyst, SO2 converts into SO by Oxidation. This is a reversible reaction. It is an exothermic reaction

The equation reveals the following points:

I. 3 volumes of the reactants convert into 2 volumes of SO. i.e. a decrease of volume accompanies the reaction.
II. The reaction is an exothermic change.
III. The catalyst may be present to increase the SO yields.

According to Le Chatelier’s principle

I. A decrease in volume of the system is favoured at high pressures. But in practice only about 2 atmospheres pressure is used. The reason for not using high pressures is acid resisting towers which can with stand high pressures cannot be built.
II. Exothermic changes are favoured at low temperatures. It is not always convenient in the industry to work at low temperatures. In such situations, an optimum temperature is maintained. At this temperature considerable amounts of the products are obtained. In the manufacture of H_2SO_4, The optimum temperature suitable for the conversion of SO2 to SO_3 is experimentally found to be 673- 723K.
III. The rate of formation of SO_3 is enhanced by the use of a catalyst. Different catalysts are in use. They are Platinised asbestos, vanadium pentoxide, finely divided Platinum deposited on MgSO4 and mixture of Fe2O_3 and cupric oxide CuO. All the catalysts in

the contact process are easily poisoned and therefore, the gases used must be extremely pure. In modern plants, excess of oxygen is used in the gaseous mixture.

Description of the plant:

Various parts of the plant are shown in the figure given below.

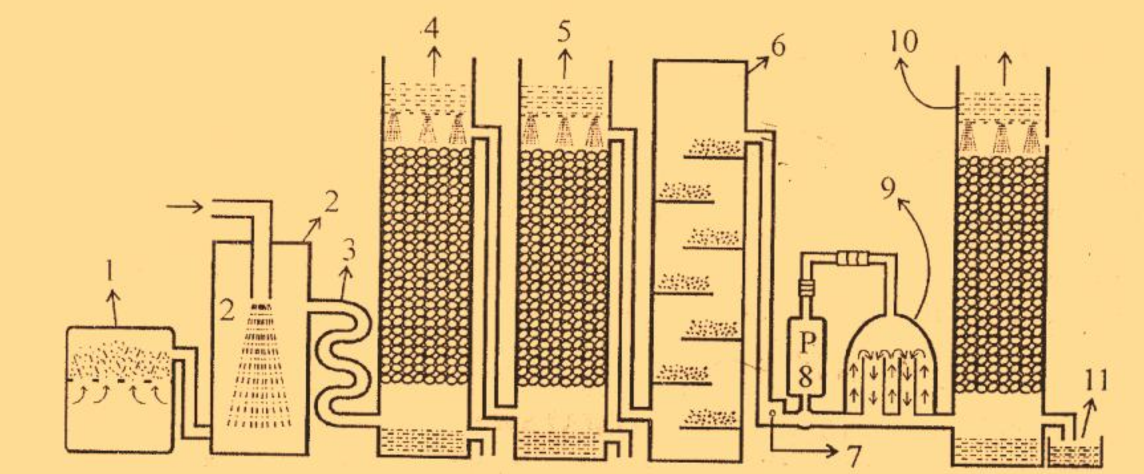


Fig.22.1.bManufactureofSulphuricacid-ContactProcess

1. Pyrites burners
2.Dusting tower
3.Cooling Pipes
4. Scrubbing tower
5.Drying tower
6. Arsenic purifier
7. Testing box
8. Pre-heater
9. Catalytic chamber
10. Absorption tower

1) *Pyrites burners or sulphur burners:* Here Soriron pyrites are burnt to produce SO_2.
2) *Dusting tower:* The dust particles in the burner gases are removed by settling down.
3) *Cooling pipes:* The gases are cooled and also dust particles settle down completely.
4) *Scrubbing tower:* The water falling from the tower cleans the up going gases.
5) *Drying tower:* The gases coming into this are dried.
6) *Arsenic purifier:* The main impurity in the gases is arsenic oxide. It is removed in this chamber by gelatinous ferric hydroxide.
7) *Testing box:* Here the gases are tested for their purity. If the gases still contain impurity As_2O_3 and the suspended particles then the gases are recycled.
8) *Pre-heater:* The pure gases are heated to 673–723K. From here they go into contact tower.
9) *Contact tower:* The contact tower has vertical pipes packed with the catalyst, V_2O_5 maintained at the required temperature. SO_2 is converted into SO_3. The catalyst is maintained at the required temperature by the heat evolved in the reaction.
10) *Absorption tower:* SO_3 is absorbed in conc.H_2SO_4 to form oleum $H_2S_2O_7$. The oleum is diluted with water to get the acid of required concentration.

Advantages of contact process over other methods.

1. Sulphuric acid obtained is extremely pure and concentrated.
2. Contact process is comparatively cheap.
3. The impurities can be tested and the reactants can be recycled.

22.1.b Intext Questions:

1. Write the chemical reactions taking place in contact process.

....

2. Name any three catalysts used in contact process

....

3. What is the oxidation state of S in H2SO4

....

What you have learnt:

1. Preparation of Sulphuric acid by contact process.

22.1. a. Answers to Intext Questions

1. $2SO_2 + O_2 \xrightarrow[\Delta]{\text{Catalyst}} 2SO_3$
2. Vanadium Pentoxide Platinised asbestos, mixture of CuO_3 and Fe_2O_3
3. +6

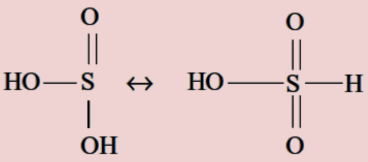
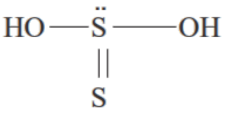
22.1.b Oxyacids of Sulphur

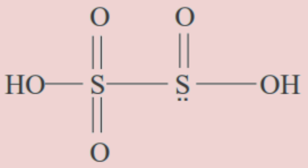
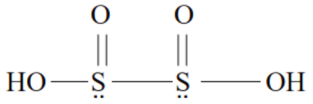
Sulphur oxoacids are numerous and more important than the oxy acids of other elements of the group. The oxoacids of S may be divided into 4 series, depending on their structural similarities. They are

i. Sulphurous acid series
ii. Sulphuric acid series
iii. Thionic acid series
iv. Peroxo acid series

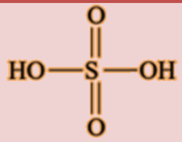
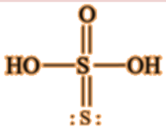
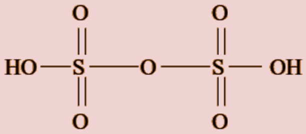
Each of these acids may have more than one structure. The structures of these acids, which is possible resonating or fantomeric form are given.

i) Sulphurous acid series:

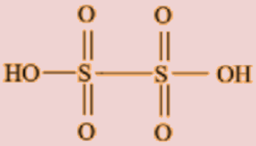
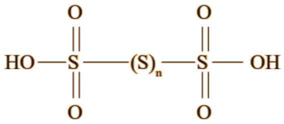
Name	M.F.	Oxidation state of S	Structure
sulphurous acid	H_2SO_3	+4	
thiosulphurous acid	$H_2S_2O_2$	+ 4	

Disulphurous acid or Pyro sulphurous	$H_2S_2O_5$	+3, & +5	
Dithionous acid or Sulphurous acid	$H_2S_2O_4$	+3	

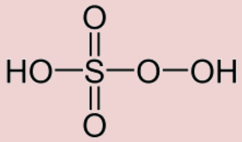
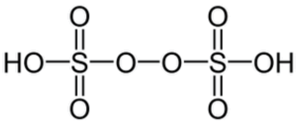
ii) Sulphuric acid series:

Name	M.F.	Oxidation state of S	Structure
sulphuric acid	H_2SO_4	+6	
thiosulphuric acid	$H_2S_2O_3$	-2, +6	
Di sulphuric acid or Pyro sulphuric acid	$H_2S_2O_7$	+8, +6	

iii) Thionic acid series:

Name	M.F.	Oxidation state of S	Structure
Dithionic acid	$H_2S_2O_6$	+5	
Poly thionic acid	$H_2S_{(n+2)}O_6$	+5	

iv) Peroxo acid series or peroxy acid series:

Name	M.F.	Oxidation state of S	Structure
Peroxo monosulphuric acid or caro's acid	H_2SO_5	+6	
Peroxo di sulphuric acid or per sulphuric acid or Marshall's acid	$H_2S_2O_8$	+6	

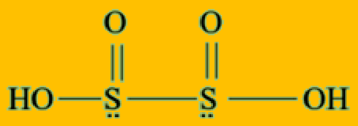
22.1.b Intext questions:

1. Write the structures of i) Dithionous acid ($H_2S_2O_4$) ii) Disulphurous acid ($H_2S_2O_5$).

2. Write the structure of Dithionic acid $H_2S_2O_6$. What are the oxidation states of S atoms in it?

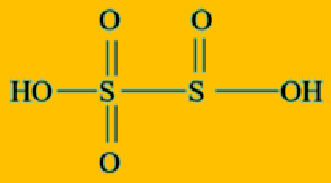
22.1.c Answers of intext questions:

1. a) Dithionous acid $H_2S_2O_4$



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\cdot\cdot}{S}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\cdot\cdot}{S}}-OH$$

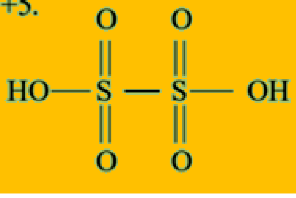
b) Disulphurous acid $H_2S_2O_5$



$$HO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle O}{\|}}{S}-OH$$

2. Dithionic acid $H_2S_2O_6$

Oxidation state +5.



$$HO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH$$

Chapter 23

d-BLOCK AND f-BLOCK ELEMENTS

You have already learnt in lesson 4 on periodic classification, that each period (except the first period) of the periodic table starts with the filling of ns subshell and ends with the filling of *np* subshell (n is the principal quantum number and also the number of the period). The long form of the periodic table is based on the filling of electrons in various levels in order of increasing energy as given by Aufbau principle. In the fourth period, filling of the 4th shell commences with the filling of *4s* subshell followed by *3d* and *4p* subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number (*3d*) starts getting filled instead of the expected subshell *4p*. This group of elements that occurs in between the *4s* and *4p* elements is referred to as *3d* elements or elements of first transition series (see periodic table). 4f Series consist of 14 members from Ce to Lu (At.No. 58 - 71), where the pen ultimate subshell, *4f* subshell is filled up. They have general electronic configuration [Xe] $4f^{1-14}\ 5d^{1,2}\ 6s^2$. La is also included in this series: it is the prototype for the succeeding 14 elements. In this lesson you will study more about these elements and also about the preparation, properties and uses of potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$).

Objectives

After reading this lesson, you will be able to:

- define transition metals and write their electronic configuration;
- list the general and characteristic properties of the transition elements;
- explain the properties of *3d* transition series: metallic character, variable oxidation state, variation in atomic and ionic radii, catalytic properties, coloured ions, complex formation, magnetic properties, interstitial compounds and alloy formation;
- recall the preparation of potassium permanganate from pyrolusite ore;
- write the chemical equations illustrating the oxidizing properties of KMnO4 in acidic, alkaline and neutral media (acidic: $FeSO_4$, SO_2 alkaline: KI and ethene, neutral: H_2S and $MnSO_4$);
- recall the preparation of potassium dichromate from chromite ore;
- write the oxidation reactions of potassium dichromate with SO_2 and ferrous sulphate in acidic medium;
- write electronic configuration of lanthanides (*4f*-elements) and
- explain lanthanide contraction.

23.1 *d*- Block Elements

d- Block elements occupy the middle portion of the periodic table i.e. between s- and p-block elements. They include elements from groups 3 to 12. In these elements the outermost shell contains one or two electrons in their outer most i.e., ns orbital but the last electron enters into the inner d-subshell i.e. (*nl*) d orbital. The elements of the d-block are metallic in nature. Their general characteristic properties are intermediate between those of the *s*-block elements, on one hand and of the *p*-block elements on the other. We can say that *d*-block elements represent a change (or transition) from the most electropositive *s*-block elements to the least electropositive *p*-block elements and are, therefore, also named as transition elements.

Transition elements are elements in which the *d*-subshell is partially filled either in atomic state or in ionic state.

There are four series of transition elements in the periodic table. The first transition series begins with scandium (At.No.21) and ends at copper (At.No.29) where as the second, third and fourth series begin with yttrium (At. No. 39), lanthanum (At. No. 57) and actinium (At. No. 89) and end at silver (At. No. 47), gold (At. No. 79) and at the element having atomic number 112 (a synthetic element), respectively. These series are also referred to as *3d*, *4d*, *5d* and *6d* series, respectively. It may be noted that although elemental copper, silver and gold as well as Cu^{1+}, Ag^{1+} and Au^{1+} have a *d*10 configuration but Cu^{2+} has a $3d^9$, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration and that is why these elements are classified as transition elements. On the other hand, zinc, cadmium and mercury do not have partially filled d subshell either in the elemental state or in any of their common ions. These elements, therefore, are not transition elements. However, zinc, cadmium and mercury are often considered along with *d*- block elements.

Intext Questions23.1

1. What are transition elements?

………………………………………………………………………………………

2. How many elements comprise the first transition series? Give names of all these elements.

....

3. Whereas copper is a transition element, zinc is not included amongst transition elements. Explain.

....

4. Although Cu^+, Ag^+ and Au^+ have d^{10} configuration but Cu, Ag and Au are transition elements, why?

....

23.2 Electronic Configuration

The general electronic configuration of transition elements is $(n1)d^{1-10}\ ns^{1-2}$. The (n-1) stands for inner shell and the *d*-orbitals may have one to ten electrons and the *s*-orbital of the outer most shell (*n*) may have one or two electrons. It is observed from the Fig.23.1 that *4s* orbital ($l=0$ and $n=4$) is of lower energy than *3d* orbitals ($l=2$ and $n=3$) upto potassium (At.No.19). The energy of both these orbitals is almost same in case of calcium (At.No.20), but the energy of *3d* orbitals decreases with further increase of nuclear charge and becomes lower than *4s*, and *4p*, (in case of scandium At.No.21). Thus after filling of *4s* orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to *3d* orbital instead of *4p*, as the former is of lower energy than the latter. This means that 21st electron enters the underlying principal quantum level with $n=3$ rather than the outer most level with $n=4$ which started filling at potassium (At.No.19), the first element of the fourth period. In the case of next nine elements following calcium, the incoming electron is filled in the *d*-subshell. Since half-filled and completely filled subshells are stable than the one in which one electron is short, an electron gets transferred from *4s* to *3d* in case of the elements with atomic number 24 and 29. Consequently, configuration of chromium and copper have only one *4s* electron (Table23.1).

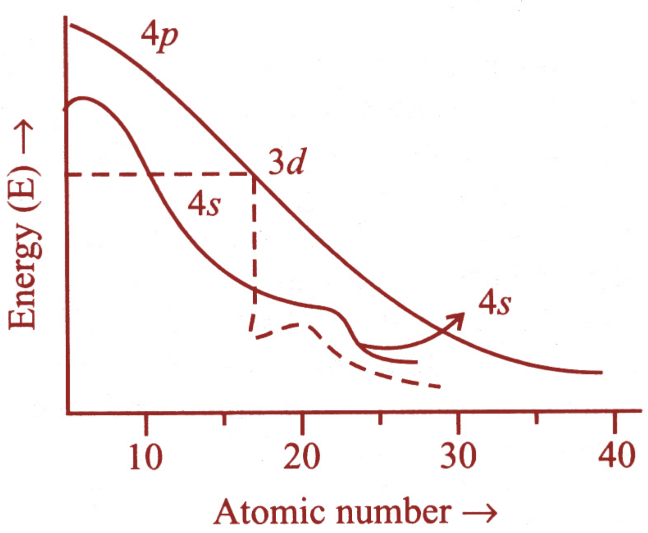


Fig.23.1: Variation of energy of orbitals *vs* atomic number

Table23.1: Electronic configuration of first series (or *3d*) transition elements

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$
Titanium	Ti	22	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$
Vanadium	V	23	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3\,4s2$
Chromium	Cr	24	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^4\,4s2$
Manganese	Mn	25	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s2$
Iron	Fe	26	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s2$
Cobalt	Co	27	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s2$
Nickel	Ni	28	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^8\,4s2$
Copper	Cu	29	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s1$
Zinc	Zn	30	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s2$

As can be seen, in case of zinc, the 30th electron goes to *4s* level and not *3d* level which is already full. Thus by definition, zinc cannot be called a member of d block elements. Besides, no compound of zinc is known to have a partially filled *3d* subshell. Thus it does not fit into the definition of a transition element either. Hence zinc cannot be rightly called either a *d*-block element or transition element. However, zinc and other members of group 12, viz., cadmium and mercury are discussed along with *3d*, *4d* and *5d* transition elements for the sake of convenience.

It is important to understand at this point, the process of ionization (i.e. oxidation) of transition elements. From what has been said above regarding filling of the orbitals, it is logical to conclude that during ionization electrons should be lost first from the *(n-l)d* subshells and then from the *4s* level. This, however, is not the case. The reason for the deviation from the expected behavior is that once the filling of the *3d* subshell commences at scandium (At. No.21) energy of *3d* subshell decreases and becomes lower than that of *4s* subshell.

Consequently, on ionization, the first row transition elements lose electrons from the *4s* subshell followed by the loss from *3d* level. For example vanadium (Z=23) has electronic configuration V = [Ar] $3d^3 4s^2$ and the electronic configuration of V^{2+} is [Ar] $3d^3$, Similarly electronic configuration of V^{3+} and V^{4+} are [Ar] $3d^2$ and [Ar]$3d^1$, respectively. In some cases, however, for example scandium, all the electrons beyond the core of 18 electrons are lost in single step. It is important to note that though *3d* orbitals are of higher energy than *4s* orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of same energy.

Intext Questions23.2

1. Write the general electronic configuration of transition elements.

....

2. Write down the electronic configuration of the following elements in ground state: Sc, Cr, Cu and Zn.

....

3. Write down the electronic configuration of the following ions: Cr^{3+}, Ti^{4+}, Ni^{3+} and Cu^{2+}.

....

4. Why the electronic configuration of Mn2+ is $3d^5$ and not $3d^2\ 4s^2$?

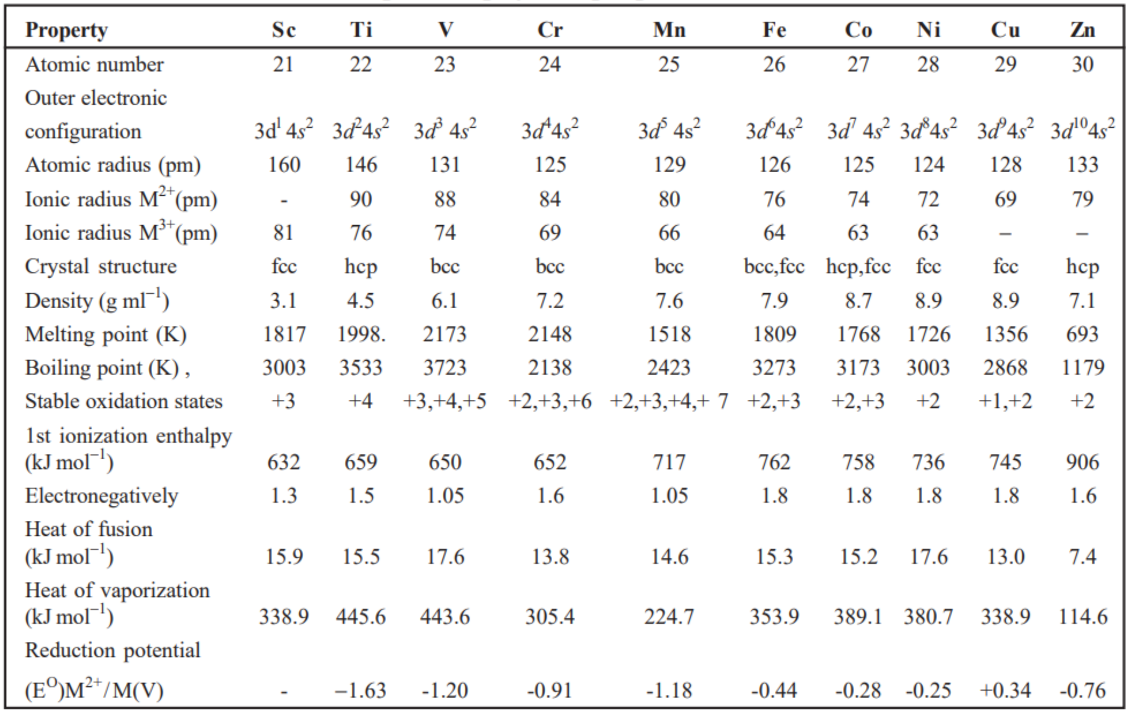
....

23.3 Physical Properties

Some important physical properties of *d*-block elements are listed in Table 23.2. Like *s*-block elements, *d*-block elements are also metals. But properties of these elements are markedly different from those of *s*-block elements. The interesting feature of the chemistry of transition elements is that similarities in the properties of transition elements are much more marked as compared to those in *s*-block. Almost all transition elements show typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lusture. All the transition elements have typical metallic structure except mercury, which is liquid at room temperature.

Transition elements show high melting and boiling points. They typically melt above 1356 K. It is due to the small atomic size and strong interatomic bonding. All the transition elements are hard except zinc, cadmium and mercury. They show high enthalpy of atomization (Table 23.2). Densities of transition elements are very high as compared to those of *s*-block elements. The density of the elements in a given transition series increases across a period and reaches a maximum value at groups 8, 9 and 10. This trend can be explained on the basis of small radii and close packed structure of the elements.

Table 23.2: Some important physical properties of 1st transition series



Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Outer electronic configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$	$3d^{10} 4s^2$
Atomic radius (pm)	160	146	131	125	129	126	125	124	128	133
Ionic radius M^{2+}(pm)	-	90	88	84	80	76	74	72	69	79
Ionic radius M^{3+}(pm)	81	76	74	69	66	64	63	63	–	–
Crystal structure	fcc	hcp	bcc	bcc	bcc	bcc,fcc	hcp,fcc	fcc	fcc	hcp
Density (g ml^{-1})	3.1	4.5	6.1	7.2	7.6	7.9	8.7	8.9	8.9	7.1
Melting point (K)	1817	1998.	2173	2148	1518	1809	1768	1726	1356	693
Boiling point (K) ,	3003	3533	3723	2138	2423	3273	3173	3003	2868	1179
Stable oxidation states	+3	+4	+3,+4,+5	+2,+3,+6	+2,+3,+4,+ 7	+2,+3	+2,+3	+2	+1,+2	+2
1st ionization enthalpy (kJ mol^{-1})	632	659	650	652	717	762	758	736	745	906
Electronegatively	1.3	1.5	1.05	1.6	1.05	1.8	1.8	1.8	1.8	1.6
Heat of fusion (kJ mol^{-1})	15.9	15.5	17.6	13.8	14.6	15.3	15.2	17.6	13.0	7.4
Heat of vaporization (kJ mol^{-1})	338.9	445.6	443.6	305.4	224.7	353.9	389.1	380.7	338.9	114.6
Reduction potential (E^O)M^{2+}/M(V)	-	–1.63	-1.20	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76

Atomic radii

The radii of the elements decrease from left to right across a row in the transition series until near the end, and then the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra electrons are added. The *d*-orbital electrons shield the nuclear charge poorly. Thus, the effective nuclear charge increases and, therefore, electrons are attracted more strongly, hence contraction in size occurs. There is an increase in atomic radii with increase in atomic number in a given group, for example Ti (146 pm), Zr (157 pm) and Hf (157 pm). The very close similarity between the radii of elements of second and third transition series is a consequence of the filling of the *4f*-subshell (causing lanthanide contraction which you will study later in this lesson).

Intext Questions23.3

1. Why do transition elements show higher melting and boiling points?

....

2. Why do the radii of transition elements decrease along a period?

....

3. Why do transition elements show higher density as compared to *s*-block elements?

....

23.4 Characteristic Properties

These are the properties shown only by transition elements. On the basis of these properties transition elements can be distinguished from *s* and *p*-block elements.

23.4.1 Variable Oxidation States

s-block, *d*-block and *f*-block elements show positive oxidation states (except H which shows -1 oxidation state also) whereas, most of the p-block elements show both positive and negative states. The number of electrons used for bonding by an electropositive element is equal to its positive oxidation state. A characteristic property of *d*-block elements is their ability to exhibit a variety of oxidation states in their compounds. This is due to the fact that for bonding, in addition to ns electrons, these elements can use inner (n-l)d electrons as well because of very small difference in their energies. Thus, depending upon the number of d electrons involved in bonding, different oxidation states arise. The lowest oxidation state is usually equal to the number of s-electrons present (except Sc). For example, copper has an electronic configuration of $3d^{10}\ 4s^{1}$ and shows oxidation state of +1 besides the usual oxidation state of +2. The highest oxidation states are observed in compounds with fluorine and oxygen, which are the two most electronegative elements. The different oxidation states of elements of the first transition series are given below:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*
+3	(+2)	+2	+2	+2	(+1)	(+1)	(+1)	+1	**(+1)**
	+3	+3	+3	(+3)	+2	+2	+2	+2	**+2**
	+4	+4	+4	+4	+3	+3	(+3)	(+3)	
		+5	(+5)	(+6)	+6	(+4)	(+4)		
			+6	**+7**					

(* Given for comparison only.) Here the rare oxidation states are given in parentheses.

An examination of the common oxidation states given above reveals the following:

Except for scandium, the most common oxidation state of *3d* elements is +2 which arises from the loss of two *4s* electrons. This means that after scandium, *d*-orbitals become more stable than s orbital. Compounds having oxidation states +2 and + 3 of these elements have ionic bonds whereas bonds are essentially covalent in higher oxidation states. For example, in case of permanganate ion, MnO, bonds formed between manganese and oxygen is covalent. Considering the acid base character of the oxides, it can be inferred that increase in oxidation state leads to decrease in basic character of the oxide and vice-versa. For example, MnO is a basic oxide whereas Mn_2O_7 is an acidic oxide.

Since transition metals exhibit multiple oxidation states, their compounds in the higher oxidation states are strong oxidizing agents as they tend to accept electrons and come to stable lower oxidation states.

Trends in the stability of higher Oxidation States:

Elements of 3d series acquire stable highest oxidation states in their halides and oxide compounds. Although +2 oxidation state is common to most of the elements in the *3d* series Cr and V show the highest stable oxidation state in their fluorides ($CrF_6$and VF_5) while Mn shows the highest oxidation state i.e., +7 in its oxyhalide MnO_3F. Fluorine provides sufficient lattice energy and covalent bond nature to its transition metal halides to stabilize the higher oxidation states.

Similar trends are observed in the oxides also. Oxygen can form multiple bonds with transition elements and exhibit prominent covalent character in its oxides in comparison with Fluorine which provides more stable higher oxidation states in oxides to that of Fluorides. The lowest stable oxidation state is found in Sc_2O_3 whereas Mn shows the highest oxidation state in Mn_2O_7.

23.4.2 Magnetic Properties

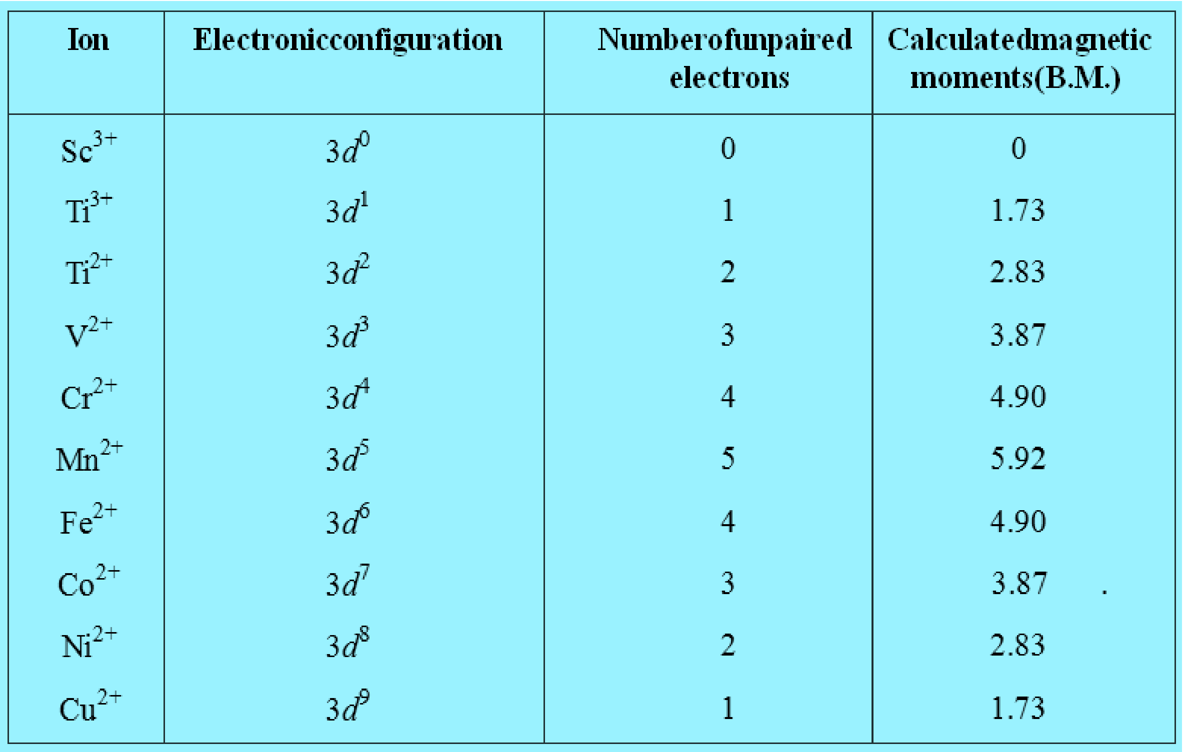
Substances possess two types of magnetic behaviour, either diamagnetism or paramagnetism. Diamagnetic substances are either repelled or remain unaffected by an applied magnetic field where as, paramagnetic substances are attracted towards the applied field.

There is a strong co-relation between the magnetic behaviour, electronic configuration and oxidation state. Paramagnetism arises due to the presence of unpaired electrons (Table 23.3). Since transition metal ions generally contain unpaired electrons a large number of transition metal ions exhibit paramagnetic behavior.

Magnetic moment (μ) of paramagnetic material can be calculated (in B.M., Bohr Magneton) by using, the expression: $\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons.

For example, Ni2+ ion has two unpaired electrons (i.e. n=2). The magnetic moment can be calculated as $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$ B.M The magnetic moments of some 3d metals ions are listed in Table 23.3 which shows that greater the number of unpaired electrons, greater is the magnetic moment.

Table23.3: Magnetic moments of some ions of the transition elements:



Ion	Electronicconfiguration	Numberofunpaired electrons	Calculatedmagnetic moments(B.M.)
Sc^{3+}	$3d^0$	0	0
Ti^{3+}	$3d^1$	1	1.73
Ti^{2+}	$3d^2$	2	2.83
V^{2+}	$3d^3$	3	3.87
Cr^{2+}	$3d^4$	4	4.90
Mn^{2+}	$3d^5$	5	5.92
Fe^{2+}	$3d^6$	4	4.90
Co^{2+}	$3d^7$	3	3.87
Ni^{2+}	$3d^8$	2	2.83
Cu^{2+}	$3d^9$	1	1.73

Compounds containing Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+} and Cu^{+} ions are diamagnetic since these ions do not contain any unpaired electron.

23.4.3. Ionisation Enthalpies

Ionisation enthalpy rises from left to right along each series of the transition elements as a result of an increase in nuclear charge caused by the filling of inner d orbitals. But there are little variances. The ionisation enthalpies of the first-row elements are represented in Table **23.2.** These numbers demonstrate that the first ionisation enthalpy usually increases the second and third ionisation enthalpies for the succeeding elements rise by a much greater amount.

The cause for the uneven trend in the first ionization enthalpy of the 3d metals is the removal of one electron, which changes the relative energies of the 4s and 3d orbitals. As the effective nuclear charge rises, the values follow the widely anticipated upward trend. The ionization value of Zn is larger because it indicates an ionization from the 4s level, while the value of Cr is lower since there has been no change in the d configuration. These metals' most prevalent lowest oxidation state is +2. To create the M^{2+} ions from the gaseous atoms in addition to the enthalpy of atomization, the sum of the first and second ionization energies are needed. Here the second ionization enthalpy is the key value; it shows exceptionally high values for Cr and Cu.

23.4.4. Trends in M^{2+}/M Standard Electrode Potentials:

In the 3d series, Redox potential (M^{2+}/M) values gradually increase from Ti to Cu but exceptionally Mn and Zn show lower Redox potential (E^{-}) i.e., -0.90 and -0.76 V respectively due to the stable electronic configuration of half-filled (Mn: d^5) and full-filled d (Zn: d^{10}) sub-shells. Cu shows positive redox potential (0.34 V) owing to that it is incapable of liberating hydrogen gas when reacts with protic acids. The trend is depicted in the **Fig.23.1.**

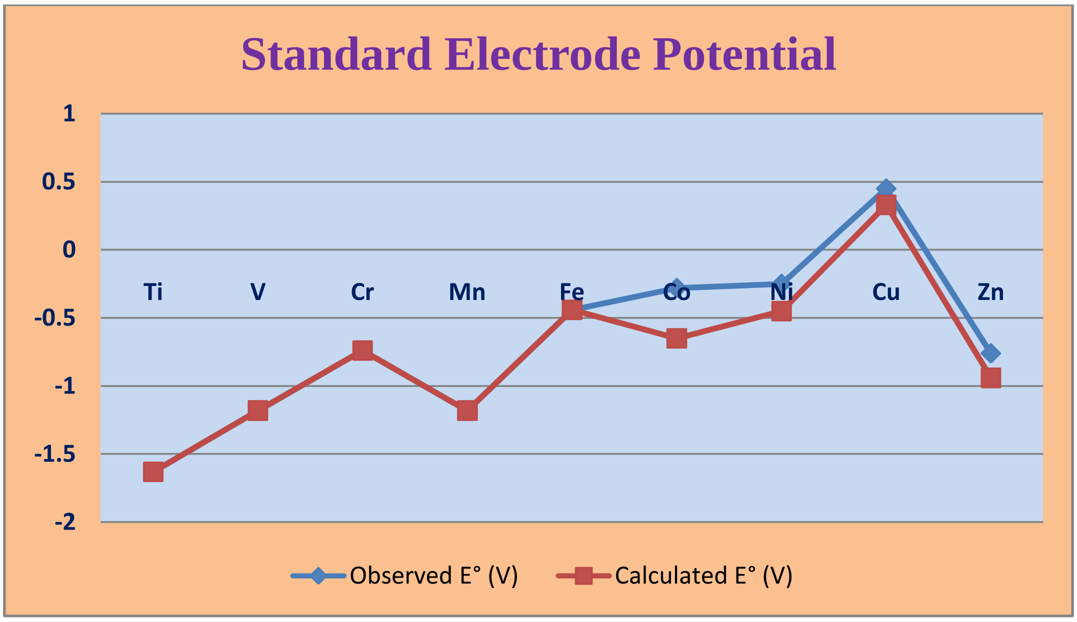


Fig. 23.1. Trends in M^{+}/M Standard Electrode Potential

Cu has a special characteristic that explains for why it cannot liberate H_2 from acids due to its positive E^{-}. Cu reacts only with oxidizing acids (nitric and hot concentrated sulfuric). Usually smaller negative E values observed along the series. It is noteworthy that the values of E (sum of the first and second ionization enthalpies) for Mn, Ni, and Zn are more negetive than would be predicted based on the trend.

The stability of Mn^{2+} in which d sub-shell is half-filled and Zn^{2+} in which completely filled d^{10} configuration in are related to their E^{-} values, whereas E^{-} for Ni is related to the highest negative $\Delta_{hyd}H^{-}$.

23.4.5. Trends in M^{3+}/M^{2+} Standard Electrode Potentials:

These values show irregular trends along the 3d series due to the variations in their electronic configurations. Sc displays the least value because of the stable noble gas configuration acquired by Sc^{+3} ion, whereas the highest value for Zn is due to the stable d^{10} configuration of Zn^{+2} ion. Similarly owing to the half-filled (d^5) configuration Mn^{+2} exhibits relatively higher redox potential (M^{3+}/M^{2+}) whereas Fe displays a comparatively decreased value due to stable d^5 configuration in the Fe^{+3} state.

23.4.6. Colour of Ions and Compounds

Most of the compounds of d-block elements are coloured or they give coloured solution when dissolved in water (Table 23.4). This property of transition elements is in marked contrast to that of the *s* and *p*-block elements, which often yield white compounds. In transition metal compounds colour is generally associated with incomplete (*n-1*) d subshell of the transition metal. When white light, which has colored constituents, interacts with a substance, a part of it is absorbed by the substance. For example, if red portion of white light is absorbed by a substance, it would appear blue (the complementary colour of red). This is observed in case of copper sulphate solution. Since most compounds of transition elements are coloured, there must be energy transition, which can absorb some of the energy of the visible light. The colour of transition metal ions containing unpaired electrons is attributed to electronic transitions from one energy level to another in the *d*-subshell. In these metals the energy difference between the various *d*-orbitals is in the same order of magnitude as the energies of the radiation of white light (λ= 4000 to 8000 Å).

Table 23.4: Colours of hydrated ions of some transition elements

Hexahydrated ion of	Number of d electrons	Color of solid/solution
Ti^{3+}	1	Violet
V^{3+}	2	Blue
V^{2+}	3	Violet
Cr^{3+}	3	Green
Mn^{3+}	4	Violet
Fe^{3+}	5	Yellow/colorless
Mn^{2+}	5	Yellow/colorless
Fe^{2+}	6	Palegreen
Co^{2+}	7	Pink
Ni^{2+}	8	Green
Cu^{2+}	9	Blue

23.4.7 Alloy and Interstitial Compound Formation

In the Table 23.2 it may be observed that the atomic size of the elements of first transition series is quite close to each other. Thus, in the crystal lattice, anyone of these elements can easily replace another element of similar size forming solid solutions and smooth alloys. Transition elements, therefore, form a number of alloys. Cr, V and Mn are used to produce alloy steel and stainless steel, copper forms brass, bronze etc. Besides, transition metals also form a number of interstitial compounds in which they take up atoms of small size, like hydrogen, carbon and nitrogen etc. These are located in the vacant spaces of metal lattices and are bound firmly there in. The products thus obtained are hard and rigid. For example, steel and cast iron become hard due to formation of an interstitial compound with carbon. In such compounds, malleability and ductility may marginally decrease but tenacity is considerably enhanced. Some examples of alloys are given in Table 23.5.

Table 23.5: Examples of some alloys

Alloy	Composition
Brass	Cu(50%-80%) and Zn(50%-20%)
Bronze	Cu(90%-93%) and Sn(10%-7%)
Gun metal	Cu(88%), Sn(10%) and Zn(2%)
Bell metal	Cu(80%) and Sn(20%)

23.4.8 Complex Formation

Transition metals exhibit a strong tendency to form complexes with different ligands due to the following reasons:

1. Small size and high charge density.
2. Variable oxidation states.
3. Availability of vacant d-orbitals to accept electron pairs from ligands.

You will learn more about complexes in the next lesson

23.4.9 Catalytic Properties

The catalytic activity of transition metals and their compounds is associated with their variable oxidation states. Typical catalysts are vanadium (V) oxide (contact process for sulphuric acid), finely divided iron (Haber's process), nickel (catalytic hydrogenation) and palladium (II) chloride and a copper (II) salt for the production of ethanol from ethane and water (Wacker's process). Haemoglobin, a large molecule containing Fe (II), acts as a catalyst for the respiration process.

Catalysis at a solid surface involves the formation of bonds between reactant molecules and the catalyst surface atoms, this has the effect of increasing the concentration of the reactants at the catalyst surface and also of weakening the bonds in the reactant molecules (the activation energy is lowered).

Transition metal ions function as catalysts by changing their oxidation states, e.g., Fe(III) cations catalyse the reaction between iodide and peroxo disulphate ions:

$$2I^-(aq) + S_2O_8^{2-}(aq) \xrightarrow{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

An over simplified, explanation of this catalysis reaction might be:

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$

It is known that both the above reactions can take place, and it would be expected that two reactions between ions of opposite charge would be faster than one reaction between ions of the same type of charge.

Intext Questions 23.4

1. Why do transition elements act as good catalysts?

....

2. Name some of the common catalysts you have studied.

....

3. Which of the following compounds are expected to be diamagnetic: $CrCl_3$, $ScCl_3$, $CuSO_4$, $CoCl_2$, $TiCl_4$ and $ZnCl_2$?

....

4. Which of the following do you expect to be coloured and why, Cr^+ and Cu^+?

....

5. Name any two alloys of transition elements.

....

6. Calculate in B.M., magnetic moments expected for the following ions: V^{4+}, Ni^{3+}, V^{4+}, Ni^{3+} and Ti^{4+}

....

23.5 Important Compounds of Transition Elements

The preparation, properties and applications of two important compounds of transition elements *viz*. $K_2Cr_2O_7$ and $KMnO_4$ which are widely used in industry and laboratory are discussed below:

23.5.1 Potassium Dichromate (K2Cr2O7)

Mineral chromite (FeO.Cr2O3) is the starting material for the manufacture of all chromates and dichromates. Soluble chromates are prepared using alkalimetaloxides, hydroxides or carbonates where as insoluble chromates are made by double decomposition of soluble chromates.

Large Scale Production of Potassium Dichromate from Chromite ore

A mixture of finely powdered chromite, sodium carbonate and quicklime is heated in a reverberatory furnace in free supply of air. Carbondioxide is evolved and sodiumchromate is formed. The function of quick lime is to keep the mass porous and prevent fusion.

$$4FeO.Cr2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

Chromite

The mass after roasting is extracted with water, which dissolves soluble sodium chromate leaving behind insoluble ferricoxide. After concentrating the solution containing sodium chromate, concentrated sulphuric acid is added.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium sulphate produced, crystallizes out and is removed. On further concentrating the solution, deliques centred crystals of sodium dichromate separate out slowly on cooling. When a hot saturated solution of sodium dichromate is mixed with a saturated solution of potassium chloride, sodium chloride separates out, followed by separation of game red tri clinic crystals of potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Since potassium dichromate is moderately soluble in cold water ($100gL^{1}$ at 298K) but easily soluble in hot water ($1000gL^{1}$) at 373K, it is readily purified by recrystallization from water.

Physical Properties

$K_2Cr_2O_7$ forms orange red prismatic crystals. Its specific gravity is 2.676 and its melting point is 696K. It is moderately soluble in cold water but highly soluble in hot water and insoluble in alcohol.

Chemical Properties

1. Since chromium forms stable compounds in low oxidation states as well, potassium dichromate in which oxidation number of chromium is +6, acts as a powerful oxidizing agent. For this reason, it is used as a primary standard in volumetric analyses. In acidic solutions, one molecule of potassium dichromate furnishes three atoms (i.e. six equivalents) of available oxygen as follows:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$$

The available oxygen then oxidizes ferrous, iodide ions and sulphur dioxide as follows:

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$2HI + [O] \longrightarrow H_2O + I_2$$

$$SO_2 + [O] + H_2O \longrightarrow H_2SO_4$$

These reactions can also be shown as ionic equations.

In acidic solution, the oxidizing action of $K_2Cr_2O_7$ can be represented as follows:

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

The ionic equation for the reducing action of Fe(II) can be represented as:

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

The complete ionic equation may be obtained by adding the half reaction of dichromate ion to the half reaction of Fe(II):

$$\begin{array}{l} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\ (Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 6 \\ \hline Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

Similarly the reactions of dichromate with iodide ion and sulphurdioxide can be written as given below:

$$\begin{array}{l}
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
(2I^- \rightarrow I_2 + 2e^-) \times 3 \\
\hline
Cr_2O_7^{2-} + 6I + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O
\end{array}$$

$$\begin{array}{l}
Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \\
(SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2e^-) \times 3 \\
\hline
Cr_2O_7^{2-} + 3SO_2 + 14H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O
\end{array}$$

2. Potassium dichromate when heated with concentrated sulphuric acid with anionic chloride (such as NaCl, KCl etc.) forms red vapours of chromylchloride, (CrO_2Cl_2) as follows:

$$\begin{array}{l}
K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O \\
[NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 4 \\
[CrO_3] + 2HCl \rightarrow CrO_2Cl_2 + H_2O] \times 2 \\
\hline
K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O
\end{array}$$

Red vapours of chromyl chloride, a derivative of chromic acid is absorbed in dilute solution of NaOH. A yellow solution of sodium chromate is formed. On acidifying this solution with acetic acid and adding lead acetate, a yellow precipitate of lead chromate, is formed which is soluble on heating and reappears on cooling. This is used as a confirmatory test to detect the presence of chloride ions in qualitative analysis.

3. When concentrated sulphuric acid is added to a solution of chromate or dichromate, a red coloured solution of chromic trioxide often called "chromic acid", is obtained. In the acidic solution it exists as dichromic acid ($H_2Cr_2O_7$). Chromium trioxide is a very powerful oxidizing agent.

4. Oxidation number of chromium is +6 in both chromates and dichromates. However, in neutral aqueous solution, dichromate ions exist in equilibrium with chromate ions as:

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O \rightleftharpoons \underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+$$

Thus in an acidic medium, equilibrium shifts to the left and dichromate ions exist where as in alkaline medium, only monomeric chromate ions exist.

Uses:

1. Potassium dichromate is used as an important volumetric reagent for the estimation of Fe2+, I^-, SO_3^{2-} etc.

2. It is used in the manufacture of chromealum, which is an important compound used for tanning of leather and dyeing of fabrics.

Intext Questions 23.5

1. Name the starting materials used in preparation of soluble chromate and dichromates.

....

2. Write down the formula of chromite ore.

....

3. How is sodium dichromate converted in to potassium dichromate?

....

4. What happens when potassium dichromate is heated with an alkali metal chloride and concentrated sulphuric acid?

....

5. Give the molecular formula of chromealum. What are its uses?

....

6. Why does dichromate act as an oxidizing agent?

....

7. What happens when a base is added to dichromate?

....

8. What is the oxidation state of chromium in (i) K_2CrO_4 and (ii) $K_2Cr_2O_7$?

....

23.5.2 Potassium Permanganate (KMnO4)

Pyrolusite ore (MnO_2) is the starting material for the manufacture of potassium permanganate. Pyrolusite is first converted into potassium manganate which is then oxidized to potassium permanganate.

Conversion of pyrolusite into potassium manganate

When pyrolusite is fused with hydroxide of sodium or potassium in the presence of air manganite first formed is converted into a dark green mass of corresponding manganate as follows:

$$MnO_2 + 2KOH \rightarrow \underset{\textbf{Potassium manganite}}{K_2MnO_3} + H_2O$$

$$2K_2MnO_3 + O_2 \rightarrow \underset{\textbf{Potassium manganate}}{2K_2MnO_4}$$

The dark green mass of potassium manganate is dissolved in a small quantity of cold water to form a dark green solution from which dark green crystals of potassium manganate may be obtained on concentration.

Conversion of potassium manganate to potassium permanganate:

Any of the following methods can be used for preparing potassium permanganate.

1. When green concentrated solution of potassium manganate is gently warmed, or largely diluted with water, the green color changes to pink owing to the formation of potassium permanganate. Potassium manganate is stable in alkaline solutions or in pure

water. But even at race of acid, like carbonic acid, is enough to bring about its disproportionation:

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

2. Potassium manganate may also be converted in to potassium permanganate by oxidation either chemically with chlorine or ozone or electrolytically at the anode.

Chemical oxidation:

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2.$$

Anodic oxidation:

$$\underset{\textbf{green}}{MnO_4^{2-}} \rightarrow \underset{\textbf{purple}}{MnO_4^-} + e^- \text{ (at anode)}$$

Physical properties:

Potassium permanganate forms dark purple red rhombic prisms. It is sparingly soluble in water (5.31 g in 100mL at 298K) giving a deep purple coloured solution which is opaque until very dilute. The crystals on heating evolve oxygen and form a black powder of potassium manganate and manganese dioxide.

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

Chemical properties:

Potassium permanganate is a powerful oxidizing agent. The action is different in acidic, neutral and alkaline solutions.

(i) In acidic solution, two molecules of permanganate furnish five atoms of oxygen as follows:

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

In ionic form the equation is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Ferrous sulphate is oxidized to ferric sulphate by acidified potassium permanganate.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

or

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Sulphur dioxide is oxidized to sulphuric acid:

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

or

$$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

(ii) In neutral solution the main reaction is:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

$KMnO_4$ oxidises Mn^{2+} salts to MnO_2 and H_2S to Sand SO_4^{2-} as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

$$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$$

(iii) In alkaline solutions the main reaction is:

$$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$$

In ionic form the equation is:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}$$

However, MnO_4 is further reduced to MnO_2 hence the complete equation representing the oxidizing behaviour of $KMnO_4$ in alkaline solution is same as in neutral medium

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2^- + 4OH^-$$

Alkaline permanganate oxidizes iodides to iodates and ethene to ethylene glycol:

$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

$$2KMnO_4 + 3CH_2 = CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2 - CH_2OH + 2KOH$$

Uses:

1. Potassium permanganate is used as an oxidizing agent in the laboratory and in industry.
2. Because of its oxidizing properties, it is used for disinfecting wells and lake water, as mouth wash, for washing wounds and gargling during throat infections.
3. It is used as a reagent in volumetric analyses for estimating Fe(II) ion, oxalic acid, oxalate ion, sulphites and hydrogen peroxide.

Intext Questions23.6

1. How is potassium manganate converted into potassium permanganate?

....

2. Give reactions of $KMnO_4$ to show that it acts as an oxidizing agent in neutral, alkaline and acidic medium..

....

3. Why is $KMnO_4$ added to wells and lakes from where water is drawn for drinking?

....

4. Write down the chemical formulae of pyrolusite ore, potassium permanganate and potassium manganate.

....

5. In which medium (acidic, basic or neutral), $KMnO_4$ acts as better oxidizing agent?

....

6. What is the color of K_2MnO_4 and of $KMnO_4$?

....

7. What are the oxidation states of Mn in MnO_2, K_2MnO_4 and $KMnO_4$?

....

23.6 f-Block Elements (Lanthanoides and Actinoides)

In addition to *d*-block elements, there are two rows of elements shown separately at the bottom of the periodic table. The elements from La to Lu (14 elements) are called lanthanoides. They are characterised by the filling up of the anti penultimate *4f* orbitals. They are extremely similar to each other in properties. Earlier these were called the rare earths. This name is not appropriate because many of these elements are not particularly rare. Now these elements are known as inner transition elements (because they form transition series within the *d*-block transition elements) or lanthanoids.

23.6.1 Lanthanoides

23.6.1.1 Electronic Configuration of Lanthanoides

Lanthanum is the first member of the third transition series, and it has one *5d* and two *6s* electrons. The next element is cerium, which while still retaining two *6s* electrons, has two electrons in the *4f* orbitals and none in the *5d* orbitals. There are 7 separate *4f* orbitals, each of which can accommodate two electrons with opposite spins. The atoms of the elements from cerium to lutetium have two to fourteen electrons in *4f* orbitals, respectively. These elements constitute the first inner transition series known as lanthanides and, although lanthanum itself does not possess any *4f* electrons, it is customary to include this element in this series.

The filling up of the4f orbitals is regular with some exceptions (Table 23.6); the element europium has the outer electronic configuration $4f^7\ 5s^2\ 5p^6\ 5d^0\ 6s^2$ and the next element gadolinium has the extra electron in the *5d* orbital. The element ytterbium has a full complement of *4f* electrons ($4f^{14}\ 5s^2\ 5p^6\ 5d^0\ 6s^2$) and the extra electron in the lutetium atom enters the *5d* orbitals ($4f^{14}\ 5s^2\ 5p^6\ 5d^1\ 6s^2$). Except for lanthanum, gadolinium and lutetium, which have a single *5d* electron, the lanthanoides do not have electrons in the *5d* orbitals.

Table 23.6a: Electronic configuration of lanthanoides

Element	Symbol	Z Atomic no.	Electronic configuration
Lanthanum	La	57	**$[Xe]\ 4f^0\ 5d^1\ 6s^2$**
Cerium	Ce	58	**$[Xe]\ 4f^2\ 6s^2$**
Praseodymium	Pr	59	**$[Xe]\ 4f^3\ 6s^2$**
Neodymium	Nd	60	**$[Xe]\ 4f^4\ 6s^2$**
Promethium	pm	61	**$[Xe]\ 4f^5\ 6s^2$**
Sarnarium	Sm	62	**$[Xe]\ 4f^6\ 6s^2$**
Europium	Eu	63	**$[Xe]\ 4f^7\ 6s^2$**
Gadolinium	Gd	64	**$[Xe]\ 4f^7\ 5d^1\ 6s^2$**
Terbium	Tb	65	**$[Xe]\ 4f^9\ 6s^2$**
Dysprosium	Dy	66	**$[Xe]\ 4f^{10}\ 6s^2$**

Holmium	Ho	67	**[xe] $4f^{11}$ $6s^2$**
Erbium	Er	68	**[Xe] $4f^{12}$ $6s^2$**
Thulium	Tm	69	**[Xe] $4f^{13}$ $6s^2$**
Ytterbium	Yb	70	**[Xe] $4f^{14}$ $6s^2$**
Lutetium	**Lu**	**71**	**[Xe] $4f^{14}$ $5d^1$ $6s^2$**

23.6.1.2 Oxidation states of Lanthanoides:

Lanthanoides in general show +3 oxidation state by losing 3 electrons from the outer valence shell (*6s*, *5d*). exceptionally +2 and +4 oxidation states are also found in the compounds of lanthanides owing to attaining stable electron configuration of $4f^0$, $4f^7$ and $4f^{14}$ shells. By attaining noble gas configuration, Ce can show +4 oxidation state. Ce (IV) is a strong oxidizing agent, even though it can be slowly turned back as Ce(III) on reaction with a reductant hence it is used as an analytical reagent in redox estimations. A similar trend is observed in Pr, Nd, Tb, and Dy which exceptionally display +4 oxidation state in their dioxides (MO_2). These oxides act as oxidizing agents. While Eu and Yb exhibit +2 oxidation state by acquiring stable $4f^7$ and $4f^{14}$ configuration respectively which acts as reducing agents by reverting to the common oxidation state i.e. +3.

23.6.1.3 Color properties of Lanthanoides

Most of the Lanthanide (III) ions are colorful due to incompletely filled *4f* orbitals. In their spectral analysis, these ions show narrow spectral bands due to *f-f* transitions. La^{+3} and Lu^{+3} ions are colorless due to the lack of unpaired electrons in f orbitals. Whereas Ce (IV) shows intense yellow colour owing to charge transfer.

23.6.1.4The lanthanoide contraction

Each succeeding lanthanoide differs from its immediate predecessor in having one more electron in the *4f* orbitals (except for some exceptions as discussed above) and one extra proton in the nucleus of the atom. The *4f* electrons constitute inner shells and are rather ineffective in screening the nucleus; thus there is a gradual increase in the attraction of the nucleus for the peripheral electrons as the nuclear charge increases, and a consequent contraction in atomic radius is observed. For example, the ionic radii of the +3 cations decrease steadily from a value of 115 pm for La^{3+} to a value of 93 pm for Lu^{3+}.The regular decrease in atomic radii with increase in atomic number is known as lanthanoide contraction. The lanthanoide contraction considerably influences the chemistry of the elements, which succeed the lanthanides in the periodic table; for instance the atomic radii of zirconium (At. No. 40) and hafnium (At. No. 72) are almost identical and the chemistry of these two elements is strikingly similar. Incidentally, the density of hafnium (which immediately follows the lanthanides) is almost twice the density of zirconium (which is in the same group).

23.6.1.5 General Characteristics of Lanthanoides:

- These are silver whitish soft solids that can be cut by a knife (Sm exceptionally steel hard).
- Their M.P.s are in the range of 1000-1200 K (Sm melts at 1623 K).

- These are good conductors of heat and electricity.
- Lanthanides on reaction with water form corresponding hydroxides by liberating hydrogen gas.
- On reaction with halogen they form trihalides (LnX_3).
- Lanthanides burn in air to form their oxides (Ln_2O_3).
- Lanthanides on reaction with non-metals like N, S and C can form Nitrides (LnN), Sulphides (Ln_2S_3), and Carbides (LnC_2) respectively only at elevated temperatures.

23. 6. 2 Actinoids

The fourteen elements from Th to Lr have unique properties and are considered Actinoids. (See the Table 23.6b for their Symbol, and electronic configuration)

Table 23.6b: Electronic configuration of Actinoides

Element	Symbol	Z Atomic No	Electronic configuration
Actinium	Ac	89	$6d^1 7s^2$
Thorium	Th	90	$6d^2 7s^2$
Protactinium	Pa	91	$5f^2 6d^1 7s^2$
Uranium	U	92	$5f^3 6d^1 7s^2$
Neptunium	Np	93	$5f^4 6d^1 7s^2$
Plutonium	Pu	94	$5f^6 7s^2$
Americium	Am	95	$5f^7 7s^2$
Curium	Cm	96	$5f^7 6d^1 7s^2$
Berkelium	Bk	97	$5f^9 7s^2$
Californium	Cf	98	$5f^{10} 7s^2$
Einsteinium	Es	99	$5f^{11} 7s^2$
fermium	Fm	100	$5f^{12} 7s^2$
Mendelevium	Md	101	$5f^{13} 7s^2$
Nobelium	No	102	$5f^{14} 7s^2$
Lawrencium	Lr	103	$5f^{14} 6d^1 7s^2$

23.6.2.1 Electronic Configurations of Actinoids

All the actinides have the electronic configuration of $7s^2$ and variable occupancy of the $5f$ and $6d$ subshells. Usually, fourteen electrons are added to the $5f$ orbital, except in thorium (Z = 90), from Pa onwards the $5f$ orbitals are progressively filled up to element lawrencium-103. Similar to lanthanoids, the actinoids' irregular electronic configurations are related to the stability of the f^0, f^7, and f^{14} occupancies of the $5f$ orbitals. As a result, Am and Cm have the configuration [Rn] $5f^7 7s^2$ and [Rn] $5f^7\ 6d^1\ 7s^2$ respectively.

23.6.2.2 Ionic Sizes of Actinoids

The actinoids exhibit the same trend in ionic sizes as lanthanoids. Over the course of the series, the size of the atoms or $M^{+`}$ ions gradually decreases. The actinoid contraction, similar to the lanthanoid contraction, may be used to describe this. However, due to inadequate *5f* electron shielding, the contraction varies more from element to element in this series.

23.6.2.3 Oxidation States of Actinoids

Due to similar energies of *5f*, *6d* and *7s* levels, actinides would exhibit wide range of oxidation states. The known oxidation states of actinoids are listed in Table **23.6c**.

Usually the actinoids have +3 oxidation state. In the first half of the series' elements maximal oxidation state rises from +4 in Th to +5, +6 and +7 in Pa, U, and Np, respectively, but falls in succeeding elements (Table **23.6c**). Similar to lanthanoids, actinoids prefers to have +3 oxidation state than +4 state. However +3 and +4 ions tend to hydrolyze.

23.6c: Oxidation states of 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									

23.6.3 General Characteristics of Actinoids and their Comparison with Lanthanoids

The actinoid metals all have a silvery appearance but differ in their structure. Because of more imperfections in metallic radii than lanthanoids, this structural diversity results. The actinoids are highly reactive metals. On reaction with boiling water form a mixture of oxide and hydride, and they can combine with the majority of non-metals at moderate temperatures. All metals are attacked by hydrochloric acid but are little affected by nitric acid due to the creation of protective oxide layers.

Compared to lanthanoids, actinoids have more complicated magnetic characteristics. The magnetic susceptibility of the actinoids varies with the number of unpaired *5f* electrons, like that of lanthanoids. Actinoids behavior makes it clear that, the early actinoids ionization enthalpies are lower than those of the early lanthanoids. This makes sense because in actinides as the *5f* orbitals begin to fill up, they will penetrate less into the inner core of the electrons. In the actinoids, the outside electrons can form bonds because they are less tightly bound.

When the actinoids and lanthanoids are compared in terms of the many features mentioned above, it becomes clear that the behavior of the actinoids is similar to that of the lanthanoids in the first half of the actinoid series. The lanthanoid and actinoid contractions, both have extended effects on the sizes.

23.7. Some Important Applications of d-block and f-block elements:

- Iron is abundantly used in the construction sector.
- Chromium, manganese, and nickel form strong alloys with carbon.
- Titanium monoxide is used in the pigment industry.

- Manganese dioxide is used in the manufacturing of dry battery cells.
- Zinc, nickel, and cadmium are extensively used in battery cells.
- Copper, silver, and gold are termed as coinage metals.
- Vanadium pentoxide is used in the oxidation of sulfur dioxide in the manufacturing of sulfuric acid.
- Titanium tetrachloride used in Ziegler-Natta Catalysis.
- Silver bromide is used in the photography industry.

Intext Questions23.7

1. How many elements constitute lanthanoide series?

……………………………………………………………………………………………………

2. Why Zr and Hf show almost same properties?

……………………………………………………………………………………………………

3. Write down the electronic configuration of the following in the groundstate: Gd, Lu, Ho, Er.

……………………………………………………………………………………………………

4. Write down the electronic configuration of the following ions: Eu^{3+}, Yb^{3+}, Ce^{4+}.

……………………………………………………………………………………………………

5. What is the maximum oxidation state of an actinoide?

……………………………………………………………………………………………………

6. Write down the electronic configuration of Am and Cm.

……………………………………………………………………………………………………

What You Have Learnt

- Transition elements have partially filled *d*-orbitals either in atomic or ionic state.
- They show general electronic configuration $(n^1)\ d^{1\text{-}10}\ ns^{1,2}$.
- They show high M.P. and B.P. due to strong inter-atomic bonding.
- They show variable oxidation states.
- They form colored ions and compounds.
- They show paramagnetic behaviour.
- They form complexes.
- They form alloy and interstitial compounds.
- Manufacture of $K_2Cr_2O_7$ and $KMnO_4$.
- $K_2Cr_2O_7$ and $KMnO_4$ act as oxidizing agents. These compounds are used in volumetric analysis.
- Electronic configuration of lanthanoids.
- Lanthanoid contraction.
- Special Characteristics of Actinoids.

Terminal Exercises

1. What distinguishes a transition metal from a representative metal?

2. Why zinc is not considered a transition metal?

3. Explain why atomic radii decrease very gradually from Sc to Cu.

4. Write down the ground state electronic configuration of the first row transition elements. Explain their regularities.

5. Write down the electronic configuration of the following ions: V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Cu^{2+}, Sc^{3+} and Ti^{4+}

6. Why do transition elements have more oxidation states than other elements?

7. Give the highest oxidation states for the elements from Sc to Cu.

8. How would you define transition elements? List the properties associated with transition elements.

9. How do the following properties vary in transition elements?

   (a) Stability of the various oxidation states. (b) Ability to form complexes.

10. What do you understand by the terms paramagnetism and diamagnetism? Predict the magnetic moments for Fe^{2+}, CO^{3+}, Ni^{3+} and Cu^{+} ions.

11. *4s* sub-shell is filled prior to *3d*-sub-shell but on ionization *4s* electrons are removed first. Explain.

12. Why does Mn(II) show maximum paramagnetic character amongst the bivalent ions of first transition series?

13. Why is Cu^{2+} ion colored and paramagnetic while Zn^{2+} ion is colourless and diamagnetic.

14. Why do transition elements.

   (a) Show variable oxidation states?
   (b) Form a large number of coordination compounds?
   (c) Give colored and paramagnetic ions?
   (d) Exhibit good catalytic properties?

15. Discuss the main characteristic features of the transition elements with special reference to their atomic size, variable oxidation states, magnetic and catalytic properties.

16. Explain the trends of variations of transition elements:

   (a) melting and boiling points.
   (b) atomic radius in the first transition series.
   (c) trends in ionization enthalpies.
   (d) trends in M^{+}/M and M^{+3}/M^{+2} redox potentials

17. A solution of KMnO4 on reduction yields either a colourless solution or a brown precipitate or a green solution depending on the pH of the solution. What different stages of the reduction do these represent and how are they carried out?

18. A black colour compound [X] of manganese when fused with KOH under atmospheric oxygen gave a green coloured compound [Y]. When the compound [Y] was treated with an oxidizing agent (chlorine or ozone), it gave a purple coloured solution [Z]' Identify X, Y, Z and write the chemical equation.

19. Compound [A] of chromium when treated with sodium carbonate in the presence of atmospheric oxygen gave a yellow coloured compound [B]. Compound [B] on treatment with

acid gave an orange coloured compound [C]. [B] can also be obtained by treatment of [C] with alkali. Identify the compound A, B, C and write the chemical equations.

20. Why do transition elements form a large number of alloys and interstitial compounds?
21. What are lanthanides? Why are they called inner transition elements?
22. What is lanthanide contraction and what are its consequences?
23. Write the electronic configurations of the following in ground state: Eu, Ho and Gd.
24. Describe two oxidizing properties of potassium dichromate.
25. Describe two oxidizing properties of potassium permanganate.
26. Differentiate the Properties of Lanthanides and Actinides.

Answers to Intext Questions

23.1

1. Transition elements are defined as “Elements whose atoms have partially filled *d*-orbitals either in the atomic or in ionic state (common oxidation state).
2. 10 elements constitute the first transition series. These are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn.
3. Since zinc does not have partially filled *d*-orbitals either in atomic or in ionic state.
4. Because there are partially filled *d*-orbitals in Cu^{2+}, Ag^{2+} and Au^{3+}.

23.2

1. General electronic configuration of transition elements is: $(n^1)\ d^{1\text{-}10}\ ns^{1\text{ or }2}$.
2. Sc = $[Ar]3d^1\,4s^2$, Cr = $[Ar]3d^5\,4s^1$, Zn = $[Ar]3d^{10}\,4s^2$, Cu = $[Ar]3d^{10}\,4s^1$
3. Cr^{3+} = $[Ar]3d^3$, Ti^{4+} = $[Ar]3d^0$, Ni^{3+} = $[Ar]3d^7$ and Cu^{2+} = $[Ar]3d^9$
4. Because less amount of energy is required to remove an electron from *4s* instead of *3d* orbital. It is due to the fact that after Sc, *3d,* becomes lower in energy than *4s.*

23.3

1. due to strong inter atomic bonding.
2. due to increase in effective. nuclear charge.
3. due to small size. Size does not increase in the same proportion as the atomic mass.

23.4

1. variable oxidation states.
2. U_2O_5 (contact process for H_2SO_4) and iron (Haber’s process)
3. $ScCl_3$ ($3d^0$), $TiCl_4$ ($3d^0$) and $ZnCl_2$ ($3d^{10}$).
4. Cr^+ because it has partially filled *d*-orbital *i.e.* $3d^5$.
5. Nichrome and brass.
6. V^{4+} $3d^1$ $\sqrt{n(n+2)} = \sqrt{n(1+2)} = \sqrt{3}$=1.73 B.M.,
   Ni^{3+} $3d^7$ n=3, $\sqrt{3(3+2)} = \sqrt{15}$ = 3.83 B.M.,

23.5

1. Chromite ore, Na_2CO_3 and O_2
2. $FeO.Cr_2O_3$.
3. $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
4. $K_2Cr_2O_7 + 4NaCl = 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$
5. $KCr(SO_4)_2.\ 12H_2O$ or $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, tanning of leather and dyeing fabrics.
6. For Cr, +3 is the stable oxidation state but in $K_2Cr_2O_7$ the oxidation state of Cr is +6.
7. $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$. Dichromate changes to chromate.
8. (i) +6 (ii) +6.

23.6

1. By oxidation with ozone or chlorine

   $K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$

   $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$

2. Alkaline:

   $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

   Neutral:

   $2MnO_4^- + 2H_2O + 3Mn^{2+} \rightarrow 5MnO_2 + 4H^+$

   Acidic:

   $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H = O$

3. Because it is used as disinfectant (kill microorganisms)
4. Pyrolusite MnO_2, potassium permanganate $KMnO_4$, potassium manganate K_2MnO_4.
5. In acidic medium, because it liberates 50 atoms or change in oxidation state of Mn is from +7 to +2.
6. K_2MnO_4, green and $KMnO_4$, purple.
7. $MnO_2 = +4$. $K_2MnO_4 = +6$ and $KMnO_4 = +7$.

23.7

1. 14.
2. Due to lanthanide contraction.(Due to same size)
3. $Gd[Xe]\ 5f^7\ 5d^1\ 6s^2$, $Lu[Xe]\ 4f^{14}\ 5d^1\ 6s^2$, $Ho[Xe]\ 4f^{11}\ 6s^2$ and $Er[Xe]\ 4f^{12}\ 6s^2$
4. $Eu^{3+} = [Xe]4f^6$, $Yb^{3+} = [Xe]4f^{13}$ and $Ce^{4+} = [Xe]4f^0$
5. +7
6. $5f^7 7s^2$, $5f^7 6d^1 7s^2$

Chapter 24

COORDINATION COMPOUNDS

You have come across compounds like $Na[Ag(CN)_2]$ and $Na_2[Zn(CN)_4]$. Such compounds are referred to as coordination compounds or complex compounds. Coordination compounds play an important role in the chemical industry and in life itself. For example, the Ziegler-Natta catalyst which is used for polymerization of ethylene, is a complex containing the metals aluminum and titanium. Metal complexes play important role in biological systems. For example, chlorophyll, which is vital for photo synthesis in plants, is a magnesium complex and hemoglobin, which carries oxygen to animal cells, is an iron complex. These are the compounds that contain a central atom or ion, usually a metal, surrounded by a number of ions or molecules. The complexes tend to retain their identity even in solution, although partial dissociation may occur. Complex ion may be cationic, an ionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

Difference between a double salt and a complex

Double salts are formed by the combination of two different salts whereas complex compounds have central metal ion surrounded by ligands. Although both double salts and complexes are formed by the combination of two or more stable compounds in a stoichiometric ratio, they differ in their dissociation pattern. Double salt such as Carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, Potash alum, $K_2Al_2(SO_4)_4.12H_2O$, etc. completely dissociate into simple ions when dissolved in water, while complex compounds dissociate to give complex ion and the counter ions. For example, $K_4[Fe(CN)_6]$ dissociates to give K^+ and $[Fe(CN)_6]^{4-}$ but not into K^+, Fe^{+2}, and CN^- .

In this lesson you will study about the complexes including their nomenclature and nature of bonding in them.

Objectives

After reading this lesson, the learner will be able to:

- State the postulates of Werner's theory;
- Define ligand, Coordination number and Coordination sphere;
- Name simple complexes by IUPAC nomenclature system
- Explain Valence Bond Theory
- Apply VB theory to explain hybridization, shape and magnetic behaviour of the following complexes: $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$
- Bonding, Isomerism and EAN
- Explain Crystal field theory-its applications

- Color properties of Coordination compounds
- Bonding in Metal Carbonyls
- Stability of Coordination complexes and
- Explain the applications of Coordination compounds in extraction of Metals, Qualitative analysis, significance in biology and industrial applications

24.1 Werners' Coordination Theory

Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like $CoCl_3$ reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds:

$CoCl_3.6NH_3$, $CoCl_3.5NH_3$, and $CoCl_3.4NH_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound is different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner's coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence.

The Important postulates of Werner's Theory are:

Metals exhibit two (02) type of valence:

(a) Primary valence (ionizable) (b) Secondary valence (non-ionizable).

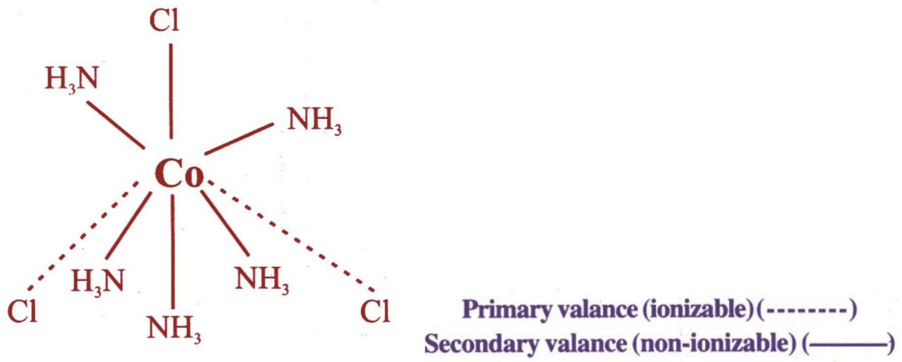
1. Primary or ionizable valence: It is satisfied by negative ions and corresponds to oxidation state of the metal. The Secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence: It is directed toward fixed positions in space *i.e.* this has spatial arrangement corresponding to different coordination number.

For the complexes $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$. the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner's postulate these compounds are formulated as:

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable Ions. On the basis of Werner's theory the structure of $[Co(NH_3)_5Cl]Cl_2$ is:



One of the three chloride ions satisfy both primary and secondary valence.

He also postulated that octahedral, tetrahedral and square planar shapes are more common for coordination compounds of transition elements. Six coordinated complexes such as $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are octahedral whereas four coordinated such as $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are tetrahedral and square planar, respectively.

Intext Questions24.1

1. Explain primary valence.

....

2. Explain secondary valence.

....

3. What is the number of the secondary valence in the following: $[Cr(H_2O)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$?

....

4. What is shape associated with a six-coordinated complex?

....

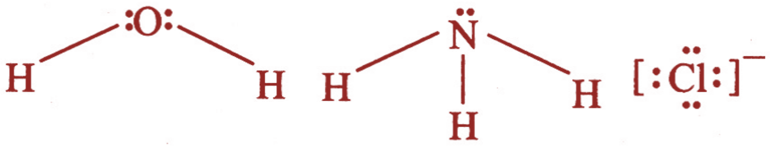
5. How many types of shapes are possible for four-coordinate complexes?

....

24.2 Definition of Some Important Terms

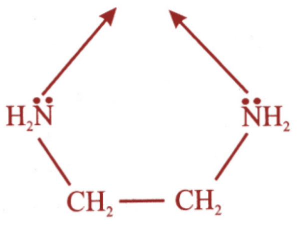
There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

Ligand: the molecules or ions that are attached to the metal in a complex ion are called ligands. The interaction between a metal atom and the ligands can be thought of as Lewis acid-base reaction. As you know a Lewis base is a substance capable of donating one or more electron pairs, every ligand has at least one unshared pair of valence electron. Few examples are shown below:



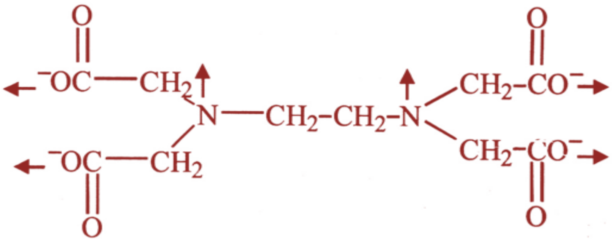
The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu^{2+} is the acceptor atom in the $[Cu(NH_3)_4]^{2+}$ complex ion.

Depending on the number of the donor atoms present, ligands are defined as monodentate, bidentate or polydentate. H_2O and NH_3) are monodentate ligands with only one donor atom in each. Ethylenediamine (en) is a bidentate ligand.



Ethylenediamine

The two nitrogen atoms can coordinate with a metal atom. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw (from the Greek Chele, meaning “claw”) one example is ethylene diaminetetra acetate ion (EDTA), a polydentate (hexadentate) ligand.



Ethylenediaminetetraccetate ion

Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in $[Co(NH_3)_6]^{3+}$ is six. Similarly the coordination number of Ag^+ in $[Ag(NH_3)_2]^+$ is 2, that of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[Fe(CN)_6]^{3-}$ is 6.

Coordination sphere: The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere. The ligands and the metal atom inside the square brackets behave as single constituent unit.

$$\overbrace{[Cr(NH_3)_4Cl_2]}\,Cl$$

Coordination sphere

Oxidation number: Another important property of coordination compounds is the oxidation number of central metal atom. The net charge on a complex ion is, sum of the charges on the central atom and its surrounding ligands. In the $[PtCl_6]^{2-}$ ion for example, each chloride ion has an oxidation number of -1, so the oxidation number of Pt must be +4. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in $[Cu(NH_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of copper is +2.

Central atom/ion: In coordination compounds, the metal atom to which ligands are bound is called Central atom. These ligands surround the central atom in a definite geometrical arrangement. These central atoms/ions are also act as **Lewis acids.**

Intext Questions 24.2

1. What is the coordination number of the metal ion in the following?

(i) $[Co(NH_3)_5C1]^+$ (ii) $[Cr(en)_2Cl_2]^+$ (iii)$[NiC1_4]^{2-}$

....

2. What is the oxidation state of the metal ion in the following?

(i) $[MnCl_6]^{4-}$ (ii) $[Fe(CN)_6]^{3-}$ (iii) $[Cr(NH_3)_6]^{3+}$ (iv)$[Ni(en)_3]^{2+}$

....

3. Give an example of a chelate ligand.

....

4. Give one example of each monodentate, bidentate and polydentate ligand.

....

5. What is the oxidation and coordination number of Co in this $[Co(en)_2(H_2O)CN]^{2+}$ complex ion Which ligand is bidentate in the above complex?

....

24.3 Rules of Nomenclature of Coordination Compounds

We have already discussed about the ligands and oxidation number of metal, our next step is, to learn how to name these coordination compounds. The rules for naming coordination compounds as recommended by IUPAC are as follows:

1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compound, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ first, respectively.
2. Within a complex ligands are named first, in alphabetical order, and the metal ion is named last.
3. The name of anionic ligand ends with the letter ‘O’, whereas a neutral ligand is usually called by the name of the’ molecule. The exceptions are H_2O (aqua), CO (carbonyl) and NH_3 (ammine).

The table given below lists some common ligands:

Table 24.1 : Some Common Ligands

Ligand	Name of the ligand in coordination compounds
Fluoride (F^-)	Fluro
Chloride (Cl^-)	Chloro
Bromide (Br^-)	Bromo
Hydroxide (OH^-)	Hydroxo
Sulphate (SO_4^{2-})	Sulphato
Oxide (O^{2-})	Oxo
Carbonate (CO_3^{2-})	Carbonato
Oxalate ($C_2O_4^{2-}$)	Oxalato
Thiocyanate (SCN^-)	Thiocyanato
Cyanide (CN^-)	Cyano
Isothiocyanate (NCS^-)	Isothiocyanato
Ethylenediamine ($NH_2CH_2CH_2NH_2$)	Etylenediamine
Ammonia (NH_3)	Ammine
Water (H_2O)	Aqua
Carbon monoxide (CO)	Carbonyl
EDTA	Ethylenediamineteracetato

4. When several ligands of a particular kind are present, we use the Greek prefix di, tri-tetra etc. to name them. Thus the ligands in cation $[Co(NH_3)_4Cl_2]^+$ are named as

"tetraammine dichloro" (note thatyrefixes are ignored when alphabetizing ligands). If the ligand itself contains a Greek prefix, we use the prefixes *bis, tris and tetrakis* etc. to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di, therefore, if two such ligands are present the name is *bis* (ethylenediamine).

5. The oxidation number of the metal is written in roman numerals following the name of the metal. For example, the roman numeral III is used to indicate the +3 oxidation state of chromium in $[Cr(NH_3)_4Cl_2]^+$, which is named as tetraamminedichlorochrornium (III) ion.
6. If the complex is an anion, its name ends in -ate. For example, in $K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the numeral (II) indicate the oxidation state of iron. Table given below gives tha name of anions containing metal atoms.
7. If the complex is either a cation or is neutral, no change is required in the name of the central metal ion. For example $[Co(NH_3)_6]^{3+}$ and $[Ni(CO)_4]$ are named as hexaammine cobalt(III)ion and tetracarbonyl nickel(0), respectively.

Table 24.2: Some anions containing metal atoms

Metal	Name of metal in anionic state
Copper	Cuperate
Zinc	Zincate
Aluminum	Aluminate
Chromium	Chromate
Tin	Stannate
Cobalt	Cobaltate
Nickel	Nickelate
Gold	Aurate
Silver	Argentate
Lead	Plumbate
Rhodium	Rhodate
Iron	Ferrate
Manganese	Manganate

A few examples are given below:

$[Co(H_2O)_6]Cl_3$	hexaaquacobalt (III) chloride
$K_2[PtCl_6]$	potassium hexachloroplatinate (IV)
$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum (IV)
$[Co(en)_2Cl_2]Cl$	dichlorobis (ethylenediamine) cobalt (III) chloride.

Intext Questions 24.3

1. Write down the name of the following complexes:

(a) $[Co(NH_3)_4Cl_2]^+$ ....

(b) $(NH_4)_3[Cr(NCS)_6]$ ....

(c) $Ni(CO)_4$ ....

(d) $K_4[Fe(CN)_6]$ ....

(e) $[Cr(en)_3]C1_3$ ....

2. Write down the formula of the following:

(a) Tetrachloronickelate(II) ....

(b) Pentaamminenitrocobalt(III) ion ....

(c) Potassium hexacyanoferrate(III) ....

(d) Dichlorobis(ethylenediammine) chromium(III) ion..

24.4.Valence Bond Theory

Linus Pauling of the California Institute of Technology developed the valance bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling's ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and magnetic properties of metal complexes.

The basic principles, which are involved in the valence bond treatment of coordination compounds are:

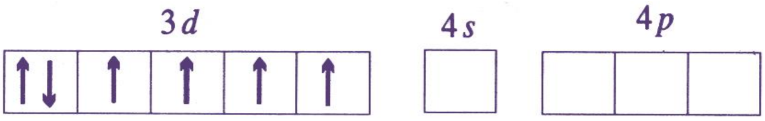
(a) Hybridization of valence orbitals of the central metal/ion

(b) Bonding between ligand and the metal ion/atom.

(c) Relation between the type of bond and the observed magnetic behaviour.

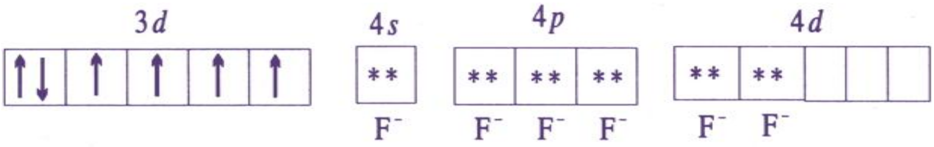
Six Coordinate Complexes

let us explain by taking simple examples such as $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, although in both these complexes the oxidation state of cobalt is +3, but $[CoF_6]^{3-}$ is paramagnetic and $[Co(NH_3)_6]^{3+}$ is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g.Co^{3+}, cobalt atom has the outer electronic configuration $3d^7\ 4s^2$. Thus Co^{+3} ion will have the configuration of $3d^6$ and the electrons will be arranged as:



Co^{+3} ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

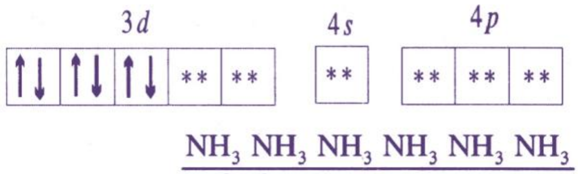
As CO^{3+} ion combines with six fluoride ligands in $[CoF_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one 4*s*, three 4*p* and two 4*d*. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The d-orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. It is shown below:



sp^3d^2, outer orbital complex

Since the outer 4d orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex will be high-spin paramagnetic, because it has four unpaired electrons.

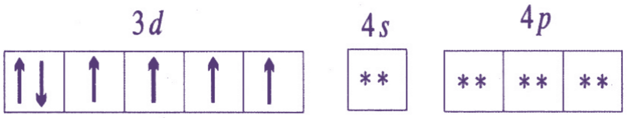
An alternative octahedral arrangement in$[Co(NH_3)_6]^{3+}$, is possible when the electrons on metal ion are arranged as shown below:



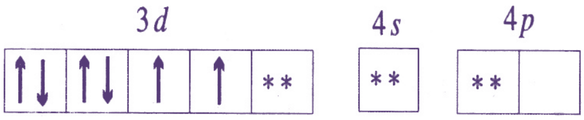
d^2sp^3, inner orbital complex

Since inner *d*-orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin and diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral (sp^3) and square planar (dsp^2):



tetrahedral sp^3



square planar dsp^2

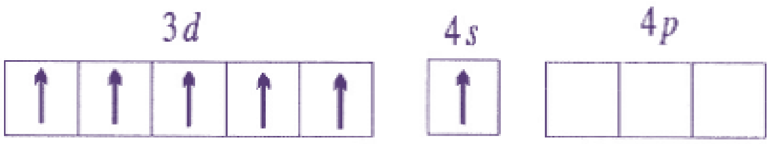
About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:

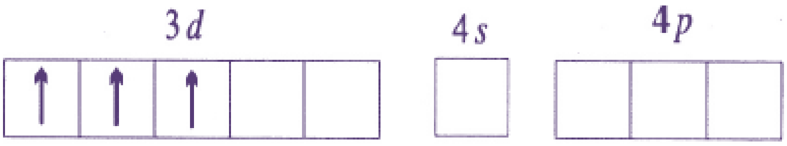
1. $Cr(NH_3)_6]^{3+}$

The electronic configuration of only 3*d*, 4*s* and 4*p* orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr^{3+} ion are given in (i) and (ii) below:

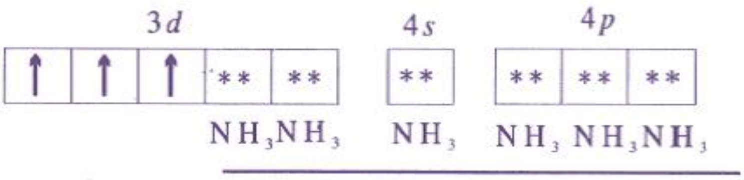
(i) Cr ground state:



(ii) Cr^{3+}



(iii) $[Cr(NH_3)_6]^{3+}$

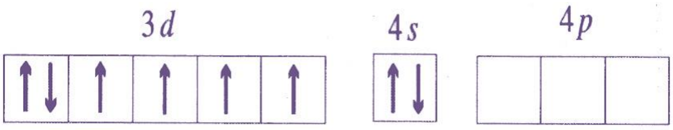


d^2sp^3 (inner orbital)

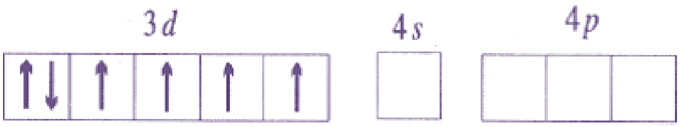
The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be: $\sqrt{n}(n+2)=\sqrt{3}(\sqrt{3+2})=\sqrt{15}=3.87\text{B.M}$

2. $[Fe(CN)_6]^{4-}$

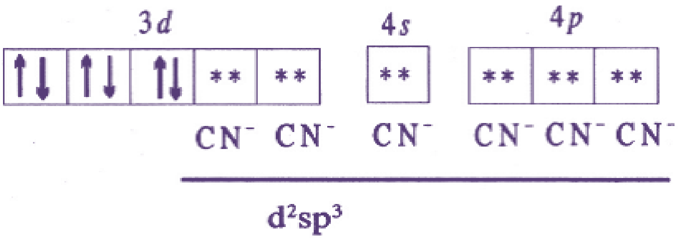
(i) Fe



(ii) Fe^{2+}



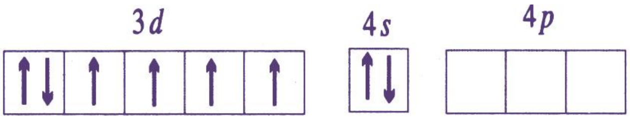
(iii) $[Fe(CN)_6]^{4-}$



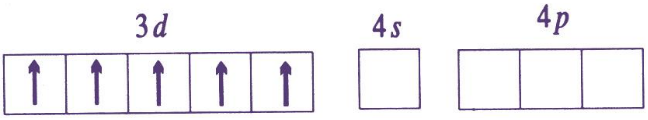
The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diagmagnetic.

3.$[Fe(CN)_6]^{3-}$

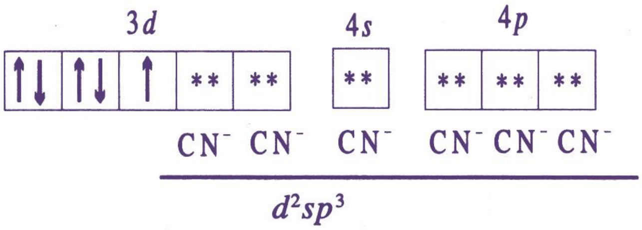
(i) Fe



(ii) Fe^{3+}



(iii) $[Fe(CN)_6]^{3-}$

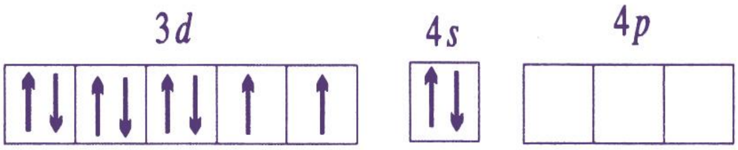


The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

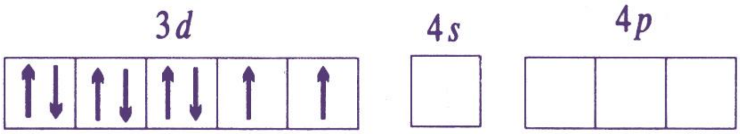
Four coordinate complexes:

1. $[NiCl_4]^{2-}$

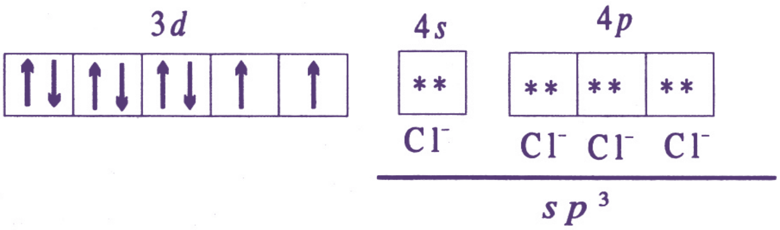
(i)Ni



(ii) Ni^{2+}



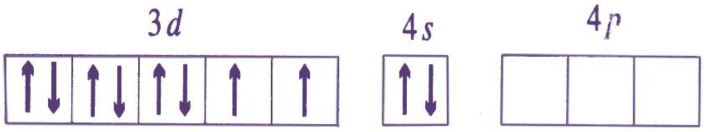
(iii) $[NiCl_4]^{2-}$



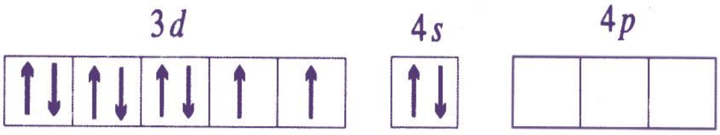
The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. $Ni(CO)_4$

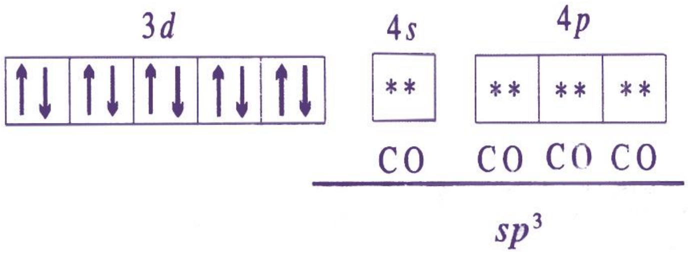
(i) Ni



(ii)Ni(0)



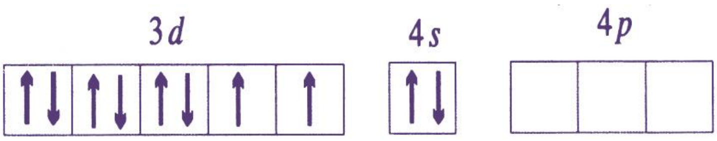
(iii) $Ni(CO)_4$



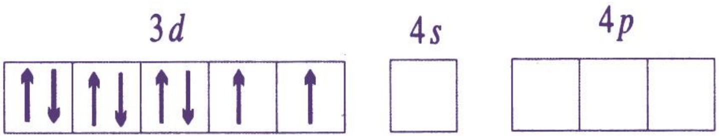
The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

3. $[Ni(CN)_4]^{2-}$

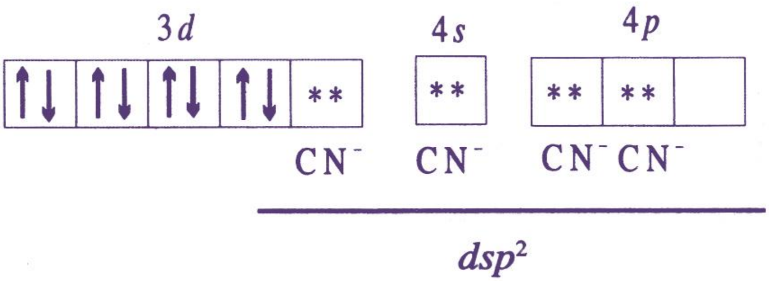
(i) Ni



(ii) Ni^{2+}



(iii) $[Ni(CN)_4]^{2-}$



The resulting complex is square planar and diamagnetic.

Limitations of Valence Bond Theory

- VBT unable to explain the Color and Magnetic properties of Coordination compounds.
- It is unable to explain thermodynamic and kinetic stabilities of Coordination Complexes.
- It does not explain the role of strong field and weak filed ligands in complex formation.
- It is unable to predict the geometries of complexes with coordination number 4{especially square planar of $[Cu(NH_3)_4]SO_4$}.

24.4 Intext Questions

1. Name the type of hybridization present in: $[Co(NH_3)_6]^{3+}$

....

2. $[Fe(CN)_6]^{3-}$ Is diamagnetic or paramagnetic?

....

3. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ have *sp* or *dsp*^{2} hybridization?

....

4. Which one is diamagnetic: $[Ni(CN)4]^{2-}$ or $[NiCl4]^{2-}$?

....

5. What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?

....

24.5. Crystal Field Theory (CFT)

To explain the magnetic properties, color properties, spectral properties, and metal-ligand bonding aspects of coordination complexes, Hans Bethe and John Hasbrouck van Vleck proposed Crystal Field Theory (CFT). According to CFT metal-ligand bonds are established purely due to electrostatic interactions between metal ions and ligands. In the coordination compounds central metal ion serves as a positive point charge and the ligand serves as a negative point charge. The d-orbitals of metal ions in the free gaseous state maintain degenerate (Energetically Equivalent) in a spherically symmetrical field until it interacts with negative point charges of ligands. The ligands when interacting with the central metal atom the symmetrical field disturbs, and the degeneracy will be lost which leads to the splitting of d-orbitals. The splitting pattern of d-orbitals in the complex formation depends on the type of crystal field and geometry of the ligand's approach.

a. Crystal Field Splitting in Octahedral Coordination complexes:

In an octahedral coordination complex, the six ligands approach the d-electron cloud along the x,y, and z axes due to which the repulsion between the electron cloud of the metal d orbitals and the electrons (or negative charges) of the ligands arises. As a result, the d_{xy}, d_{yz}, and d_{xz} orbitals that are directed between the axes will feel lower energies in comparison to the average energy in the spherical crystal field, and the d_{x2-y2} and d_z^2 orbitals that point towards the axes in the direction of the ligand will experience more repulsion. Hence the d_{x2-y2} and d_z^2 orbitals attain higher energy and are denoted as e_g set of orbitals while d_{xy}, d_{yz}, and d_{xz} orbitals attain lower energy which is denoted as t_{2g} set of orbitals.

Crystal field splitting is the splitting of the degenerate levels caused by the presence of ligands in a specific geometry, and the energy separation is given by Δ_o(the subscript 'o' stands for octahedral) (**Fig. 24.1**). As a result, the energy of the three t_{2g} orbitals will decrease by $(2/5)\Delta_o$while the energy of the two e_g orbitals increases by $(3/5)\Delta_o$.

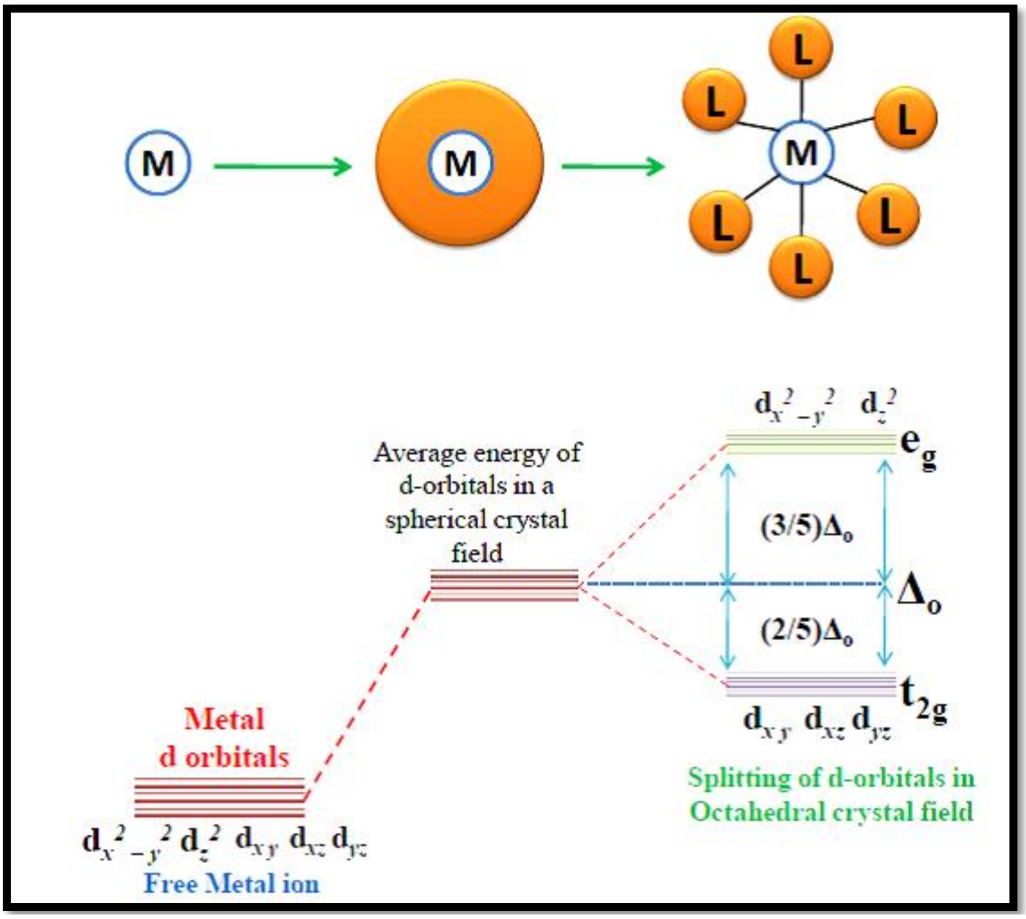


Fig 24.1: Splitting of d-orbitals in an octahedral crystal field

The field generated by ligands and the charge of the metal ion decides the magnitude of Δ_o. The arrangement of increasing order of field strength of various ligands is called a ***Spectrochemical series***.

The increasing field strength arrangement of some ligands given below:

$$\mathbf{I^- < Br^- < S^{-2} < SCN^- < Cl^- < N^{-3} < F^- < OH^- < C_2O_4^{-2} < H_2O < NCS^- < NH_3 < en < CN < CO}$$

The strength of these ligands was calculated by estimating the light absorption capacities of their complexes experimentally. The filling of these degenerate orbitals is based on Hund's rule hence first 3 electrons filled in t_2g set of orbitals (d^1, d^2, d^3) but from d^4 onwards there are two possibilities of filling the incoming electrons which depends on the two factors namely magnitude of Crystal field splitting (Δ_o) and the pairing energy (P). If $P>\Delta_o d^4$ and d^5 electrons get filled in eg set of orbitals ($t_2g^3eg^1$, $t_2g^3eg^2$) whereas if $P < \Delta_O$ the d^4, d^5 and d^6 electrons filled and paired in t_2g set of orbitals ($t_2g^4eg^0$, $t_2g^5eg^0$, $t_2g^6eg^0$). The ligands with $P > \Delta_O$ are known as weak field ligands and those with $P < \Delta_O$ are known as Strong field ligands.

b. Crystal Field Splitting in tetrahedral Coordination complexes:

While in the formation of tetrahedral coordination complex, splitting pattern of *d*-orbital is in a reverse manner to that of octahedral complexes due to the 4 ligands approach in between the axes hence d_{xy}, d_{yz}, and d_{xz} orbitals face more repulsion and acquire higher energy after splitting (**See Fig. 24.2**). This set of orbitals is denoted as '$t_2{}'$ set. Whereas the d_{x2-y2} and $d_z{}^2$ orbitals face comparatively lesser repulsion and acquire lower energy which is denoted as 'e' set of orbitals. The crystal field splitting energy of *d*-orbitals in tetrahedral coordination complexes is 44% lesser than octahedral coordination complexes ($\Delta_t = (4/9)\Delta_o$) which is insufficient for the pairing of the electrons in a lower energized set of orbitals (e set) hence low spin complexes are rarely found with tetrahedral geometry.

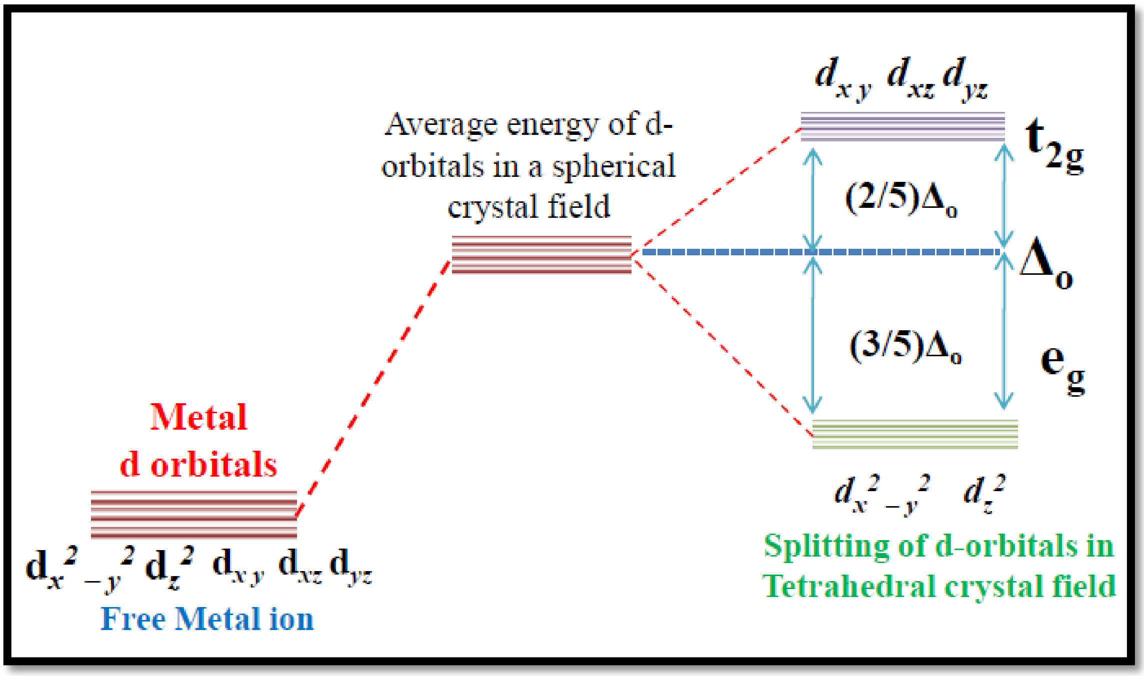


Fig 24.2: Splitting of d-orbitals in tetrahedral crystal field

Limitations of CFT:

- It does not consider the covalent nature of the M-L bond.
- It does not explain why some ligands are weak field and some are strong field.

24.6. Color properties of Coordination complexes:

Most of the d-block elements develop unique colors upon complex formation. The color of the complex depends on several factors like crystal field splitting energy (CFSE), nature of ligand, the charge of the metal ion, etc. The visible color of the complex is complementary to a certain specific electromagnetic radiation that is absorbed. For example, if the complex absorbs red color, which leads to the transmission of blue-green color and appeared in the same color i.e., blue-green. (**see table 24.3**)

According to CFT, the electronic transition from a lower energy level to a higher energy level is allowed and the energy required for this transition was absorbed in the form of its equivalent electromagnetic radiation. For instance, in octahedral complexes, the transition of electrons from t_{2g} to e_g needs certain energy, and light corresponding to that particular energy will be absorbed and its complementary transmitted color will appear.

Table 24.3 Correlation between wavelength of light absorbed and the color appeared in few coordination complexes

Wave length of light absorbed by the complex (in nm)	Colour of the absorbed light	Colour of the transmitted light
400-435	Violet	Yellow green
435-480	Blue	Yellow
480-490	Green blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow green	Violet
580-595	Yellow	Blue
595-605	Orange	Green blue
605-750	Red	Blue-green

24.7 Bonding in metal carbonyls:

Most of the transition elements can form complexes with carbonyl ligands with a variety of structures (fig. 24.3). These complexes are known as Metal carbonyls which usually have a central metal atom with a zero-oxidation state. These complexes although show simple structures but some complexes exhibit metal-metal bonding. Both σ and π bonding characteristics are found in metal-carbon bonding in these complexes. When the lone pair of electrons present in the p-orbital of carbon donated to a metal atom's empty d-orbital leads to M-C σ-bond formation whereas the pair of electrons of filled *d*-orbitals donated to vacant anti-bonding π* orbital of CO leads to M-C π-bond formation. Due to this mutual electron sharing between metal and CO results in strong and stable bonding. (See fig. 24.4)

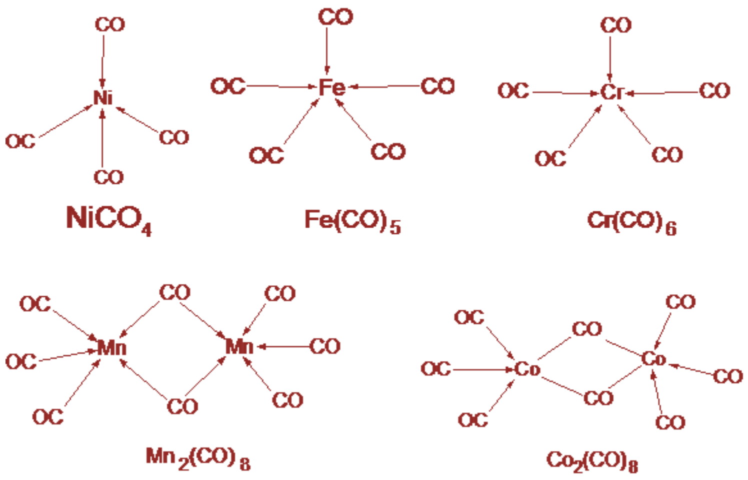


Fig. 24.3: Structures of few basic metal carbonyls

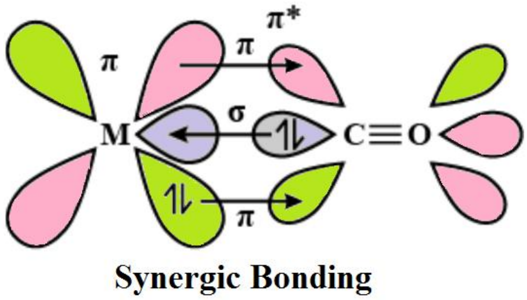


Fig. 24.4: Representation of synergic bonding in metal carbonyl.

24.8 Stability of coordination compounds:

The Stability of a coordination compound in solution refers to the degree of association between the metal ion and the ligands involved in the equilibrium. The value of equilibrium constant or the degree of association is related to its stability. Consider a reaction of the type:

$$M + 4L \rightleftharpoons ML_4$$

If the value of stability constant is more, higher proportion of ML_4 exists in solution than free metal. Usually, free metal ion does not exist, as it prefers to surround itself by solvent molecules, and also it competes with the ligand, L, successively replaced by them. Following are the reactions takes place with 4 stability constants:

$$M + L \rightleftharpoons ML \quad K_1 = [ML] / [M][L]$$
$$ML + L \rightleftharpoons ML_2 \quad K_2 = [ML_2] / [ML][L]$$
$$ML_2 + L \rightleftharpoons ML_3 \quad K_3 = [ML_3] / [ML_2][L]$$
$$ML_3 + L \rightleftharpoons ML_4 \quad K_4 = [ML_4] / [ML_3][L]$$

Where K_1, K_2 etc., are referred to as **stepwise stability constant**. Alternatively, we can write this as:

$$M + 4L \rightleftharpoons ML_4 \quad \beta_4 = [ML_4] / [M] [L]^4$$

The stepwise and overall stability constant are therefore related as follows:

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \text{ or more generally,}$$
$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots\ldots K_n$$

If we take as an example, the steps involved in the formation of Cuprammonium ion we have the following:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+} \quad K_1 = [Cu(NH_3)^{2+}]/ [Cu^{2+}][NH_3]$$
$$Cu(NH_3)^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+} \quad K_2 = [Cu(NH_3)_2^{2+}]/[Cu(NH_3)^{2+}][NH_3] \text{ etc.}$$

Where K_1 , K_2 are the stepwise stability constants and overall stability constant is

$$\beta_4 = [Cu(NH_3)_4^{2+}] / [Cu^{2+}][NH_3]^4$$

The addition of the four amine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case the four constants are:

$$\log K_1 = 4.0,\ \log K_2 = 3.2,\ \log K_3 = 2.7,\ \log K_4 = 2.0 \text{ or } \beta_4 = 11.9$$

The **dissociation constant** of coordination compounds is defined as reciprocal of the formation constant$(\frac{1}{\beta n})$.

24.5 Intext Questions5

1. According to CFT in octahedral complexes the energy of the three t2g orbitals will decrease by how much?

…………………………………………………………………………………………

2. Write the increasing field strength arrangement of following ligands?

CO, en, Cl^-, I^-, Br^-, S^{-2}

…………………………………………………………………………………………

3. How much crystal field splitting energy of *d*-orbitals in tetrahedral coordination complexes is lesser than octahedral coordination complexes?

…………………………………………………………………………………………

4. What are the factors which will affect the colour of coordination complexes?

…………………………………………………………………………………………

5. What is the usual oxidation state of metal in metal carbonyl?

…………………………………………………………………………………………

6. What is the dissociation constant of coordination compounds?

…………………………………………………………………………………………

24.9 Applications of Coordination Compounds

Coordination compounds are found in living systems and have many uses in the home, in industry and in medicines. A few examples are given below:

Extraction of metals:

cyanide ions are used for the extraction of gold and silver. The crushed ore is heated with an *aq.* cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion $[Au(CN)]^-$.

$$4Au(s) + 8CN(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq) + 4\,OH^-(aq)$$

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound $Ni(CO)_4$ and then decomposing the latter to pure nickel.

Medicines:

EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin cis$[Pt(NH_3)_2Cl_2]$ is used in the treatment of cancer. Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ is used to lower blood pressure during surgery.

Qualitative Analyses:

complex formation is useful for qualitative analyses.

a) Separation of Ag^+ from Pb^{2+} & Hg^{2+}
   a. $Ag^+ + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+$
      Soluble
b) Separation of IIA and IIB groups:
   a. The cations of IIB group form soluble complex with yellow ammonium sulphide.
c) Cu^{2+} ion forms complex on addition of ammonia $[Cu(NH_3)_4]^{2+}$.
d) Fe^{2+} forms a blue complex with $K_3Fe(CN)_6$, i.e. $K\,Fe^{II}[Fe^{III}(CN)_6]$.
e) Cobalt (II) gives color with HCl due to the formation of complex $[CoCl_4]^{2-}$.
f) Nickel forms a red complex $[Ni(DMG)_2]$with dimethylglyoxime (H_2DMG).
g) Due to the unique color formation during the formation of coordination compounds, many metal ions are qualitatively and quantitatively analyzed using the complex formation especially with chelating ligands like DMG (dimethylglyoxime), EDTA, Cupron, β-Naphthol, etc. For example, the hardness of water can be estimated by calculating the concentration of Ca^{+2} and Mg^{+2} ions using their complex formation with EDTA by applying titrimetric methods.

Significance in Biology:

Coordination complexes play an important role in biological and physiological pathways. The photosynthetic pigment, chlorophyll is a coordination complex of Mg while Hemoglobin which is an oxygen-carrier pigment contains a Fe-coordination complex. Vitamin B_{12} (Cyanocobalamin) is also the coordination complex having Cobalt as a central metal atom.

Industrial Applications:

- Many catalysts with synthetic and industrial importance were designed using coordination complexes. Wilkinson catalyst used in the hydrogenation of alkenes is as Coordination complex of Rhodium ($[(Ph_3P)_3RhCl]$).
- Formation of complex $Ag[S_2O_3)_2]^{-3}$is used in Photography to dissolve non-reactive AgBr using Hypo solution.

24.6 Intext Questions

1. Name two elements which are extracted by complexation.

....

2. What is the use of EDTA in medicine?

....

3. Name the compound of platinum which is used as anti-cancer agent?

....

4. Give two uses of complexes in qualitative analyses

....

What You Have Learnt

- Coordination compounds are compound in which a central metal ion is attached to a group of surrounding ligands by coordinate covalent bond. Ligands can be monodentate or polydentate, depending upon the number of donor atoms attached to the metal. Polydentate ligands are also called chelating agents. They form complexes that have rings of atoms known as chelate rings.
- The number of donor atoms bonded to a metal is called the coordination number of the metal. Common coordination number and geometries are 2(linear), 4(tetra hedral and square planar), and 6(octahedral).
- Systemic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.
- Valence Bond Theory describes the bonding in complexes in terms of two-electron, coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands; sp(linear), sp^3(tetrahedral), dsp^2(squareplanar) and d^2sp^3 or sp^3d^2(octahedral).
- Crystal field theory describes the splitting pattern of *d*-orbitals due to metal ligand interactions. This splitting factor is different in octahedral and tetrahedral coordination complexes. CFT explains geometries, color properties and magnetic properties of coordination complexes.
- According to CFT, the electronic transition from a lower energy level to a higher energy level is allowed and the energy required for this transition is absorbed in the form of its equivalent electromagnetic radiation.
- The Stability of a coordination compound in solution refers to the degree of association between the metal ion and the ligands involved in the equilibrium. The value of equilibrium constant or the degree of association is related to its stability.
- Complexes are very useful in qualitative analyses, in medicine and industry. Coordination complexes play a significant role in biological systems.

Terminal exercise:

1. Differentiate the coordination complexes and double salts.

2. Define the following: (i) Coordination number (ii) Coordination sphere
(iii) Oxidation number (iv) Central metal atom/ion

3. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.

4. Write the postulates of Werner's theory of coordination compounds.

5. Write down the name of the following complexes:
(i) $K_3[Cr(C_2O_4)_3]$ (ii) $[Co(NH_3)_2(H_2O)_2Cl_2]^+$ (iii) $[Pt(en)_2]^{2+}$ (iv) $[NiCl_4]^{2-}$ (v) $[Fe(CN)_6]^{4-}$

6. Write down the formulae of the following complexes:
(i) Tris(ethylenediamine)platinum(IV) (ii)Tetraaquadibromo cobalt(III)ion
(iii)Sodiumtetraiodozincate(II) (iv)Tetracyanonickelate(II)ion
(v)Dichlorotetrathiocyanatochromium(III)ion

7. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?

8. $[NiCl_4]^{2-}$ and $Ni(CO)_4$ are tetrahedral but differ in magnetic behaviour ,explain.
9. $Ni(CO)_4$and $[Ni(CN)_4]^{2-}$ are diamagnetic but have different geometries, explain.
10. $[NiCl_4]^{2-}$is paramagnetic whereas $[Ni(CN)_4]^{2-}$ is diamagnetic, explain.
11. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:
(i) $[Fe(CN)_6]^{4-}$ (ii) $[Cr(NH_3)_6]^{3+}$ (iii) $[Fe(CN)_6]^{3-}$ (iv) $[NiCl_4]^{2-}$ (v) $Ni(CO)_4$
12. Explain the application of complexes in extraction of elements, medicines, qualitative analysis and industries.
13. Explain the splitting pattern of *d*-orbitals in octahedral and tetrahedral complexes.
14. Explain the color properties of coordination complexes.
15. Explain the bonding in the metal carbonyls with examples.
16. Explain the stability constants of coordination compound formation.

Answers to Intext Questions

24.1

1. Primary valence corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions only.
2. Secondary valence of the metal corresponds to coordination number and is satisfied by negative ions or neutral molecules.
3. In both secondary valence is 6.
4. Octahedral.
5. Two *i.e.* Tetrahedral or square planar.

24.2

1. (i) 6 (ii) 6 (iii) 4
2. (i) +2 (ii) +3 (iii) +3 (iv) +2
3. EDTA
4. NH_3, ethylene diammine and EDTA
5. +3, 6, Ethylene diammine.

24.3

1. (i) Tetra ammine dichloro cobalt (III) ion
   (ii) Ammonium hexa isothio cyanatochromate (III)
   (iii) Tetracarbonyl nickel (0)
   (iv) Potassium hexacyano ferrate (II)
   (v) Tris(ethylenediamine)chromium (III) chloride
2. i) $[NiCl_4]^{2-}$ ii) $[Co(NH_3)_5NO_2]^{2+}$ iii) $K_3[Fe(CN)_6]$ iv) $[Cr(en)_3Cl_2]^{+}$

24.4

1. d^2sp^3
2. $[Fe(CN)_6]^{3+}$ is paramagnetic because it has one unpaired electron.
3. Both the complexes have sp^3 (tetrahedral) hybridization.
4. $[Ni(CN)]^{2-}$ is diamagnetic because it is square planar (dsp^2 hybridization). It has no unpaired electron.

5. Inner d^2sp^3, outer sp^3d^2

24.5

1. $(2/5)\Delta_o$ 2. 44% 3. $I^- < Br^- < S^{-2} < Cl^- < en < CO$

4. CFSE, nature ligand, charge of the metal ion.

5. Zero.

6. Reciprocal of the formation constant ($1/\beta n$).

24.6

1. Gold and silver are extracted by cyanide process.
2. EDTA forms soluble complex with elements. It is used in the treatment of lead poisoning.
3. Cis-platin
4. $[Cu(NH_3)_4]^{2+}$ & $[Ni(DMG)_2]$

24.1.a Bonding, Isomerism and EAN rule

Bonding, EAN rule:

- A transition element shall have an incompletely filled d-sub level either in its elemental form or in its chemically significant oxidation state.
- Werner's views of the complex formation were given an electronic basis by N.V. Sidgwick.
- In Complex formation the electron transfer corresponds to the electro valency of the metal. These electrovalent bonds are the primary valencies of Werner.
- The non-ionizable valencies of the metal corresponds to the co-ordinate covalent bonds.
- The ligands possess lone pair or pairs of electrons which are donated to fill the vacant orbitals of the metal and form co-ordinate covalent bonds (or) semi-polar bonds.
- These bonds are indicated by an arrow starting from the donar atom in the ligand to the acceptor metal atom or ion " →"
- The total number of electrons the central metal in a complex possesses after coordination is known as Effective Atomic Number (EAN) of the metal in that complex.
- Effective Atomic Number (EAN) = (z) Atomic number of metal – number of electrons lost by the metal + number of electrons gained by the metal coordination.
- (or)
- EAN = Z- no. of electrons lost by metal (x) + 2 x coordination number (y).
- The metal ion tends to accept the electrons or election pairs from ligands until the total number of electrons on the metal is equal to that of the next inert gas.

EAN of various metals in complexes:

Complex Compound	Central metal	At. no of the metal (z)	no. of electrons lost (x)	no. of electrons gained (y)	EAN z-x+Y
$K_4[Fe(CN)_6]$	Fe	26	2	12	26-2+12=36
$K_3[Fe(CN)_6]$	Fe	26	3	12	26-3+12=35
$[Cu(NH)_4]Cl_2$	Cu	29	2	8	29-2+8=35
$Na_4[PtCl_6]$	Pt	78	4	12	78-4+12=86

24.1.a Intext Questions:

1. What is ligand.

....

24.1.a Answers to Intext Questions:

1. Those groups or atoms or ions possess lone pair or pairs of electrons which donate electron pair to the central metal or metal ion in complex are called ligands.

24.1.b Isomerism in complexes:

Two or more chemical substances with identical chemical composition but with different properties are called isomers. This phenomen on is known as isomerism.

The isomerism in complexes is broadly divided into two types. They are

1) Structural isomerism 2) Stereo isomerism

1) Structural isomerism: Compounds having same chemical formula but different kinds of bonds between the metal and the ligands are called structural isomers and this phenomenon as structural isomerism.

Structural isomerism is further sub-divided into five types.

a) Ionization isomerism:

Compounds which have the same stoichiometric composition but yield different ions in solution are called ionization isomers and this phenomenon as ionization isomerism.

Eg :- $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_5SO_4]B$

b) Hydrate isomerism:

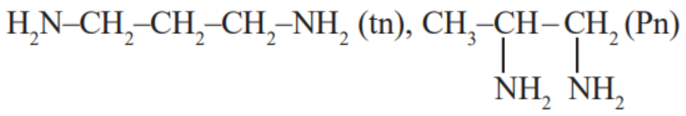
Compounds having same chemical formula, complexes have different places for aqua molecules and this type of isomerism is called hydrate isomerism.

Eg: $[Co(H_2O)_6Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$

c) Ligand isomerism:

When the ligands in different complexes are themselves isomers then this isomerism is called Ligand isomerism.

Trimethylenediamine (tn) and propylene diamine (Pn) are ligand isomers.



$$H_2N\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2\ (tn),\ CH_3\text{–}\underset{NH_2}{\underset{|}{CH}}\text{–}\underset{NH_2}{\underset{|}{CH_2}}\ (Pn)$$

Eg:- $[Co(tn)_2Cl_2]\,Cl\,;\,[Co(Pn)_2Cl_2]Cl$

d) Linkage Isomerism

Linkage isomerism arises in coordination compounds containing ambidentate ligand because ambidentate ligand has two different donor atoms so it can bind to the metal ion in two different ways. Eg: Thiocyanate ligand, (SCN^-) ligand may bind to the metal ion to give M-NCS or M-SCN. Jorgensen observed this ambidentate behavior in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, when the nitrite ligand is bound through oxygen (-ONO), and as the yellow form, when ligand is bound through nitrogen ($-NO_2$)

e) Coordination Isomerism

Coordination isomerism arises due the interchange of ligands between complex cationic and complex anionic parts with different metal ions present in single coordination compound.

Eg: $[Co(NH_3)_6][Cr(CN)_6]$ - In this complex NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}

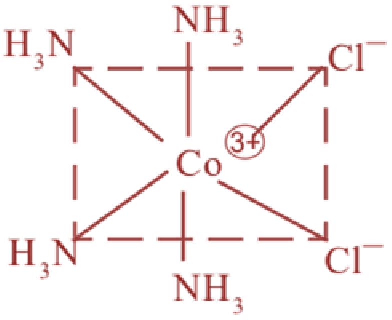
2) Stereo isomerism: Complexes having identical composition of coordination sphere but differ in the relative positions of co-ordination groups are called stereo isomers and this phenomenon as stereo isomerism.

It is sub-divided into two types.

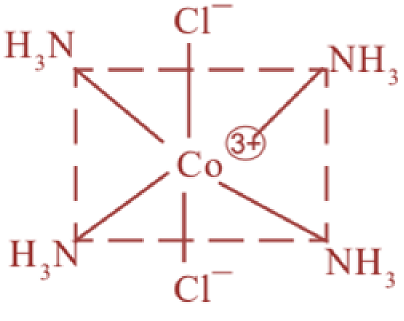
a) Geometrical isomerism: This is known as cis-trans isomerism. The isomers having same geometrical shapes but may differ in the position of the ligands around metal ion is called geometrical isomerism.

If the same ligands are arranged on one side of the metal ion, they are called cis and if they are arrangedin opposite direction, they are called trans isomers.

Eg:-$[Co(NH_3)_4Cl_2]$+



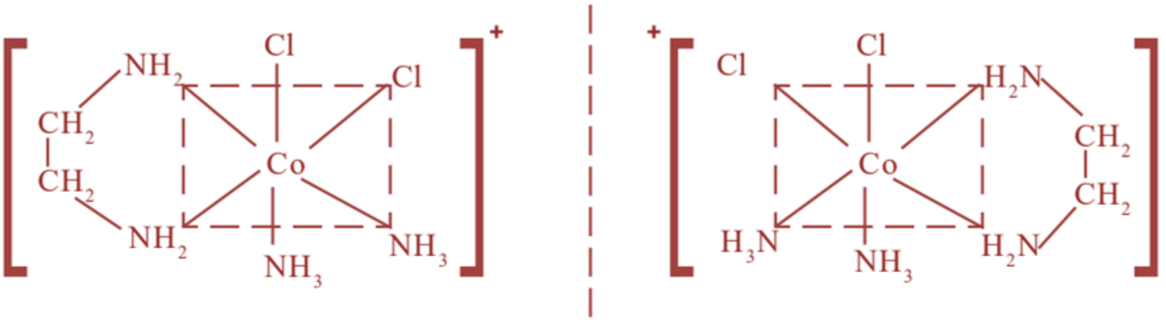
Cis form



Trans form

b) Optical isomerism: It is also called mirror-image isomerism. In two isomers the arrangement of ligand groups around the central metal atom in one isomer is the mirror image of the other and they are non-superimposable. It is called optical isomerism and they are optical isomers. Isomers can rotate the plane polarized light. If the light is rotated to right the substance is called dextro rotatory (or) d-form and if the light is rotated to left it is called Laevo rotator (or) l-Form.

Eg. $[Co(en)(NH_3)_2Cl_2]^+$



24.1.b Intext Questions:

1. How many types of structural isomerism shown in co-ordinate complexes.

....

24.1.b Answers to Intext Questions:

A. five types of structural isomerism are shown co-ordinate complexes these are

1. Ionization Isomerism
2. Hydrate isomerism
3. Ligand isomerism
4. linkage isomerism
5. Coordination isomerism

Module - VII

Chemistry of Organic Compounds

25. Nomenclature and General Principles

26. Hydrocarbons

27. Compounds of Carbon Containing Halogens (Haloalkanes and Haloarenes)

28. Alcohols, Phenols and Ethers

29. Aldehydes, Ketones and CarboxylicAcids

30. Compounds of Carbon Containing Nitrogen

31. Biomolecules

Chapter 25

NOMENCLATURE AND GENERAL PRINCIPLES

Organic compounds are around us in several forms. They are present in a vast range of substances like fuels, foods, polymers and plastics, textiles, dyes, drugs, medicines, explosives, cosmetics, paints and pesticides. The word organic is derived from the word organ because the body of living things is composed mainly of organic compounds. In addition to the organic compounds of animals and plants origin, a large number of them have been synthesized in the laboratory. All organic compounds are known to contain carbon. The carbon atoms have a unique property called 'catenation' which is the ability to form long chains, rings and networks of carbon atoms resulting into the formation of large number of carbon compounds.

The basic organic compounds are hydrocarbons (compounds of carbon and hydrogen) which can be converted to different types of organic compounds by performing different reactions. Organic chemistry is the branch of chemistry which deals with the study of compounds of carbon. Some compounds containing carbon are not studied in this branch of chemistry such as oxides of carbon, metal carbides, metal cyanides, and metal carbonates and these come under 'Inorganic Chemistry'.

This lesson describes various rules for naming of organic compounds based upon IUPAC system. A distinction between different types of bond fission in organic compounds is explained. Various types of reactions and electronic effects are discussed with examples. This lesson also covers types of isomerism.

Objectives

After reading this lesson, you will be able to:

- name various types of organic compounds according to IUPAC system;
- distinguish different types of bond fission;
- explain different types of reactions: substitution, addition, elimination and molecular rearrangements;
- identify nuclophiles and electrophiles;
- explain electronic effects in a covalent bond such as inductive effect, electromeric effect, resonance, hyper conjugation and steric hindrance, and
- explain structural isomerism and stereoisomerism.

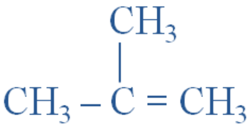
25.1 Classification of Hydrocarbons

All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

1. Open-chain or Aliphatic compounds: This class includes all hydrocarbons (saturated and unsaturated) and their derivatives which have open-chain structures. Saturated hydrocarbons are those which contain single bonds between all carbon atoms such as

$$CH_3 - CH_3 \qquad CH_3 - CH_2 - CH_3$$

On the other hand, unsaturated compounds contain a double (C = C) or a triple (C≡C) bond between two carbon atoms. For example:

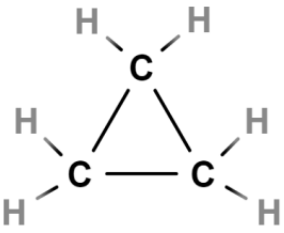


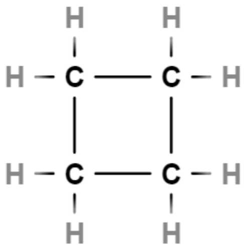
$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_3 \qquad CH_3 - CH = CH_2 \qquad CH_3 - C \equiv CH$$

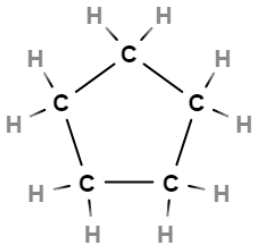
2. Closed-chain or Cyclic compounds: These compounds have atleast one ring (cyclic) system. These are further divided into two sub-classes: homocyclic and heterocyclic based on the atoms present in the ring. They are called homocyclic or carbocyclic when the ring is formed by carbon atoms only.

Homocyclic (carbocyclic) compounds may again be divided into two groups namely alicyclic and aromatic compounds.

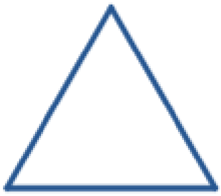
(i) Alicyclic compounds: This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:

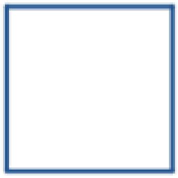


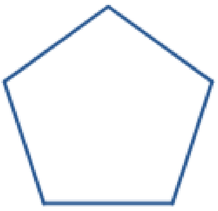




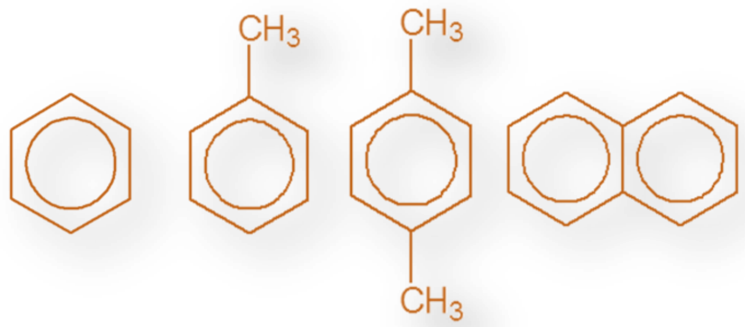
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a CH_2group.



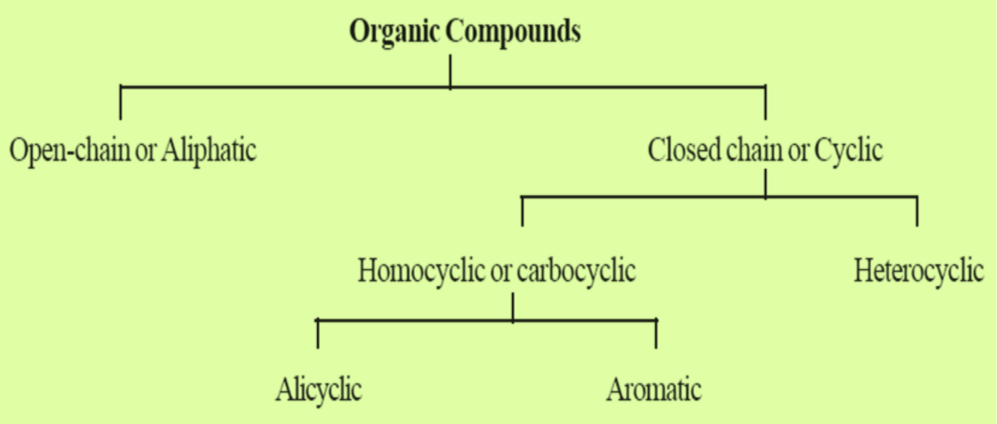




(ii) Aromatic compounds: The group of homocyclic compounds having alternate single & double bonds are called *aromatic compounds*, which will be discussed in Lesson 26. They also have characteristic smell or aroma and hence called *aromatic*. These include aromatic hydrocarbons and their derivatives are examples of such compounds are as follows:

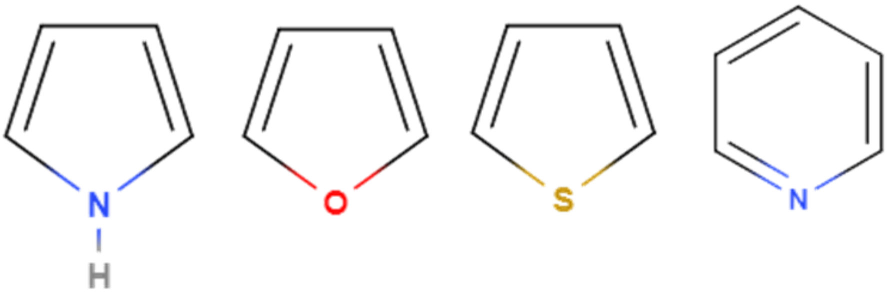


The above classification of the organic compounds can be summarized as below:



On the other hand, heterocyclic compounds contain one or more atom (usually O, N or S atom) other than the carbon atoms.

Some examples of heterocyclic compounds are as follows:



25.2 Nomenclature of Organic Compounds

In the beginning, the organic compounds were named after the source from which they were obtained *e.g.* methane was named as marsh gas as well as damp fire because it was obtained from marshy places. Similarly, formic was named so because it was obtained from red ants (Latin name *formica*). These names of organic compounds are called common names or trivial names. There was no systematic basis for naming them and it was very difficult task to remember the names of so many organic compounds. Even the same compound was known by different names. In order to bring uniformity and rationality in naming the organic compounds throughout the world, International Union of Chemistry (in 1958) came out with a system of nomenclature later known as IUPAC (International Union of Pure and Applied Chemistry) system. Before explaining IUPAC system of nomenclature, we shall discuss about homologous series.

Homologous Series:

A series of compounds in which the molecular formula of a compound differs from those of its neighboring compounds by the CH group, is known as a homologous series. Each of such homologous series is given a general name. For example, homologous series of open chain saturated hydrocarbons is known as alkanes and open chain unsaturated hydrocarbons form two series of compounds namely alkenes and alkynes which contain carbon - carbon double bond and triple bond, respectively. Some members of homologous series of aliphatic hydrocarbons are listed in the Table 25.1.

Table 25.1 : Homologous series of hydrocarbons

Saturated		**Unsaturated**			
General Name : Alkanes		**Alkenes**		**Alkynes**	
General Formula : C_nH_{2n+2}		**C_nH_{2n}**		**C_nH_{2n-2}**	
CH_4	Methane				
C_2H_6	Ethane	C_2H_4	Ethene	C_2H_2	Ethyne
C_3H_8	Propane	C_3H_6	Propene	C_3H_4	Propyne
C_4H_{10}	Butane	C_4H_8	Butene	C_4H_6	Butyne
C_5H_{12}	Pentane	C_5H_{10}	Pentene	C_5H_8	Pentyne
C_6H_{14}	Hexane	C_6H_{12}	Hexene	C_6H_{10}	Hexyne
---	---	---	---	---	---

25.2.1 IUPAC Nomenclature of Acyclic Hydrocarbons

Acyclic hydrocarbons include straight chain as well as branched chain compounds.

(a) Straight chain Hydrocarbons : The names of these hydrocarbons consist of two parts. The first one is word root and second one is suffix. The word root designates the number of carbon atoms in the chain. Special word roots *(Meth-, Eth-, Prop-, But-, etc.)* are used for chains containing one to four carbon atoms but for chains of five and more carbon atoms, Greek number roots such as *Pent -, Hex - etc.* are used in the IUPAC word roots for a few carbon chains are given below in **Table 25.2.**

Table 25.2 : Some Word Roots and corresponding number of carbon atoms

Number of C- Atoms	Word root	Number of C- Atoms	Word root
1	Meth-	6	Hex-
2	Eth-	7	Hept-
3	Prop-	8	Oct-
4	But-	9	Non-
5	Pent-	10	Dec-

The general word root for any carbon chain is *alk*. In order to write the IUPAC name, a suffix is added to the word root to indicate saturation or unsaturation in the hydrocarbons. These suffixes are listed below in the **Table 25.3.**

Table 25.3: Types of hydrocarbons and suffixes in their name

Class of compound	Suffix	General name
Saturated	- ane	Alk**ane**
Unsaturated **($>C=C<$)**	- ene	Alk**ene**
Unsaturated **($-C\equiv C-$)**	- yne	Alk**yne**

Let us consider some examples:

Compound	IUPAC Name	Word root	Suffix
$CH_3CH_2CH_3$	Propane	Prop-	-ane
$CH_3CH_2CH_2CH_2CH_3$	Pentane	Pent-	-ane
$CH_2 = CH_2$	Ethene	Eth-	-ene
$CH_3{-}C \equiv CH$	Propyne	Prop-	-yne

b) Branched chain Hydrocarbons

In branched chain hydrocarbons, one or more alkyl groups are present as side chain attached to the main straight chain of carbon atoms. The carbon atoms of the side chain constitute alkyl groups. These alkyl groups are written as prefixes in the IUPAC name. An alkyl group is obtained from an alkane by removing one hydrogen atom. Since the general formula of alkane is C_nH_{2n+2}, the general formula of alkyl group is C_nH_{2n+1}. The alkyl groups are generally represented by R- and named by replacing the suffix *-ane* of the corresponding alkane by *-yl*. Let us see some examples of the alkyl groups given in the **Table 25.4.**

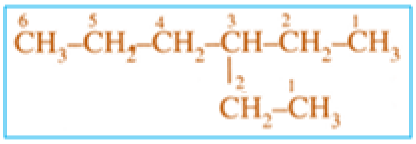
Table 25.4 : Some alkyl groups

Parent Chain	Formula R-H	Alkyl group R	Name
Methane	CH_4	CH_3 -	Methyl
Ethane	CH_3CH_3	CH_3CH_2 -	Ethyl
Propane	$CH_3CH_2CH_3$	$CH_3CH_2CH_2$ -	Propyl
		| CH_3CHCH_3	Isopropyl
Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2$ -	Butyl
		| CH_3CH_2CHCH3	sec-Butyl
Isobutane	CH_3 | H_3C - CH - CH_3	CH_3 | H_3C - CH - CH_2 -	Isobutyl
		CH_3 | H_3C - C - CH_3 |	tert-butyl

Branched chain hydrocarbons are named using the following rules in IUPAC system:

Rule 1. Longest chain Rule: According to this rule, the longest possible chain of carbon atoms is considered and the compound is named as the derivative of the corresponding alkane. *If some multiple bond is present, the selected chain must contain the carbon atoms of the multiple bond.* The number of carbon atoms in the selected chain determines the wordroot and the saturation or unsaturation will determine the *suffix*.

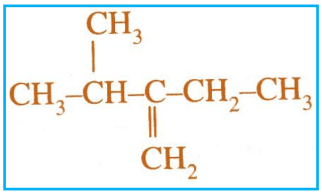
Let us consider the following example:



$$\overset{6}{C}H_3{-}\overset{5}{C}H_2{-}\overset{4}{C}H_2{-}\overset{3}{C}H(\overset{2}{C}H_2{-}\overset{1}{C}H_3){-}\overset{2}{C}H_2{-}\overset{1}{C}H_3$$

Word root **-Hex** + Suffix **-ane**

Since it has a main chain of six carbon atoms; hence, it will be named as a derivative of hexane. Similarly,

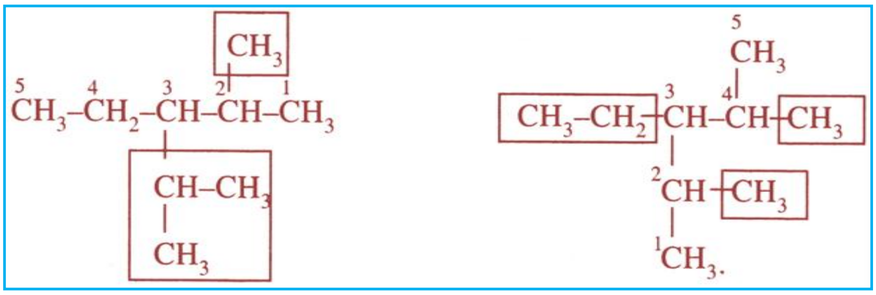


$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_3$

Wordroot -**But** + Suffix -**ene**

The main chain of carbon atoms containing double bond consists of four carbon atoms. Therefore, the compound will be a derivative of butene.

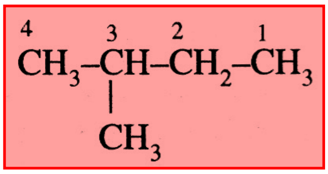
If two equally Long chains are possible, the chain with maximum number of side chains is selected as the main chain.



Main chain has 2 branches **(Wrong)** *Main chain has 3 branches* **(Correct)**

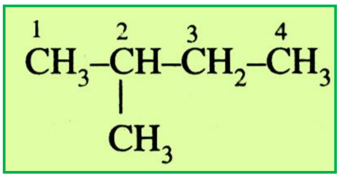
Rule 2: Lowest number or lowest sum rule: The longest carbon chain is numbered from one end to another and the positions of the side chain are indicated by the number of carbon atoms to which these are attached. The numbering is done in such a way that:

a) The substituted carbon atoms have the lowest possible numbers.



$\overset{4}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

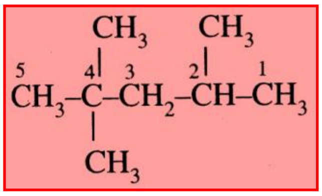
wrong numbering



$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

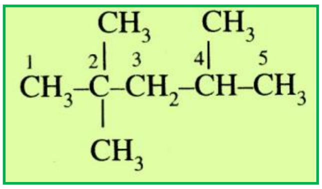
Correct numbering

b) The sum of numbers used to indicate the positions of various alkyl groups must be the lowest.



$\overset{5}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{4}{C}}}-\overset{3}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$

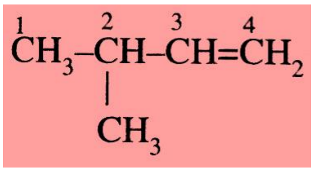
Sum of positions = 2+4+4 = 10
(Wrong)



$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_3}$

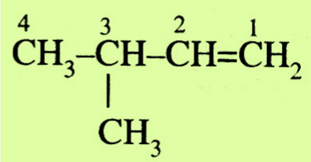
Sum of positions = 2+ 2+4 = 8
(Correct)

Rule 3: If some multiple bond is present in the chain the carbon atoms involved in the multiple bond should get the lowest possible numbers. For example:



$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH}=\overset{4}{CH_2}$

Wrong numbering



$\overset{4}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$

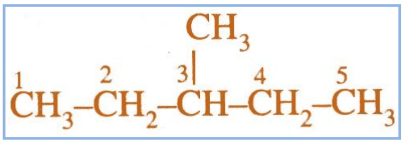
Correct numbering

Rule 4: Naming of compounds with one alkyl group as the substituent (side chain)

The name of a substituted hydrocarbon consists of the following parts.

Position of substituent - Name of *substituent*, Word root, *Suffix*.

Let us consider a compound represented by the following structure:

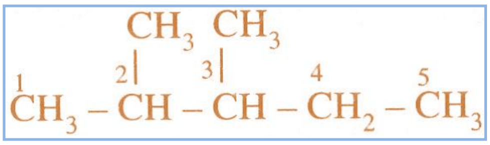


$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{\overset{CH_3}{3|}}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_3$$

In the given structure, we find that the longest chain consists of five carbon atoms and the substituent is *methyl* group at position number 3. The word root is **Pent** and suffix is **ane**. Hence, the name is *3-methylpentane*.

Rule 5: Naming the same alkyl groups at different positions or more than one alkyl groups

If the compound contains more than one identical alkyl groups, their positions are indicated separately and the prefixes *di* (for two), *tri* (for three) etc. are attached to the name of the substituents. The positions of the substituents are separated by commas (,). In the following structure, two methyl groups are attached to the main chain of five carbon atoms.



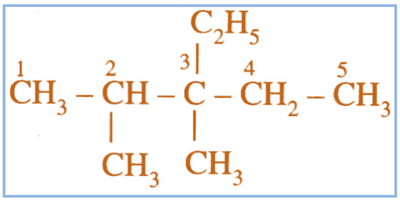
$$\overset{1}{C}H_3-\overset{\overset{CH_3}{2|}}{C}H-\overset{\overset{CH_3}{3|}}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_3$$

You can see that they are attached to the positions 2 and 3 of the main chain. Hence, the name of the compound is 2,3-dimethylpentane.

Rule 6: Naming different alkyl substituents

If there are different alkyl substituents present in the compound, their names are written in the alphabetical order. However, the prefixes *di*, *tri*, etc. are not considered in deciding the alphabetical order.

For example, in the compound shown below the longest chain consists of five carbon atoms; hence, the parent hydrocarbon is pentane. The main chain has two methyl groups at C_2 and C_3 and one ethyl group at C_3 as substituents. The names of these alkyl groups are written before the name of parent alkane and their positions are indicated by number of carbon atom to which they are attached. Thus, the name of the compound will be 3-ethyl-2, 3-dimethylpentane.



$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{3|}}{C}}-\overset{4}{C}H_2-\overset{5}{C}H_3$$

Intext Questions 25.1

1. Identify word *root* and *suffix* for the following:

(i) $CH_3CH_2CH_2CH_2CH_2CH_3$

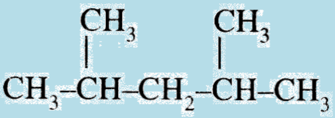
(ii) $CH_3CH_2CH = CHCH_2$

(iii) $CH_3C \equiv CH$

....

2. Give IUPAC name to the following compounds

(i) $CH_3 - CH = CH-CH_2-CH_2-CH_2-CH_2-CH_3$

(ii) 

$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$

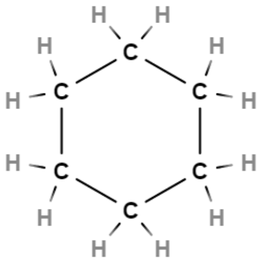
....

25.2.2 Nomenclature of Cyclic Hydrocarbons

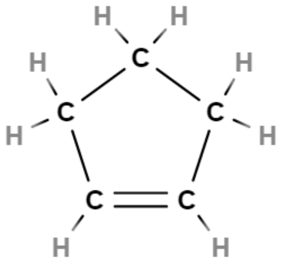
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) Alicyclic Compounds

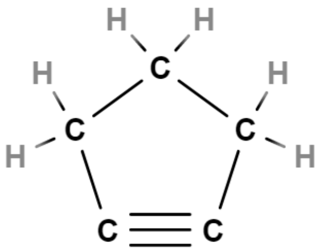
As we have already discussed (in Section 25.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix* **'cyclo'** before the word *root*. The suffix **ane, ene** or **yne** are written according to the saturation or un saturation in the ring structure. Given below are some examples of alicyclic compounds.



Cyclohexane

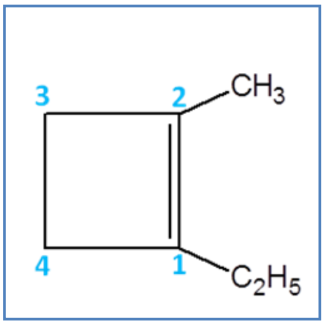


Cyclopentene

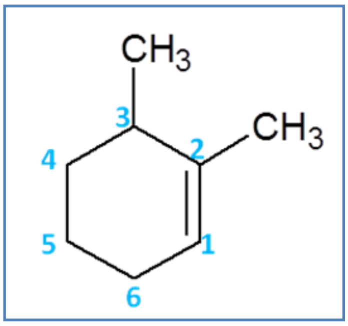


Cyclopentyne

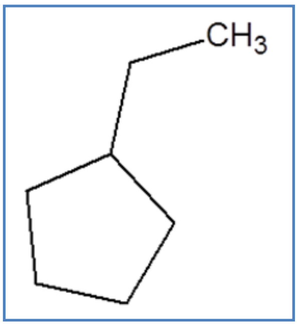
If an alkyl substituent is present, it is indicated by the appropriate prefix and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



l-Ethyl-2-methylcyclobutene



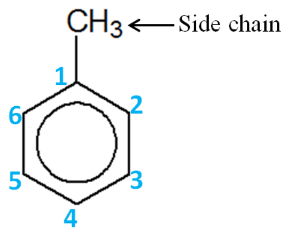
2,3-Dimethylcyclohexene



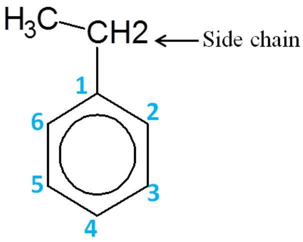
Ethylcyclopentane

b) Aromatic Compounds

The most important members of this class are benzene and its derivatives. For naming an alkyl substituted benzene, the carbon atoms of benzene are numbered from 1 to 6 by giving the lowest possible number to the position of the side chain or substituent. This is shown below.

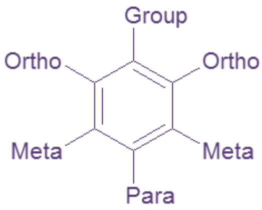


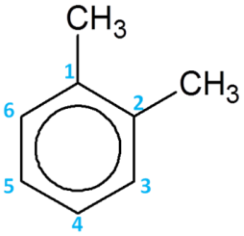
Methylbenzene



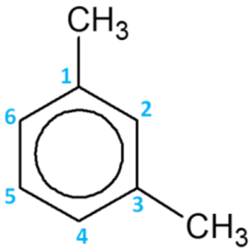
Ethylbenzene

Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1, 2; 1, 3 and 1, 4 derivatives. These are also known as *ortho*- (or *o*-), *meta*- (or *m*-) and *para*- (or *p*-) substituted compounds, respectively.

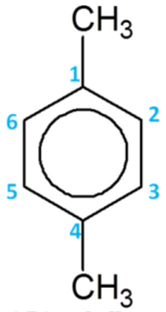




1,2-Dimethylbenzene (Ortho-Xylene)



1,3-Dimethylbenzene (Meta-Xylene)



1,4-Dimethylbenzene (Para-Xylene)

25.2.3 Writing Structure of Hydrocarbons from their IUPAC Names

Till now, we have named hydrocarbons from their structures using IUPAC nomenclature. Let us now do the reverse exercise i.e. writing structure of hydrocarbons when their IUPAC names are given. Let us take some examples to write structures for given IUPAC names.

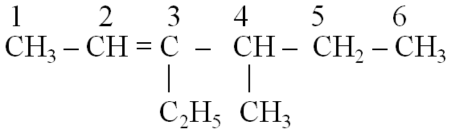
Example 1. Writing the structure of **4-Ethyl-5-methylhex-2-ene**

Step-1: The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C_2 is drawn.

$$\begin{array}{ccccccccccc} 1 & & 2 & & 3 & & 4 & & 5 & & 6 \\ C & - & C & = & C & - & C & - & C & - & C \end{array}$$

Step-2: Attach ethyl group at C_4 and methyl group at C_5.

Step-3: Attach H-atoms to the C-atoms of main chain to satisfy tetravalency of all the carbon atoms, Thus, the correct structure of the compound is as given below:



$$\begin{array}{ccccccccccc} 1 & & 2 & & 3 & & 4 & & 5 & & 6 \\ CH_3 & - & CH & = & C & - & CH & - & CH_2 & - & CH_3 \\ & & & & | & & | & & & & \\ & & & & C_2H_5 & & CH_3 & & & & \end{array}$$

Example 2. Writing the structure of **Octa-3, 5-diene**

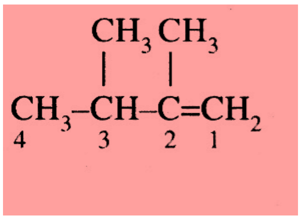
Step 1 The skeleton of parent hydrocarbon chain of **eight** carbon atoms is drawn,

Step 2 Make C = C at C_3 and at C_5.

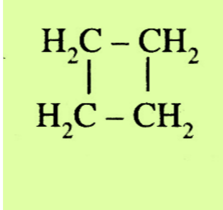
Step 3 Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms, The correct structure of the compound is as follows :

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH}=\overset{6}{CH}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

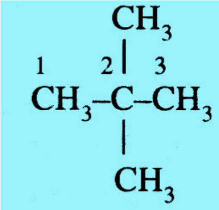
The following compounds illustrate some more examples:



(i) 2,3-Dimethylbut-1-ene



(ii) Cyclobutane



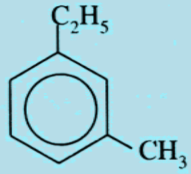
(iii) 2,2-Dimethylpropane

After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.

Intext Questions 25.2

1. Write IUPAC names for the following compounds:

(i)



(ii)

(iii)

....

2. Write the structural formula for the following compounds:
   (i) 1,3-Dimethylcyclohexane (ii) Ethylcyclobutane (iii) n-Propylbenzene

....

25.2.4 IUPAC Nomenclature of Aliphatic Organic Compounds Containing Functional Groups

A **functional group** is an atom or group of atoms which is responsible for characteristic properties of a compound. For example :

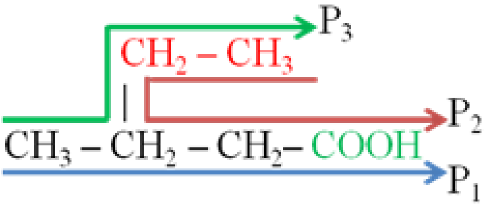
–Cl, –Br, –I, –COOH, –OH, $–NH_2$ etc.

a) Compounds with one functional group (monofunctional Derivatives):

The derivatives of hydrocarbons containing only one functional group are called monofunctional derivatives.

Most of the IUPAC names of functional derivatives of hydrocarbons are derived by replacing the suffix ***-ane*** of the parent alkane (corresponding to the number of carbon-atoms in the longest chain) by a specific *suffix* for the functional groups, (***see Table 25.5***). There are some derivatives in which a particular *prefix* is added to the parent alkane name as in *nitroalkanes, haloalkanes, and haloarenes etc.* Given below are some rules for the IUPAC nomenclature of organic compounds containing functional groups. In addition to the *rules listed below*, all the general rules discussed earlier for naming of hydrocarbons are also applicable to such compounds.

Rule 1: First of all the longest chain of carbon atoms containing the functional group is identified. In case of carbon containing functional group, (-CHO, - COOH) the main chain must include the carbon atom of the group.

For Example: 

$CH_3-\overset{CH_2-CH_3}{\overset{|}{CH_2}}-CH_2-COOH$

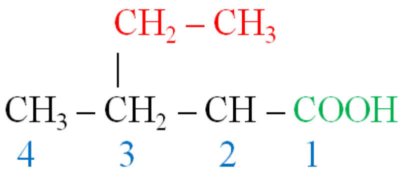
Structure-I

P_1 or P_2 are correct selections of chain of carbon atoms whereas P_3 is wrong selection as it does not include the carbon atom of the functional group.

Rule 2: The longest continuous carbon atom chain is numbered from that end which will give the lowest number to the carbon atom bearing the functional group (-*COOH is 1*).

Rule 3: There is a specific suffix for each functional group that replaces the ending -e in the name of the corresponding parent alkane. For –COOH, it is –*oic acid.*

Rule 4: If the carbon chain is branched, then the attached alkyl groups are named and numbered as in Structure I (rule 1) main chain contain a branch of two carbon atoms i.e., ethyl group at position 2.



$\underset{4}{CH_3}-\underset{3}{\overset{CH_2-CH_3}{\overset{|}{CH_2}}}-\underset{2}{CH}-\underset{1}{COOH}$

Structure-I

Rule 5: While writing the name of the compound, place the substituents in the alphabetical order.

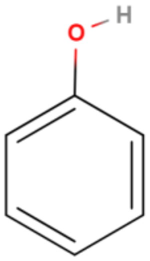
Table 25.5 list of some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

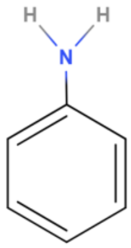
Table 25.5. Some Common Functional Groups and their Aliphatic Derivatives

Functional Group	Suffix/Prefix	General Name	Example (IUPAC name)
–OH(Hydroxy)	*–ol*	Alkanol(Alcohols)	CH_3CH_2OH(Ethanol)
–COOH(Carboxyl)	*–oic acid*	Alkanoic acid	CH_3COOH (Ethanoic acid)
$–SO_3H$(Sulphonic)	–sulphonic acid	Alkysulphonic acid	$CH_3CH_2SO_2H$ (Ethyl sulphonic acid)
–CHO(Aldehydic)	*–al*	alkanal	CH_3CHO (Ethanal)
>CO(Ketonic)	*–one*	Alkanone	CH_3COCH_3(Propanone)
$–CONH_2$(Amide)	*–Amide*	Alkanamide	CH_3CONH_2 (Ethanamide)
–COX(Carboxyl halide)	*–oyl halide*	Alkanoyl halide	CH_3COCl (Ethanoyl chloride)
–COO– (Ester)	*–oate*	Alkanoyl alkanoate	CH_3COOCH_3 (methyl ethanoate)
–CN(Cyano)	*–nitrile*	Alkanenitrile	CH_3CH_2CN (Propanenitrile)
–SH(Thiol)	*–Thiol*	alkanethiols	CH_3CH_2SH(Ethanethiol)
$–NH_2$(Amino)	*–amine*	Alkanamine	$CH_3CH_2NH_2$(Ethanamine)
–O– (Ether)	*–oxy*	Alkoxyalkane	CH_3-O-CH_3 (Methoxymethane)
–C≡C– (yne)	*–yne*	Alkyne	$CH_3C= CCH_3$(But-2-yne)
–C=C– (ene)	*–ene*	Alkene	$CH_3CH=CHCH_3$

X = –F –Cl –Br –I	*–Halo (Prefix)*	Haloalkane	CH_3CH_2-X (Haloethane)
$–NO_2$(Nitro)	*–Nitro (Prefix)*	Nitroalkane	$CH_3CH_2NO_2$ (Nitroethane)

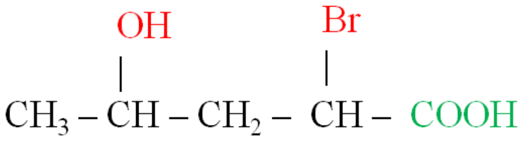
Certain derivatives have some specific general names e.g. monohydroxybenzene is called and monoaminobenzene as aniline.


Phenol


Aniline

b) Naming of Organic compounds with more than one functional group : In case of organic compounds containing more than one functional group, one group is given preference over the other(s) in deciding the parent compound. The priority order of the various functional groups is as follows;

-COOH, -COOR, $-SO_3H$, -COX, $-CONH_2$, -CHO, -CO, -CN, -OH, -SH, -O, $-NH_2$, -X (halogen), $-NO_2$, C = C, and C ≡ C. Let us try to name a polyfunctional compound by following the priority of the functional groups.



$$CH_3-\underset{}{\overset{OH}{\overset{|}{CH}}}-CH_2-\overset{Br}{\overset{|}{CH}}-COOH$$

2-Bromo-4-hydroxypentanoic acid

In the above example, -COOH group is given priority over the OH and Br (halo) groups.

25.3 Types of Reactions in Organic Compounds

You are aware that a chemical reaction occurs when one substance is converted into another substance(s). A chemical reaction is accompained by breaking of some bonds and by making of some others. In organic chemistry, this can happen in more than one way involving a variety of reactions. The different types of reactions in organic compounds are: (i)Substitution (ii) Elimination (iii) Addition and (iv) Molecular Rearrangements.

These different ways of occurrence of organic reactions can be understood by the study of reaction mechanisms. A reaction mechanism gives the detailed knowledge of the steps involved in a process in which the reactant molecules change into products. Let us explain first, some of the terms used in reaction mechanism.

25.3.1 Breaking of a Covalent Bond - Types of Bond Fission

Chemical reactions involve breaking of one or more of the existing chemical bonds in reactant molecule(s) and formation of new bonds leading to products. *The breaking of a covalent bond is known as bond fission.* We know that a covalent bond is formed by the sharing of two electrons from two atoms. During bond breaking or bond fission, the two shared electrons can be distributed equally or unequally between the two bonded atoms. There are two types of bond fission.

1. Homolytic fission : *"The fission of a covalent bond with equal sharing of bonding electrons is known as homolytic fission."*

Homolytic fission in a hypothetical molecule: $A-B \longrightarrow A^{\bullet} + B^{\bullet}$

Now consider the following C - C bond fission:

$$CH_3-CH_3 \xrightarrow[Light]{Heat} \bullet CH_3 + \bullet CH_3$$

(Free radicals)

The neutral species so formed are known as **free radicals**.

Free radicals are neutral but reactive species having an unpaired electron and these can also initiate a chemical reaction.

2. Heterolytic fission : "*The fission of a covalent bond involving unequal sharing of bonding electrons is known as heterolytic fission*". The heterolytic fission of a hypothetical molecule is shown below.

$$A : B \longrightarrow A^+ \quad + \quad B^-$$

Carbocation Carbanion

This type of bond fission results in the formation of *ions*. The ion which has a *positive charge on the carbon atom*, is known as the carbonium ion or a carbocation. For example,

$CH_3\ C^+\ H_2$ (Ethyl carbocation) and $CH_3\ C^+\ HCH_3$ (Isopropyl carbocation)

On the other hand, an ion with a negative charge on the carbon atom is known as the carbanion. For example,

$CH_3C^-H_2$ (Ethyl carbanion), C^-H_3 (Methyl carbanion)

The charged species obtained by the heterolytic fission initiate chemical reactions and they are classified as electrophiles and nucleophiles.

Electrophiles: An electrophile is an electron deficient species and it may be positively charged or neutral. Examples are H^+, NO^+, Br^+, Cl^+, Ag^+, CH_3C^+O, []BF_3 etc. Thus, an electrophile is an electron seeking species and hence, it attacks at a position of high electron density.

Nucleophiles: A nucleophile is negatively charged or electron rich neutral species. Examples of nucleophiles are OH^-, NO^-_2 ; H_2O, **:**NH etc. Nucleophiles attacks a position of low electron density.

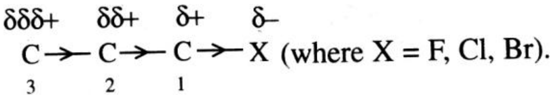
25.3.2 Electron Displacements in a Covalent Bond

For a reaction to take place by breaking of a covalent bond, with the attack of a nucleophile or electrophile, the molecule or bond under attack must develop polarity on some of its carbon atoms. This polarity can only be developed by the displacement (partial or complete) of bonding electrons due to certain effects. Some of these electronic effects are permanent (e.g. inductive) and others are temporary (e.g. electromeric) in nature. Such changes or effects involving displacement of electrons in the substrate molecules (molecule under attack of a reagent) are known as electron displacement or **electronic effects**. Some of these effects are discussed below.

a) Inductive effect: In a covalent bond between the two dissimilar atoms, the shared electron pair is attracted more towards the atom having greater electronegativity. Let us consider the case of a haloalkane (higher than halomethane). The halogen atom (X) being more electronegative than carbon atom, pulls the bonded electrons of the CX bond. Thus, the C-X bond is polarised as shown below.

$$\mathbf{C^{\delta+} \longrightarrow X^{\delta-}}$$

The carbon atom gets a partial +*ve* charge (δ+) and halogen atom a partial negative charge (δ-). This positively charged C, attracts bonded electrons of C_1 - C_2 bond, thus making C_2 atom a little less positive than C_1. Similarly, this +*ve* charge is shifted to C_3 but to a very less magnitude (nearly zero +*ve* charge is present after third atom)



$$\overset{\delta\delta\delta+}{\underset{3}{C}} \rightarrow \overset{\delta\delta+}{\underset{2}{C}} \rightarrow \overset{\delta+}{\underset{1}{C}} \rightarrow \overset{\delta-}{X} \text{ (where X = F, Cl, Br).}$$

“*This transmission of induced charges along a chain of (bonded carbon atoms is known as inductive effect)*”. The inductive effect is a permanent polarisation in the molecule and it decreases as we move along a chain of carbon atoms, away from the electronegative atom. Many of the properties of organic compounds such as acidic strength of carboxylic acids are explained on the basis of inductive effect.

Groups with - I Effect (Electron Withdrawing Groups):

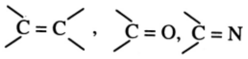
Any atom or group of atoms that withdraws electrons more strongly than the H-atom, is said to have - I effect. Following are various groups arranged in the decreasing order of their -I effect.

$$(CH_3)_3N^+ > -NO_2 > -CN > -F > -Cl > -Br > -I > -OH > -OCH_3 > -C_6H_5 > -H$$

Groups with + I Effect (Electron Releasing Groups):

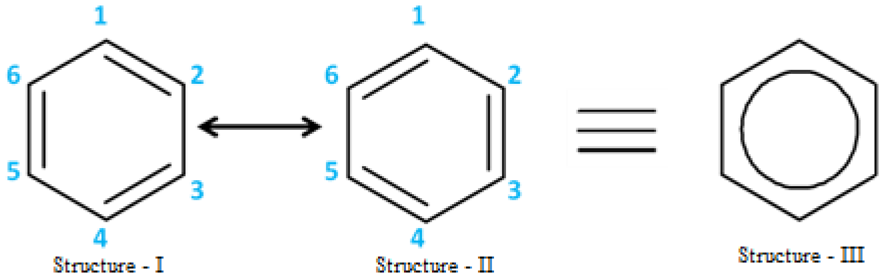
Any atom or group of atoms that releases electrons more strongly than hydrogen, is said to have +1 effect. Following are the various groups in the decreasing order of +I effect.

$$(CH_3)_3C^+– > (CH_3)_2C^+H– > CH_3C^+H_2– > –^+CH_3 > –H$$

(b) Electromeric effect : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g  etc.). It involves the complete transfer of electrons resulting into the development of +*ve* and -*ve* charges within the molecule. The electromeric effect takes place in the direction of more electronegative atom and is generally shown by an arrow starting from the original position of the electron pair and ending at the new position of the electron pair. In a carbonyl group it operates as follows :

The electromeric effect is represented by the symbol **E**. It is known as **+E** effect when displacement of electron pair is away from the atom or group, or E effect when the displacement is towards the atom or group. As in above example it is +E effect for C and -E effect for O.

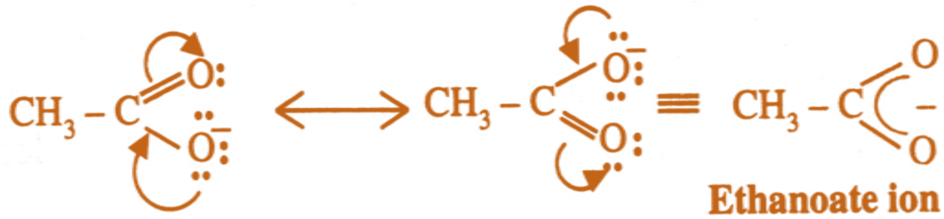
(c) Resonance: This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound are arrived at by the redistribution of valence electrons. The true structure of the compound between all the possible resonating structures or canonical structures and thus called a ***resonance hybrid***. For example, the benzene molecule (C_6H_6) may be represented by the following two structures, I and II.



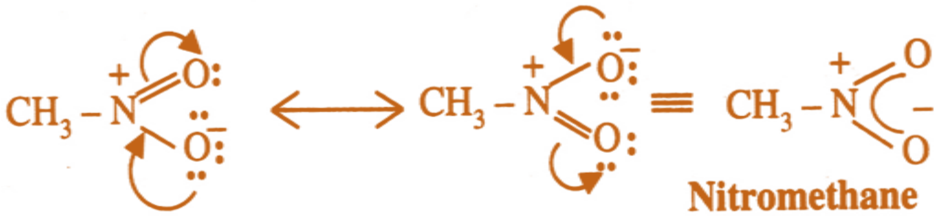
Resonating or Canonical Structures   Resonance hybrid

The evidence in support of the hybrid structure (III) of 'benzene' is available from the bond length data. Equal bond lengths of all C-C bonds (139 pm), which is an intermediate value of C-C single bond (154 pm) and C=C double bond (130 pm) lengths, indicates that each C-C bond in benzene (structure III) has a partial double bond character. Hence, structure III, a resonance hybrid, represents the benzene molecule.

Some more examples of resonance structures are as follows:

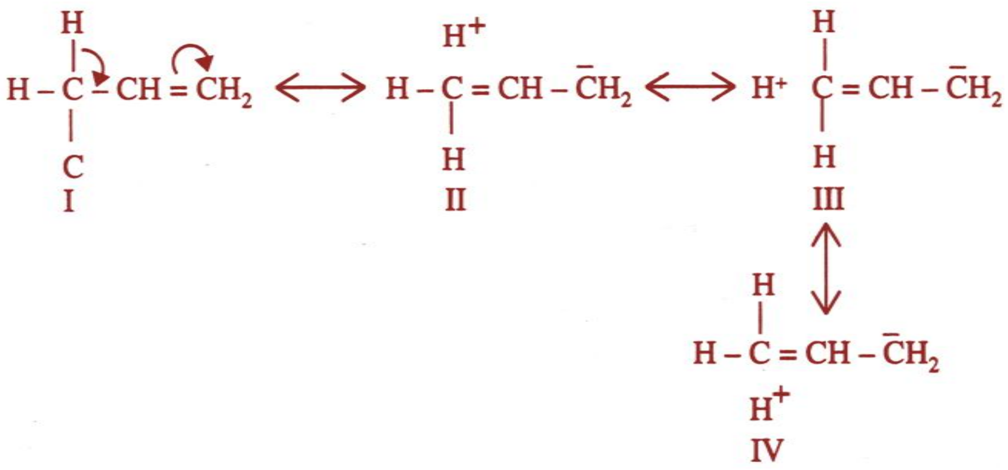


Ethanoate ion



Nitromethane

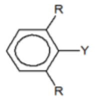
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance*. It involves the conjugation of σ(sigma) bond with π(pi) bond. *For example*, hyperconjugation in propene can be represented as follows:



The structures II to IV have no bond between one of the H-atom and the C-atom.

25.3.3 Steric Hinderance

The effect is caused by the large bulky groups present in the vicinity of the reaction centre. This effect was fIrst observed by Hofmann (1872) and Meyer (1874). They regarded it as mechanical hinderance for the attacking species to approach the reaction site.

Hofmann (1872) observed that when a compound of the type  (where, Y = -COOH, -CONH$_2$, -CHO, -NH$_2$ etc. and R = -CH$_3$, -C$_2$H$_5$ etc) is treated with the reagents such as Cl$^-$, Br$^-$, I$^-$, $^-$OH, etc., the reaction is hindered or retarded by the substituents at 'R'. The magnitude of hinderance is proportional to the size and number of substituents present in the vicinity of reaction site. Meyer (1874) observed that rate of esterification of aliphatic carboxylic acids and found that their activity was decreased by increasing the number of substituents at the carbon atom adjacent to the COOH group.

$$\underrightarrow{CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH}$$

decreasing order of reactivity with alcohols

Intext Questions 25.3

1. What is the condition of polarity for a covalent bond?

....

2. Identify the groups with -I and +1 effect from the following species:

-NO$_2$, -CH$_3$, -CN, -C$_2$H$_5$, -C$_6$H$_5$ and -CH$_3$CHCH$_3$

....

3. What is the difference between electromeric and inductive effects?

....

4. Classify the following species as electrophiles or nucleophiles :

(i) H$_3$O$^+$ (ii) NO$^+$ (iii) Br (iv) C$_2$H$_5$O$^-$ (v) CH^{3}COO$^-$
(vi) SO^3 (vii) CN (viii) $^+$CH3 (ix) :NH$_3$

....

With the above general background, let us study various types of reactions in a little more details.

25.3.4 Substitution Reactions

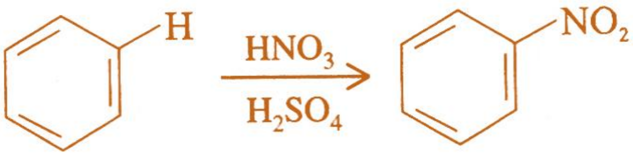
A substitution reaction involves the displacement of one atom or group in a molecule by another atom or group. Aliphatic compounds undergo nucleophilic substitution reactions. For example, a haloalkane can be converted to a wide variety of compounds by replacing halogen atom (X) with different nucleophiles as shown below.

$$\overset{\delta+}{R} - \overset{\delta-}{X} + Nu: \longrightarrow R - Nu + X^-$$

Haloalkane

(where R- is an alkyl group and Nu: = OH, NH2, CN, SH, O R , NH R etc.)

There is yet another type of substitution reaction which takes place in an aromatic hydrocarbons. In this case, an electrophilic reagent attacks the aromatic ring because the latter is electron rich. The leaving group, in this case, is always one of the hydrogen atom of the ring.

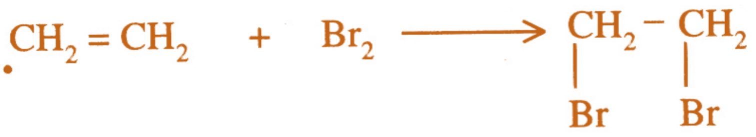


Nitrobenzene

For example, in case of nitration the NO_2 group replaces one hydrogen atom of benzene.

25.3.5 Addition Reactions

Unsaturated hydrocarbons such as alkenes and alkynes are extremely reactive towards a wide variety of reagents. The carbon-carbon double bond (-C=C-) of an alkene contains two types of bonds; one σ(sigma) bond and another π(pi) bond. In alkynes, out of the three carbon-carbon bonds, one is σ(sigma) bond and the other two are π(pi) bonds. The π(pi) bond is weaker than the σ(sigma) bond and breaks easily. For example, the colour of bromine solution disappears when added to the unsaturated hydrocarbons. This is due to the following addition reaction.



$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}}$$

1, 2-Dibromoethane
(Colourless)

Similarly, hydrogen, halogen acids and chlorine add on to a C=C double bond, as shown below.

$$CH_3 - CH = CH_2 + H_2 \xrightarrow{\text{(Ni/ Pt catalyst)}} CH_3\,CH_2\,CH_3$$

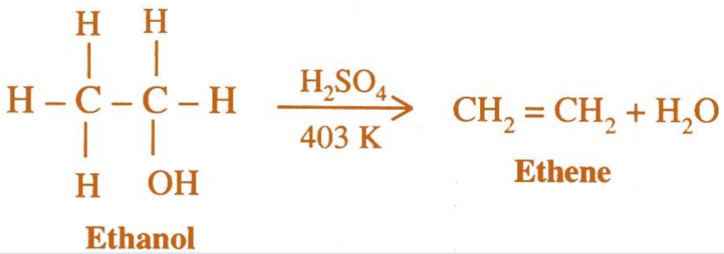
The multiple bond of an alkene or alkyne is a region of high electron density. Therefore, it is easily attacked by the electrophilic reagents. One of the most thoroughly studied addition reactions is that of halogen acids.

In alkynes (– C ≡ C –), two molecules of hydrogen add; first to give an alkene and finally the corresponding alkane, as shown below:

$$CH_3C \equiv CH + H_2 \xrightarrow{\text{(Ni/ Pt catalyst)}} CH_2CH = CH_2 + H_2 \xrightarrow{\text{(Ni/ Pt catalyst)}} CH_3CH_2CH_3$$

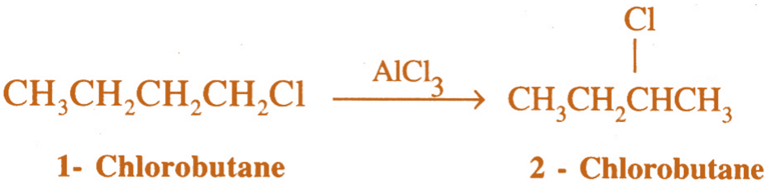
25.3.6 Elimination Reactions

From the above discussion, you know that we get a saturated compound by the addition reaction of an alkene. The reverse reaction i.e. the formation of an alkene from a saturated compound, can also be carried out and is called an elimination reaction. An elimination reaction is characterized by the removal of a small molecule from adjacent carbon atoms and the formation of a double bond. For example, when alcohols are heated with a strong acid as the catalyst, a molecule of water is removed and a double bond is formed.



25.3.7 Molecular Rearrangements

A molecular rearrangement proceeds with a fundamental change in the hydrocarbon skeleton of the molecule. During this reaction, an atom or group migrates from one position to another. For instance, l-chlorobutane in the presence of a Lewis acid (AlCl) rearranges to 2-chlorobutane.



Intext Questions 25.4

1. Write the products of each of the following reactions:

(i) $CH_3CH_2Br + CN^- \longrightarrow$

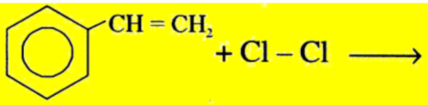
(ii) $CH_3Cl + RNH_2 \longrightarrow$

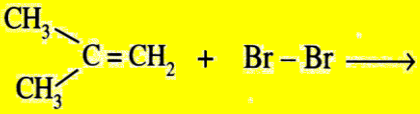
2. Write the conditions for nitration of benzene.

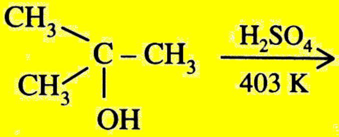
……

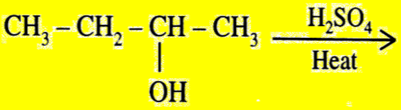
3. Predict the products of the following reactions:

(i) $CH_2 = CH_2 + \mathbf{HBr} \longrightarrow$

(ii) 

(iii) 

(iv) 

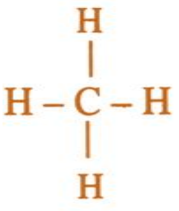
(v) 

$$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Heat}]{H_2SO_4}$$

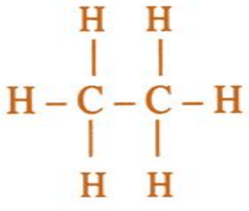
....

25.4 Isomerism

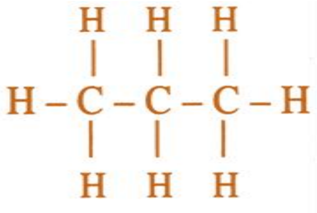
The simple alkanes containing up to three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below:



Methane

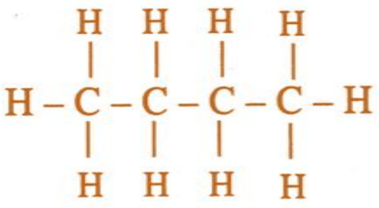


Ethane

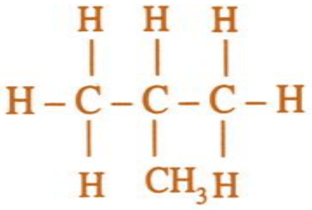


Propane

But for next higher hydrocarbon i.e. butane (C_4H_{10}), there are two possible ways in which the carbon atoms can be linked together. They may be linked to form a **straight chain** or **a branched chain**.

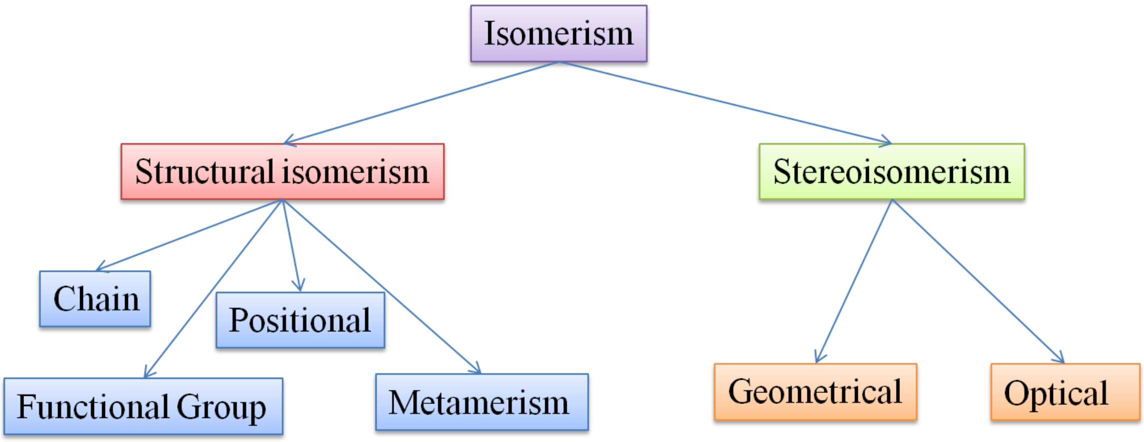


Butane (b.p.- –5 °C) 268 K



(2-Methylpropane) (b.p.- 12 °C) 261 K

Thus, there are two types of butane which are different compounds and they show different properties. *Different substances which have the same molecular formula but differ in their structures, physical or chemical properties are called isomers* and this phenomenon is known as isomerism. The isomerism can be of various types as shown below :

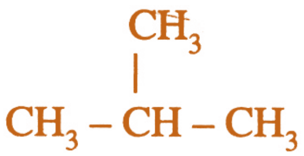


1. Structural Isomerism : Compounds which have the same molecular formula but differ in their structure are called structural isomers and the phenomenon is called structural isomerism. This is further subdivided into four types; chain, functional, positional isomerism, and metamerism.

(i) Chain isomerism: These isomers differ in the chain of the carbon atoms, for instance, n-butane and isobutane are two isomers of C_4H_{10}.

$$CH_3-CH_2-CH_2-CH_3$$

***n*-Butane**



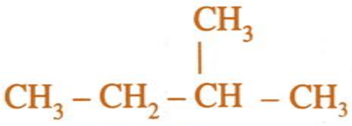
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Isobutane

Similarly, pentane (C_5H_{12}) has the following three isomers:

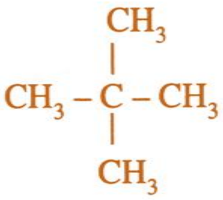
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

***n*-Pentane**



$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-Methylbutane
(*Iso*pentane)



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2,2- Dimethylpropane
(*Neo*pentane)

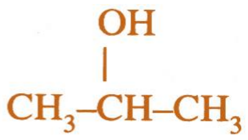
Similarly, hexane (molecular formula C_6H_{14}) can have five chain isomers.

(ii) Functional isomerism : These isomers differ in the type of functional group. For example; ethanol and ether the two isomers having molecular formula C_2H_6O, belong to two different classes of organic compounds. Similarly, the two isomers corresponding to molecular formula $C_3H_6O_2$ are, an acid and an ester having quite distinct structures and properties.

Molecular Formula : C_2H_6O	C_2H_5OH Ethanol (alcohol)	CH_3 - O - CH_3 Methoxymethane (ether)
Molecular Formula : $C_3H_6O_2$	CH_3CH_2COOH Propanoic acid	CH_3-$COOCH_3$ Methyl ethanoate

(iii) Positional isomerism: These isomers differ in the attachment of the functional group to the chain at different positions. Examples are as follows :

$CH_3CH_2CH_2OH$ and

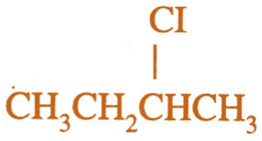


$$\overset{\large OH}{CH_3{-}CH{-}CH_3}$$

Propan-1-ol

Propan-2-ol

$CH_3CH_2CH_2CH_2Cl$ and



$$CH_3CH_2\overset{\large Cl}{C}HCH_3$$

1-Chlorobutane

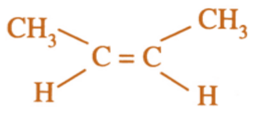
2-Chlorobutane

(iv) Metamerism: Exhibited by those compounds in which functional group comes in between the carbon chain and breaks the continuity of the chain. This breaking occurs at different positions and different isomers are formed which are called Metamers. For example, 1-methoxypropane and ethoxyethane are two metamers differing in chain length (size of alkyl groups) on the two sides of oxygen atom as shown below.

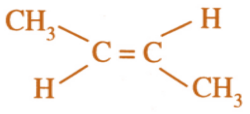
$CH_3OCH_2CH_2CH_3$	$CH_3CH_2OCH_2CH_3$
1-Methoxypropane	Ethoxyethane

2. Stereoisomerism : Stereoisomerism is exhibited by the compounds which have similar attachment of atoms but differ in their arrangement in space. There is two types of stereoisomerism-geometrical and optical.

(i) Geometrical Isomerism: Consider two isomers of 2-butene as shown below.

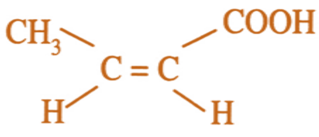


cis– **But-2-ene**

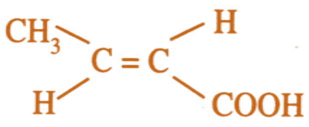


trans– **But-2-ene**

A *cis- isomer* is the one having identical groups on same side of double bond. On the other hand, a *trans-isomer* has identical groups on opposite side. In the above structures, *cis-2- butene* (two-CH_3 groups on the same side) and *trans-2-butene* (two - CH_3 groups on different sides) are two geometrical isomers (stereoisomers) as they differ in the geometries of the groups around the double bond. Another example of *cis*-and *trans*-isomerism is 2-butenoic acid or But-2-enoic acid.



cis- **But-2-enoic acid**

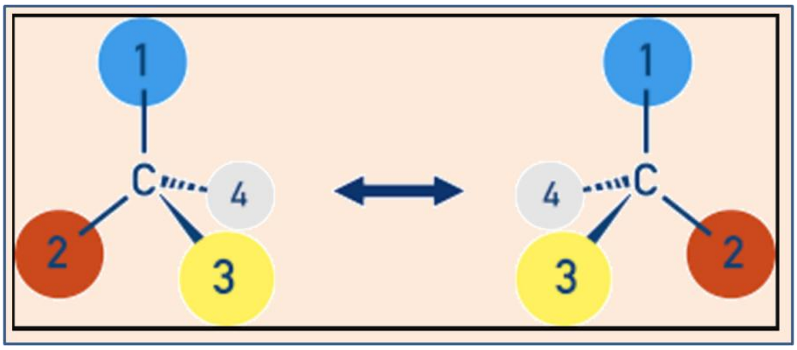


trans-**But-2-enoic acid**

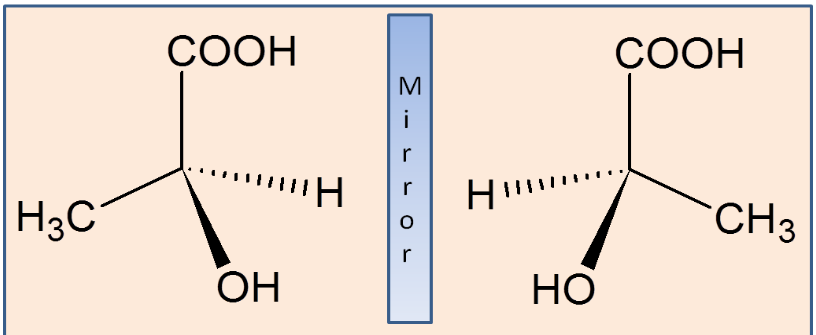
Note that in the above examples, the two isomers exist because the rotation of groups across C=C bond is not possible (it is also called as restricted rotation). Geometrical isomerisms is also shown by cyclic compounds and compounds containing -C=N- bond, about which you will study at higher level.

(ii) Optical Isomerism: The optical isomerism is shown by the compounds having at least one carbon atom joined to four different atoms or groups. Such a carbon atom is called asymmetric or chiral carbon atom and those which are not chiral (do not have four different groups) are called achiral. A chiral compound can have two different arrangements of groups attached to the chiral carbon as shown below for 1,2-dihydroxypropane.

The wedge sign (▲) shows that the direction of the bonds is towards the viewer and dotted line (.....) indicates backward direction of the bonds.



The resulting isomers are non-superimposable mirror images of each other and are called enantiomers. Thus, the enantiomers differ in the three-dimensional arrangement of atoms or groups. Another example of enantiomers is that of lactieacid as shown below:



Enantiomers of lactieacid

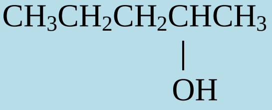
The optical isomers have identical physical properties except optical activity. They rotate the plane of plain polarized light in opposite directions. The plain polarized light is defined as the light that vibrates in one plane only. The rotation of the plane of polarized light is called optical activity. Those substances that can rotate the plane of polarized light are said to be **optically active**. Compounds that rotate the plane of plane polarized light to the right (clockwise) are said to be **dextrorotatory**. The dextrorotatory is denoted by ‘d’ or (+) before the name of the compound. Similarly, compounds that rotate the plane to the left (anticlockwise) are called **laevorotatory** and this is denoted by placing *‘l’* or (-) before the name of the compound. A mixture containing equal amounts of *d*- and *l*- isomers is called a *recemic mixture* and is optically inactive denoted by *dl or* ±.

Intext Questions 25.5

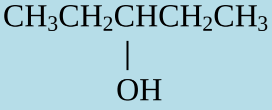
1. Is 1-butene a structural isomer of *cis*- or *trans*-2-butene?

....

2. Identify the type of isomerism exhibited by the following pairs of compounds:

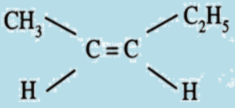
(i) 

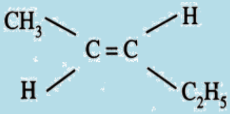
$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_3$

and 

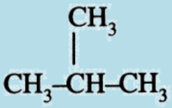
$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3$

....

(ii) 

and 

....

(iii) $CH_3CH_2CH_2CH_3$ and 

$CH_3-\underset{}{\overset{\overset{CH_3}{|}}{C}}H-CH_3$

....

(iv) $CH_3CH_2CH_2-OH$ and $CH_3CH_2-O-CH_3$

....

3. Write the structures of all the isomers of hexane (C_6H_{14}).

....

4. Which one of the following compounds would show geometrical isomerism?

(i) $CH_3CH_2CH = CHCH_2CH_3$ (ii) $FCH = CHF$ (iii) $CH_2=CHCH_2CH_3$

....

What You Have Learnt

- Organic compounds are classified into aliphatic (open-chain), homocyclic (closed ring) or carbocyclic (alicyclic and aromatic) hydrocarbons and their derivatives, and heterocyclic compounds (contain at least one heteroatom i.e., N,S,O in the ring).
- **Homologous series** of organic compounds differ by $-CH_2-$ group.
- The substitution, elimination, additions reactions and molecular rearrangements .
- Homolytic fission of a covalent bond produces free radicals because each of the parting away atoms takes away its shared electron.
- Heterolytic fission of a covalent bond produces ions because one of the atoms takes away both the shared electrons.
- Electrophiles are positively charged or electron deficient species.
- Nucleophiles are negatively charged or electron rich species.
- Benzene ring undergoes aromatic substitution reactions.
- A functional group is an atom or group responsible for specific properties of a compound.

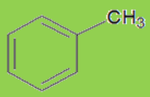
- The compounds which have the same molecular formula but different structure are called structural isomers.
- Isomerism is classified into structural isomerism and stereoisomerism.
- A carbon atom attached to four different groups is called chiral atom or asymmetric carbon atom.
- The non-superimposable mirror image isomers of a compound are called enantiomers. They are optically active and rotate the plain of plain polarized light in opposite directions.

Terminal Exercise

1. What are hydrocarbons? Explain giving two examples.
2. Give two examples of aromatic hydrocarbons.
3. Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names.

(i) $(CH_3)_3CH$ (ii) $CH_3CH = CH_2$ (iii) $(CH_3)_4C$

(iv) $CH_3C\equiv CH$ (v) $CH_3C\equiv CCH3$ (vi) $CH_2= CH_2$

(vii) 

(viii) 

(ix) 

4. Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula:

(i) C_5H_{10} and (ii) C_5H_8

5. Write the structures of the following compounds:

(i) Isobutylbenzene (ii) 4-Methyl-2-pentene

(iii) Hepta-l,6-diene (iv) Cyclobutene

6. Write the structures for the following compounds:

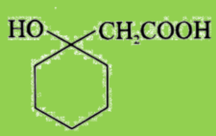
(i) 1-Bromo-3-methylhexane (ii) 3-Chloro-2,4-dimethylpentane

(iii) 3-Methylbutanal (iv) Ethyl propanoate

(v) 2-Methylbutanenitrile (vi) Cyclohexene

(vii) 3-Methylhexan-2-one

7. What are electrophilic aromatic substitution reactions? How will you prepare nitrobenzene from benzene?
8. Draw all the possible structural isomers having the molecular formula C_4H_9Cl and give their IUPAC names.
9. What is a nucleophilic aliphatic substitution reaction? Give one example.
10. Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.
11. Write a short note on the following; (i) Structural isomerism (ii) Stereoisomerism
12. Define a functional group. Identify the functional group(s) present in following compounds:

(i) 

(ii) 

(iii) $CH_3COCH_2C \equiv CH_3$ (iv) $CH_3 - CH_2 - CH_2 - O - CH_3$

(v)  $CH_3-CH(Cl)-CH_2-CHO$ (vi) CH_3CONH_2

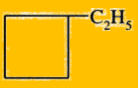
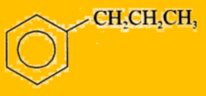
15. Describe hyperconjugation in terms of resonance.

Answers to Intext Questions

25.1

1. **Word root Suffix**
   (i) Hex ane (ii) Pent 2-ene (iii) Prop yne
2. (i) Oct-2-ene (ii) 2, 4-Dimethylpentane

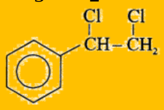
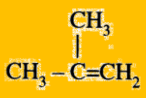
25.2

1. (i) l-ethyl-3-methylbenzene
   (ii) Cycloheptane
   (iii) Cyclopenta- l,3-diene
2. (i)  (ii)  (iii) 

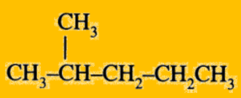
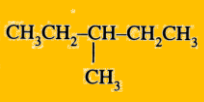
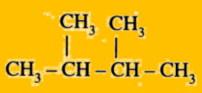
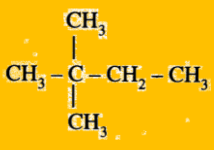
25.3

1. Covalent bond between two different atoms having large difference in their electronegativities.
2. -I effect groups $-NO_2$, $-CN$, $-C_6H_5$
   +I effect groups $-CH_3$, $-C_2H_5$, CH_3CHCH_3
   |
3. Electromeric effect is temporary polarization, whereas inductive effect is permanent polarisation of a covalent bond.
4. (i) Electrophile (ii) Electrophile (iii) Nucleophile (iv) Nucleophile
   (v) Nucleophile (vi) Nucleophile (vii) Nucleophile (viii) electrophile
   (ix) Nucleophile

25.4

1. (i) CH_3CH_2CN (ii) CH_3NHR 2. HNO_3 in presence of H_2SO_4.
3. (i) CH_3CH_2Br
   (ii)  (iii) $(CH_3)_2CBr - CH_2Br$ (major product) (iv)  $CH_3-C(CH_3)=CH_2$
   (v) $CH_3CH = CHCH_3$ (major product)

25.5

1. Yes
2. (i) Positional isomerism (ii) Geometrical isomerism
   (iii) Chain isomerism (iv) Functional group isomerism
3. (i) $CH_3CH_2CH_2CH_2CH_2CH_3$
   (ii)  $CH_3-CH(CH_3)-CH_2-CH_2CH_3$ (iii)  $CH_3CH_2-CH(CH_3)-CH_2CH_3$ (iv)  $CH_3-CH(CH_3)-CH(CH_3)-CH_3$ (v)  $CH_3-C(CH_3)_2-CH_2-CH_3$
4. (i) Yes (ii) Yes (iii) No

Methods of Purification

The organic compounds obtained from natural sources or synthesized in the laboratory are not pure. They are contaminated with impurities. So they must be purified.

Methods of Purification of solid organic compounds:

1. Crystallization:-

The Principle involved in this processes is that substance to be purified should be sparingly soluble at room temperature in the given solvent but highly soluble at high temperature and impurities are either not soluble or soluble and go into filtrate.

Process:

The impure substance is dissolved in a suitable solvent, a saturated solution is prepared. Animal charcoal is added which adsorbs the colored impure substance and solution is concentrated by heating. The solution is filtered in hot condition. The filtrate is allowed to cool without any disturbance. Slowly crystals of pure compound separate out. Care should be taken in choosing the solvent. For fast crystal formation to take place, a crystal of the same substance is to be added. The added crystal is called mother crystal and the process is called seeding.

2. Fractional crystallization:

The Principle is based on the differential solubilities of different compounds in a solvent. The compound which is less soluble in the solvent crystallizes out first on cooling. For better results, sometimes mixture of two solvents is used.

Example: 1) Alcohol & Water 2) Alcohol & Ether, etc.

3. Sublimation:

This process is used for solids which go directly into vapor state when heated and comes back directly from vapour state to solid state on cooling. This is known as sublimation. This method is suitable for organic compounds which sublime while impurities do not. If the sublimating substances have lower vapour pressure are decompose on heating before sublimation, then sublimation is carried out under low pressure.

Methods of purification of liquids:

25.a Distillation:

The process of vaporization of liquid by heating and subsequent condensation of vapours to get the liquid is called distillation. This method of purification is suitable for liquids which contain non- volatile impurities and the compound to be purified does not undergo decomposition on heating.

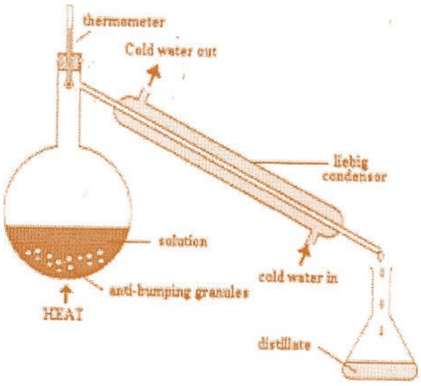


Fig. 25.a Distillation

Process:

The impure liquid is taken in a distillation flask and heated to its boiling point. The vapours are cooled and the distillate is pure liquid. The impurities remain in the distillation flask. **Fig. 25.a.**

25.b Fractional Distillation:

This process is used for separating two or more volatile liquids having boiling points close to each other.

Process:

The mixture of liqids is taken in a distillation flask fitted with a fractionating column. When the mixture is heated, the vapours of liquids pass through the fractionating column. While moving through the fractionating column the vapours of high boiling fractions condense and fall back into distillation flask. The process is repeated until the fractions of high volatile liquid go up. They are collected separately. **Fig. 25.b.**

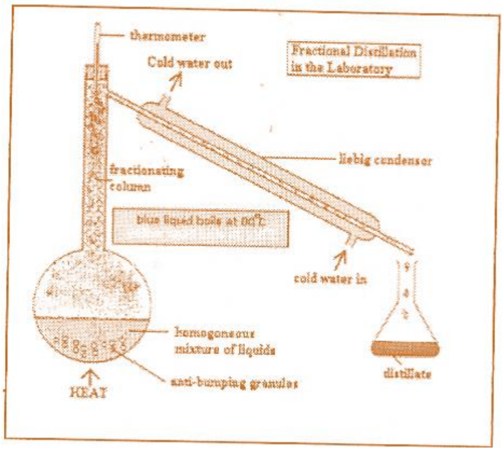


Fig. 25.b Fractional Distillation

25.c Distillation under reduced pressure:

Liquids which undergo decomposition when heated to their boiling Point are purified by this method.

Process:

When the pressure is reduced, liquid boils at lower temperature than its normal boiling point without decomposition. So liquids can be purified by distillation under reduced pressure, the process is same as distillation. Liquids like glycerol, formaldehyde etc., are purified by this method. **Fig. 25.c.**

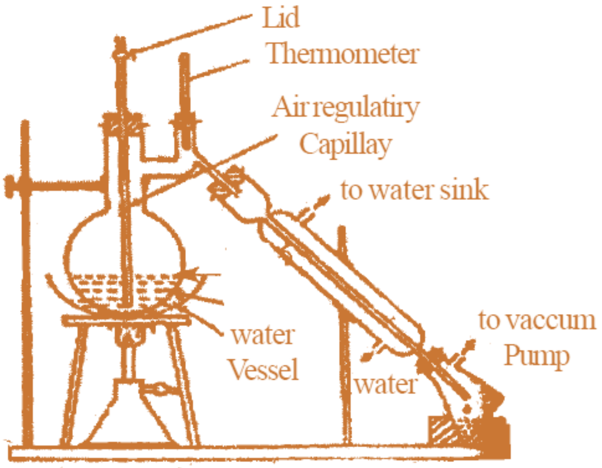


Fig. 25.c Distillation under reduced pressure

25.d Steam distillation:

Liquids which are insoluble in water but are steam volatile in nature are purified by this method, impurities are not steam volatile.

Process:

The impure liquid is taken in a distillation flask fitted with two holed stopper. Inlet for steam is fitted to one hole and condenser to the second. When steam is passed into the distillation flask, the mixture of steam and vapours of volatile organic compound come out which are condensed and collected in the receiver. Using separating funnel, the aqueous and organic layers are separated. The impurities remain in the distillation flask. Eg. Aniline is purified by this method. Fig. 25.d

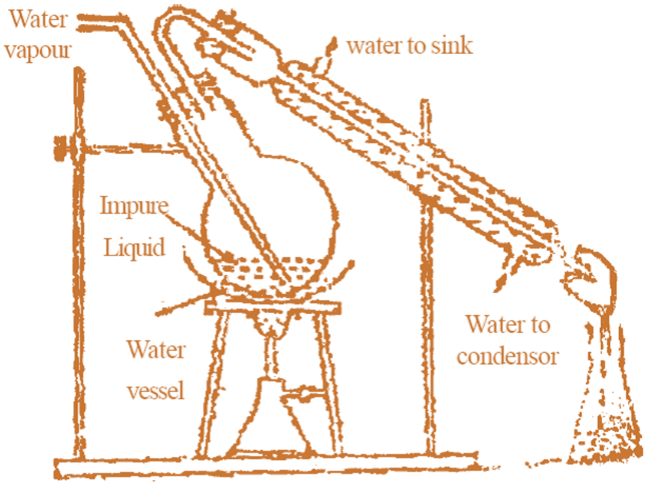


Fig. 25.d. Steam distillation

Solvent Extraction:

If the organic compound is more soluble in organic solvent than in water this method is suitable.

Process:

The aqueous solution of the compound is shaken with the organic solvent, the compound goes into organic layer. The aqueous and organic layers are separated. The organic layer is distilled to remove the solvent. The compound remains in the distillation flask.

25.a.3 Chromatographic methods:

Tswett, a Botanist separated chlorophyll, xanthophylls and other compounds by percolating the vegetable extracts through a column of calcium carbonate.

Principle:

Selective adsorption of various components of mixture between two phases – fixed or stationary phase and moving or mobile phase.

The techniques of chromatography involve three steps.

1) Adsorption and retention of mixture of substances on stationary phase followed by separation of adsorbed substances by mobile phase.

2) Elution *i.e.*, recovery of the substances separated by mobile phase.

3) Analysis of eluted substances both qualitative and quantitative.

Classification:

Depending upon the physical states of stationary and mobile phases, and also on the basis of principle of adsorption chromatography is classified into several types.

Process of Chromatography	Stationary Phase	Mobile Phase
1. Column Chromatography	Solid	Liquid
2. Liquid-liquid Partition	Liquid	Liquid
3. Paper Chromatography	Liquid	Liquid
4. Thin Layer (T L C)	Liquid or Solid	Liquid
5. Gas-liquid (G L C)	Liquid	Gas
6. Gas-Solid (G S C)	Solid	Gas
7. Ion exchange	Solid	Liquid

The mixture of substances is passed over the stationary phase which may be solid or liquid. A pure solvent or gas which is mobile phase is allowed to move slowly over the stationary phase. The components of the mixture get separated from one another. Two important techniques of chromatography are **1)** Adsorption Chromatography, **2)** Partition Chromatography.

Adsorption Chromatography:

This is based on the principle of adsorption of different compounds on an adsorbent to different degrees. Generally used adsorbents are silica gel and alumina. The mobile phase is allowed to move over the stationary phase. The components of the mixture are moved to different distances over the stationary phase. This principle is used in **a)** column chromatography and **b)** Thin layer chromatography.

25.e Column Chromatography:

The stationary phase generally alumina or silica gel are packed in glass tube (Column) fitted with a stop cock at its lower end. The mixture to be adsorbed is placed to the top of the column packed with the adsorbent A. Suitable mobile phase is continuously poured from the top of the column. This continuous pouring of solvent from the top of the column is known as elution and the solvent is known as eluent. The component which is weakly adsorbed is eluted first by least polar solvent while more strongly adsorbed component is eluted later. **Fig. 25.e.**

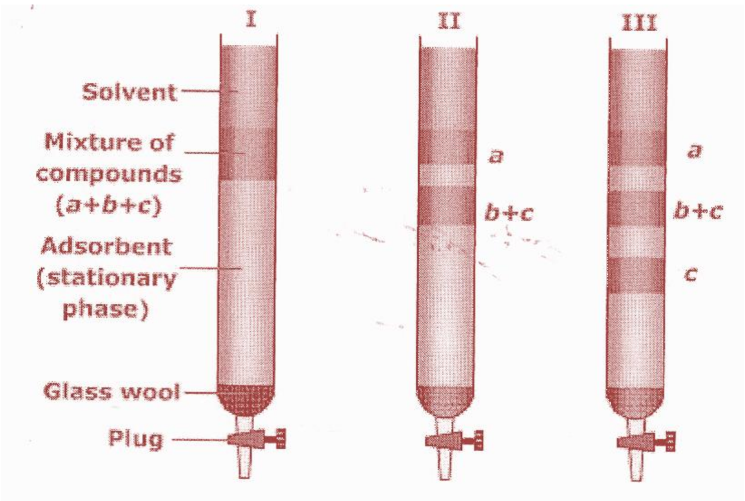


Fig. 25.e Column Chromatography

25.f Thin Layer Chromatography:

This also involves differential adsorption by the components of the given mixture. The adsorbent is silicon gel or alumina coated on a glass plate in uniform thickness (0.2 mm thick). The plate is called T L C Plate. A line is drawn about two centimeters from the bottom of the plate and the solution of the mixture to be separated is applied as a small spot with the help of micro pipette. The plate is then kept in a closed jar containing the eluent. As the eluent rises up, the components of the mixture also move up along with the eluent to various distances depending upon the degree of adsorption. The relative adsorption of a component of the mixture is expressed in terms of its retardation factor (R_f)

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

Coloured components are easily spotted. The colourless compounds are spotted with the help of UV Light or by spraying an appropriate reagent. **Fig. 25.f.**

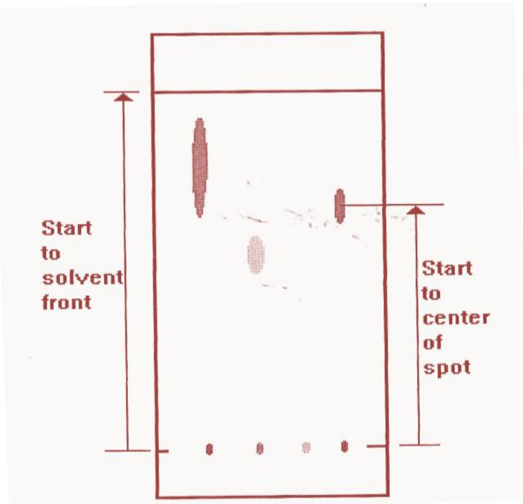


Fig. 25.f Thin layer chromatography

25.g Partition Chromatography:

Depending upon the physical state of the stationary and mobile phase we have liquid-liquid partition chromatography and liquid-gas partition chromatography. In paper chromatography a special paper called chromatography paper is used which contains water trapped in it (Stationary Phase). The solution of the mixture is spotted on the chromatography paper at the base and is suspended in a suitable solvent (Mobile Phase). Due to capillary action the solvent rises up and moves over the spot. As per the differing partition in mobile and stationary phases, the paper selectively retains different compounds. This paper strip is called chromatogram. The spots of separated coloured compounds are detected while the colourless compounds by spraying suitable reagents. **Fig. 25.g.**

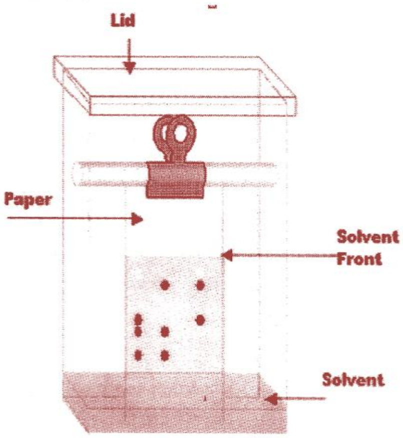


Fig. 25.g. Partition Chromatography

Qualitative Analysis of Organic Compound

The first step in the analysis of Organic compound is to find the elements present in the compound qualitatively. Following experiments are carried out for detecting the various possible elements in any organic compounds.

25.h.a Detection of Carbon and Hydrogen:

The given organic compound is taken in a dry test tube, mixed with three times its weight pure and dry copper oxide and heated strongly. The CO_2 and H_2O produced due to combustion are passed through lime water and anhydrous copper sulphate. If carbon is present it forms CO_2 gas which turns lime water milky. If hydrogen is present in the compound, it forms H_2O vapour which when passed over anhydrous $CuSO_4$ it terms to blue forming $CuSO_4.5H_2O$ **Fig.25.h.**

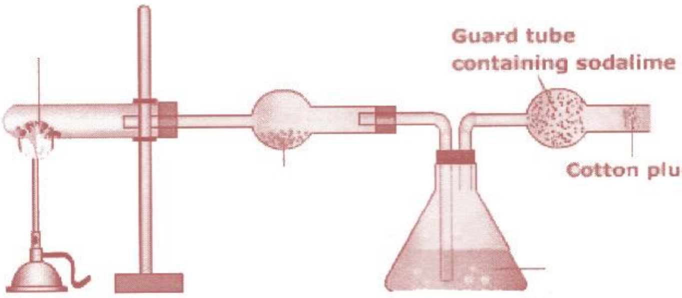


Fig. 25.h.a Detection of Carbon and Hydrogen

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

in the compound

$$2H + CuO \longrightarrow H_2O + Cu$$

In the compound

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

Lime water milky

$$5H_2O + CuSO_4 \longrightarrow CuSO_4 . 5H_2O$$

(anhydrous)

b) Detection of Halogens, Nitrogen and Sulphur (Lassaigne's test):

Elements like nitrogen, sulphur and halogens in any organic compound are detected by 'Lassaigne's test'. Organic compound is fused with sodium metal. If nitrogen, sulphur or halogens are present, they are converted to ionic compounds as follows.

$$C + N + Na \xrightarrow{\text{fusion}} NaCN$$

present in organic compound sodium cyanide

$$S + 2\,Na \xrightarrow{\text{fusion}} Na2S$$

from organic compound sodium sulphide

$$X\ (Cl, Br, I) + Na \xrightarrow{\text{fusion}} NaX\ (X=Cl, Br, I)$$

from organic compound sodium halide

The fused mass is extracted with water by plunging the red hot tube in distilled water, boiled for few minutes and filtered. The filtrate is called sodium fusion extract.

i. Test for nitrogen:

If nitrogen is present in the organic compound, on fusion with sodium metal it gives cyanide (NaCN) soluble in water. The sodium extract on reaction with ferrous sulphate, gives sodium ferrocyanide. Some of the ferrous salt is oxidized to the ferric salt on heating and this reacts with sodium ferrocyanide to form ferric ferrocyanide. A Prussian blue or green precipitate indicates the presence of nitrogen.

$$6NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

Sod. Ferrocyanide

$$2Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$$

prussianblue

ii. Test for sulphur:

To a small quantity of sodium extract taken in a test tube, 2 to 3 drops of sodium nitroprusside are added to the solution. A deep violet color indicates the presence of sulphur.

$$Na_2S + Na_2\,[Fe(CN)_5NO] \longrightarrow Na_4\,[Fe(CN)_5NOS]$$

Sod. nitroprusside violet colour

When nitrogen and sulphur both are present in any organic compound, sodium thiocyanate is formed during fusion. It gives ‘blood red coloration’ when FeCl is added due to the formation of ferric thiocyanate.

$$\mathrm{Na + C + N + S \longrightarrow NaCNS}$$

From organic compound — Sod. thiocyanate

$$\mathrm{3Na\ CNS + Fe^{3+} \longrightarrow Fe(CNS)_3 + 3\ Na^{+}}$$

blood red colour

Lead acetate test:

A small portion of sodium extract is acidified with acetic acid and lead acetate solution is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$\mathrm{(CH_3COO)_2\ Pb + Na_2S \longrightarrow PbS + 2CH_3COONa}$$

lead acetate — in sodium extract — black ppt

iii. Tests for halogens:

The sodium fusion extract is acidified with nitric acid and treated with AgNO3. Different coloured precipitates are formed which confirm halogens.

$$\mathrm{NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3}$$

White ppt

$$\mathrm{NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3}$$

pale yellow ppt

$$\mathrm{NaI + AgNO_3 \longrightarrow AgI + NaNO_3}$$

yellow ppt

c) Detection of Phosphorous:

The compound is heated with an oxidizing agent (Na_2O_2) the ‘P’ in the organic compound is oxidized to Phosphate. The solution is boiled with conc. HNO_3 and treated with ammonium Molybdate. Formation of canery yellow precipice indicates the presence of phosphorous.

$$\mathrm{2P_2 + 3Na_2O_2 + \underset{air}{O_2} \longrightarrow 2\ Na_3PO_4}$$

$$\mathrm{Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO}$$

$$\mathrm{H_3PO_4 + 12(NH_4)2MoO_3 + 21\ HNO_3 \longrightarrow (NH_4)_3PO_412MoO_3 + 21NH_4NO_3 + 12H_2O}$$

d) Detection of Oxygen:

There is no direct test for Oxygen. After determining the % composition of all the elements and if it does not come to 100% then the remaining is oxygen.

Quantitative Organic analysis:

After detecting the different elements present in the organic compound the percentage composition of the different elements is to be found out, which is called Quantitative analysis. *i.e.*, estimating the number of grams of each element per every 100 grams weight of the compound. The quantitative analysis of different elements are as follows.

25.i.a Estimation of Carbon and Hydrogen:

Carbon and Hydrogen are estimated in the same experiment simultaneously. A know weight of the organic compound is burnt completely in excess of air and dry cupric oxide. The carbon is converted to CO_2 and H to H_2O. CO_2 is absorbed in U shaped tube containing Potash and H_2O in the U shaped tube containing anhydrous $CaCl_2$. The increase in the weights of the two tubes gives the weight of CO_2 & H_2O respectively. From the weight of CO_2 & H_2O the percentage of C & H are calculated.

Percentage of carbon = $\frac{12}{44}\ X\ \frac{W_2}{W}\ X\ 100$

Where W_2 is the weight of CO_2 formed, W is the weight of organic compound

Percentage of water = $\frac{2}{18}\ X\ \frac{W_1}{W}\ X\ 100$

Where W_1 is the weight of H_2O formed, W is the weight of organic compound

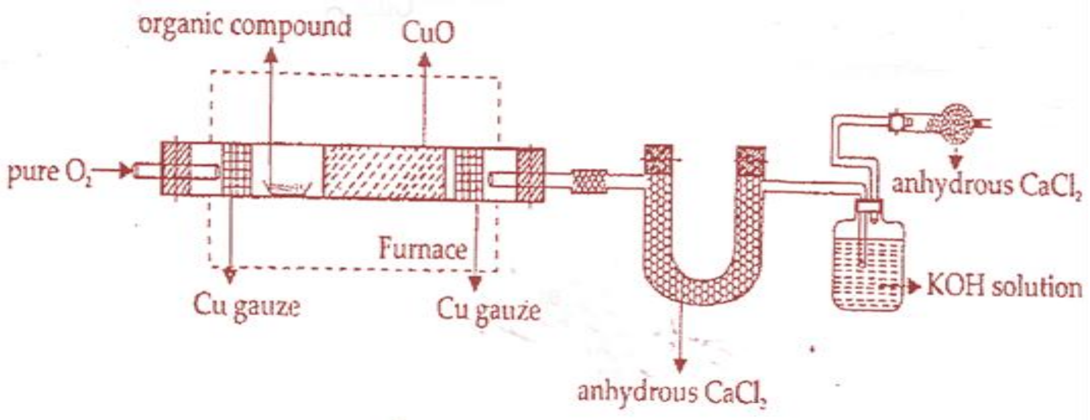


Fig. 25.i.a Estimation of Carbon and hydrogen

b) Estimation of nitrogen:

There are two methods for the estimation of nitrogen.

i) Duma's method ii) Kjeldahl's method

25.j Duma's method:

A known weight of the organic compound is heated with cupric oxide. Carbon and hydrogen get oxidized, while nitrogen is set free. It is collected over caustic potash. CO_2 is absorbed by KOH solution. Nitrogen is collected over KOH solution and its volume is found out. **Fig.25.i.**

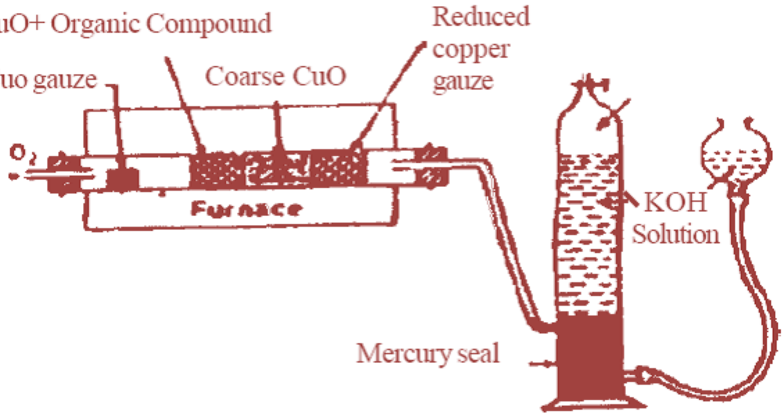


Fig. 25.j. Duma's method for the estimation of nitrogen

Calculations

Let, the mass of the organic compound taken be = W g
Volume of nitrogen collected = V_2 ml; Atmospheric pressure = 760 mm Hg
Temperature at which gas is collected = T_1K
Therefore, Pressure of the N2 gas, $P_1 = (P – p)$ mm of Hg

Volume of nitrogen at $STP = \frac{P_1V_1 \text{ x } 273}{760 \text{ x } T_1} = VmL$

(Using $P_1V_1/ T_1 = P_2V_2/T_2$)

28g of nitrogen at STP occupies 22400ml 1 mol of N_2 = 28g = 22400 mL
Mass of V mL of nitrogen at STP =28V/22400 g
Therefore,

Percentage of nitrogen in the compound =28V/22400 X 100/W

25.k Kjeldahl’s method:

To estimate the amount of nitrogen in organic compounds the most widely used method is Kjeldahl’s method.
The principle involved in Kjeldahl’s method for estimation of nitrogen is

1. Treating the organic compound with conc. Sulphuric acid to reduce the nitrogen of the compound into ammonium sulphate. This is called **digestion**.
2. The ammonium sulphate is distilled in presence of excess base so that it decomposes into ammonia gas. This is called **distillation**.
3. The ammonia gas is then absorbed in a known, excess volume of acid solution that has been standardized. This acid is generally HCl or H_2SO_4. The excess acid is then estimated by titration using standard NaOH solution. This is called **estimation**.

The quantity of ammonia produced is thus determined and from this the percentage of nitrogen in the organic compound is calculated. **Fig. 25.k**.

$$\text{Organic compound } + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

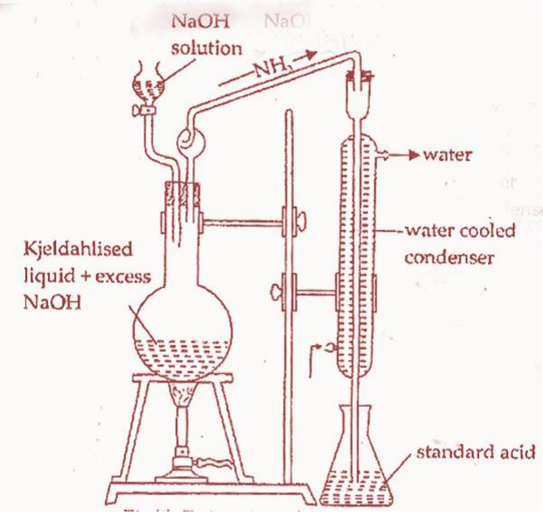


Fig. 25.k Estimation of Nitrogen

Calculation

Let the weight of organic compound be w gram

Volume of acid taken = V_1 ml Normality of acid = N

Volume of alkali of normality N required to neutralize unreacted acid = V_2 ml

Volume of acid to nuetralise ammonia = V_1 ml of acid – V_2 ml of acid

(V_2 ml of alkali is the same amount of acid neutralized as the normality is same for acid and alkali)

= $(V_1 – V_2)$ ml of N acid soln.

= $(V_1 – V_2)$ ml of alkali soln of N normal.

Now 1000 ml of (N) ammonia soln. has 17 g NH_3 *i.e.* 14 g Nitrogen

So $(V_1 – V_2)$ ml (N) NH_3 has 14 x $(V_1 – V_2)$ ml x 1/w x 1/1000 gram

So the % of N in the w gm organic compound is

14 x $(V_1 – V_2)$ x 1/w x 1/1000 x 100

i.e. 1.4 x $(V_1 – V_2)$ /w %N

25.l. Estimation of halogens:

The amount of halogen in an organic compound is estimated by Carius method. In Carius method a known mass (0.2 to 0.3 g) of the organic compound is heated with fuming nitric acid in the presence of silver nitrate at about 2000C in a sealed tube (called Carius tube) for 5 to 6 hours. Carbon and hydrogen are oxidized to carbon dioxide and water while halogen forms a precipitate of silver halide (AgX). After filtration and washing, the precipitate of silver halide is dried and weighed. Fig. **25.l.**

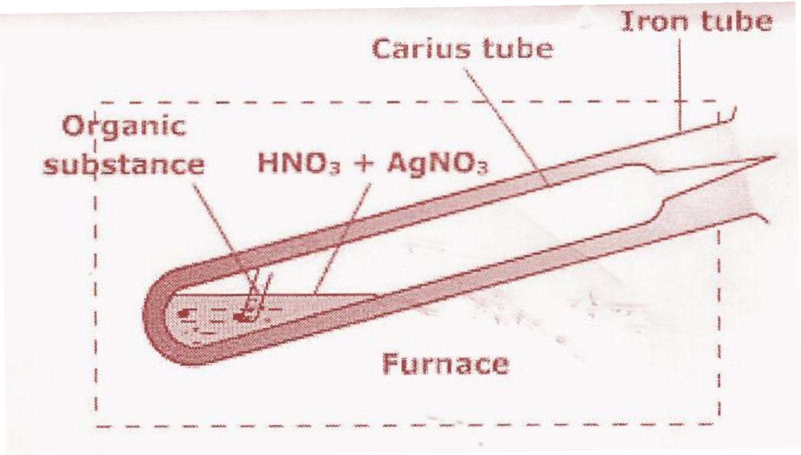


Fig. 25.l. Carius method for the estimation of halogens. Calculations

Calculation

Let, the mass of the organic compound taken be = W g

Mass of AgX formed = W_1g

From stoichiometry, 1 mole of AgX contains 1 mole of X

Therefore,

Mass of halogen inW1 = $\frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}}$ x W_1

Percentage of halogen = $\frac{\text{Mass of ha logen in } W_1 \text{ of AgXAtomic mass of X}}{\text{Molecular mass oMass of organic compound takenf AgX}}$ x 100

$$= \frac{\text{Atomic mass of X x } W_1}{\text{Molecular mass of AgX}}$$

Estimation of sulphur:

To estimate the amount of sulphur in the organic compound, a known mass of organic compound is heated strongly with fuming HNO_3 or sodium peroxide in a Carius tube for about 2 hours. If sulphur is present it is oxidized to sulphuric acid.

The contents of the Carius tube are cooled and treated with excess of barium chloride ($BaCl_2$) solution to precipitate SO^{2-} ions present in the solution as $BaSO_4$. The precipitate of barium sulphate ($BaSO_4$) is filtered, washed, dried and weighed.

Calculations

Let, the mass of the organic compound be = W g

Mass of the precipitate of $BaSO_4$ = W_1 g

From stoichiometry, 1 mol $BaSO_4$ = 1 mol S

1 molecular mass of $BaSO_4$ = 233g & 1 atomic mass of S = 32g

Therefore,

1 mole of $BaSO_4$ ……... contains 32g of sulphur

Mass of sulphur in W_1g of $BaSO_4$ precipitate = $W_1 \times \frac{32}{233}$ g

If W_g of organic compound has $W_1 \times \frac{32g}{233}$

Percentage of sulphur in the compound = $\frac{W1\ x\ 32}{233}$ X $\frac{100}{W}$

Estimation of Phosphorous:

To estimate the amount of phosphorous in the organic compound, a known mass of the organic substance is heated with fuming nitric acid in a Carius tube for about 2 hours. The phosphorus of the organic compound gets converted into phosphoric acid. The total phosphate content of the solution is precipitated using magnesia mixture (mixture of a solution containing 100g magnesium chloride, 100g ammonium chloride in water and 50ml of conc. Ammonia). The precipitate of $MgNH_4PO_4$ is filtered, washed, dried and then ignited to give magnesium pyrophosphate ($Mg_2P_2O_7$).

Calculations

Let, the mass of the organic compound taken be = W g

Mass of $Mg_2P_2O_7$ obtained = W_1 g

From stoichiometry, 1 mol $Mg_2P_2O_7$ = 2 mol P

(1 x molecular mass $Mg_2P_2O_7$ = 2 x atomic mass of P)

222 g 2 x 31 g = 62 g

Therefore,

Mass of phosphorusin W1 g of $Mg_2P_2O_7$ = W_1 X $\frac{62}{222}\,g$

Percentage of phosphorus in the compound = W_1 X $\frac{62}{222}$ X $\frac{100}{W}$

Estimation of oxygen:

There is no direct method for the estimation of oxygen present in any organic compound. The percentage of oxygen in an organic compound is usually obtained by subtracting the sum of the percentages of all other elements from 100.

% of oxygen in an organic compound = 100 – (Sum of the % of all other elements present in the compound).

25.a-l. Intext Questions:

1. Who prepared the first organic compound.
2. Which unique property of carbon is responsible for such large number of organic compounds?
3. Mention the methods of purification of solid organic compounds.
4. Mention the methods of purification of liquid organic compounds.
5. Write the principle involved in chromatographic technique.
6. What is the adsorbent used in TLC
7. How are ‘C’ ‘H’ detected in organic compound?
8. Name the test used to detect presence of Nitrogen in an organic compound.
9. How is nitrogen estimated in organic compound.
10. Name the method used to estimate halogens.

What you have learnt:

- Carbon forms numerous compounds due to its unique property called catenation.
- Solid organic compounds can be purified by Crystallization, fractional & sublimation.
- Distillation is a process to separate mixture of liquids.
- Liquids which undergo decomposition on heating are purified by distillation under reduced pressure.
- Chromatography is based on the principle of selective adsorption of various components of mixture between two phases. Stationary phase, mobile phase.
- Halogens, Nitrogen & Sulphur are detected in organic compound by lassaigne's test.
- Quantitative estimation of organic compounds.

Terminal Exercise

1. Write the different methods of purification of solid carbon compounds.
2. Explain distillation with the help of a diagram
3. Write briefly about the following :
    1. Partial Distilation 2. Distilation under reduced pressure 3. Steam distilation

25.a-l. Answers to intext questions

1. Wholer
2. Catenation
3. Crystallization, fractional crystallization and sublimation.
4. Distillation, fractional distillation, distillation under reduced pressure, steam distillation.
5. Selective adsorption of various components of mixture between two phases – stationary & mobile phase.
6. Silica gel or Alumina
7. C or H are converted to CO & H_2O respectively.
8. Lassaigne’s test.
9. By Duma’s method, Kjeldahl’s method
10. Carius method.

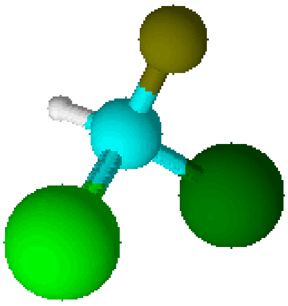
25.4.a Configuration and Fisher Projections

To convey stereo chemical information in an abbreviated form, **Fisher** described a method. In **Fisher projection formulae**, the molecule is oriented in such a way that the vertical bonds at the stereogenic centre are directed away from the viewer and the horizontal bonds point towards the viewer and the projection of the bonds is by a cross.

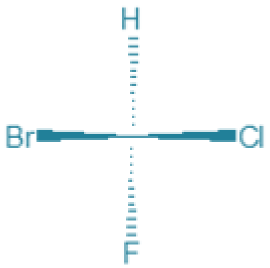
If chain contains more than one carbon, the chain is written vertically.

The carbon atoms of the chain are at the centre of crosses and not shown through symbols.

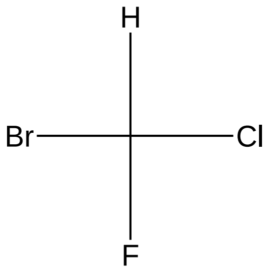
Eg:



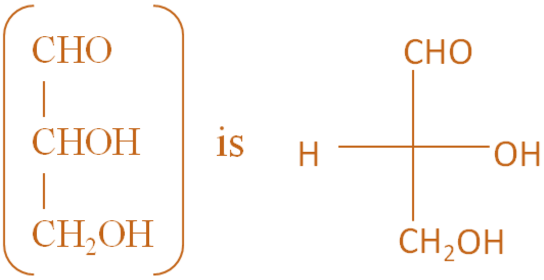
Ball - and - stick model



Wedge - and - dash model



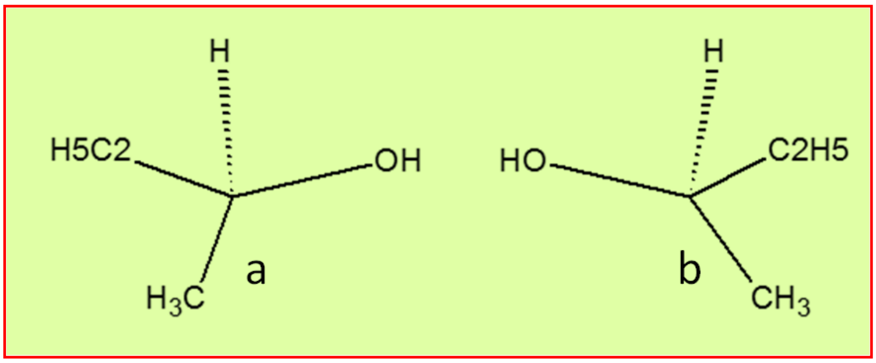
Fisher Projection formula



Fisher Projection formula for glyceraldehyde

Absolute and Relative configuration

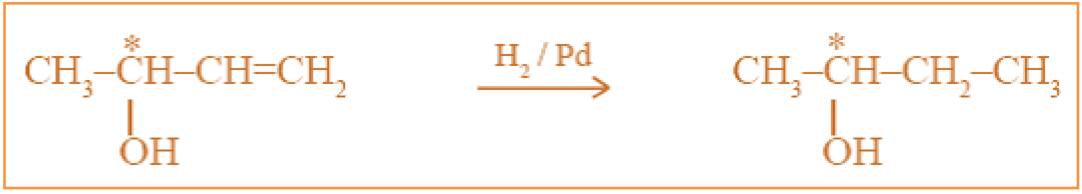
The three dimensional arrangement of substituents at a stereogenic centre is called its absolute configuration. The sign or magnitude of rotation does not provide any information about the absolute configuration of a substance.



correction

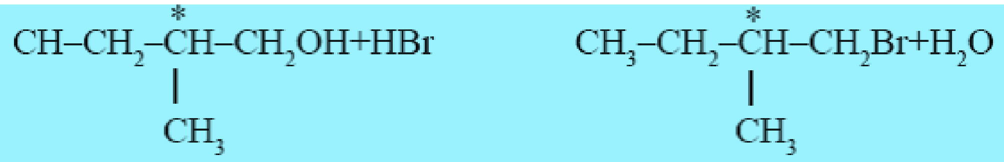
a and **b** represent absolute configuration of 2-butanol. Without any additional information it is difficult to say which is (+) 2-butanol and which is (-) 2- butanol. Hence the configurations of thousands of molecules were determined relative to one another. ***It is called relative configuration. It is determined experimentally through chemical inter conversion.***

Eg: When (+) -3- butane -2-ol is hydrogenated the product is (+)-2-butanol.



$$CH_3-\underset{\substack{|\\OH}}{\overset{*}{C}H}-CH=CH_2 \xrightarrow{H_2/Pd} CH_3-\underset{\substack{|\\OH}}{\overset{*}{C}H}-CH_2-CH_3$$

Since no change takes place at the stereogenic centre due to hydrogenation substituents must have been arranged in the same manner in both the reactants (+)-3- butene -2-ol & (+)-2- butanol. As they have the same sign of rotation, their identical configuration is established. It is to be noted that some compounds with the same relative configuration could have opposite sign of optical rotation.



$$CH{-}CH_2{-}\underset{\displaystyle |\atop CH_3}{\overset{*}{C}H}{-}CH_2OH+HBr \qquad CH_3{-}CH_2{-}\underset{\displaystyle |\atop CH_3}{\overset{*}{C}H}{-}CH_2Br+H_2O$$

2-methyl -1- butanol 1-bromo 2-methyl butane

$(\propto)^{25}_{D} = +5.8^{o}$ $(\propto)^{25}_{D} = +4.0^{o}$

25.4.a Intext questions:

1. Write the fisher projection formula for bromo, chloro fluoro methane.

……

2. Write the fisher projection formula for glyceraldehyde.

……

What you have learnt:

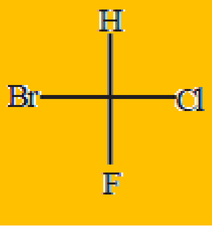
to draw the fisher projection formula of stereo isomers.
different methods of notation of stereo isomers.
absolute and relative configuration of stereo isomer.

Terminal Questions:

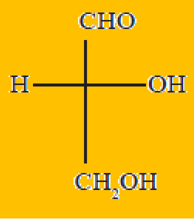
1. How do you represent fisher projection formula of stereo isomers?
2. What is meant by relative and absolute configuration?

25.4. a Answers for intext questions:

1.



2.



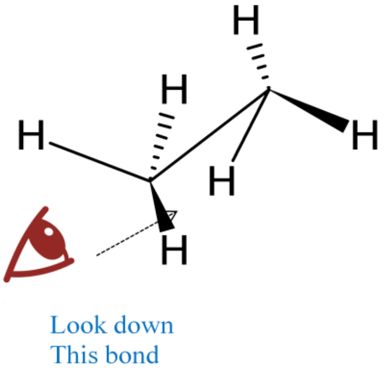
25.4(b) Asymmetric carbon and elements of symmetry

25.4.b Conformations of ethane

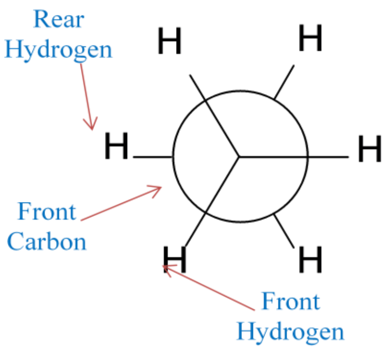
The different spatial arrangements formed by rotations about a single bond are called conformations or conformers. Let us consider the cylindrically symmetric nature of sigma bonds. The sigma bond can maintain a full degree of overlap while its two ends rotate. Hence, the energy barrier to rotate about sigma bonds is generally very low.

Several methods are used by organic chemists to visualize the conformations of molecules. One of these methods uses **wedges** to denote bonds that are extending out from the plane of the page toward the reader and **dashes** to indicate bonds that are going into the plane of the page away from the reader. This notation is frequently used to represent the tetrahedral geometry of sp^3 hybridized carbons.

A Newman projection can be used to specify the conformation of a particular bond with clarity and detail. A Newman projection represents the head-on look down the bond of interest. The circle in the Newman projection represents the atom in front of the bond, and the lines radiating from the center are the bonds of that atom. The bonds of the rear atom emerge from the sides of the circle.

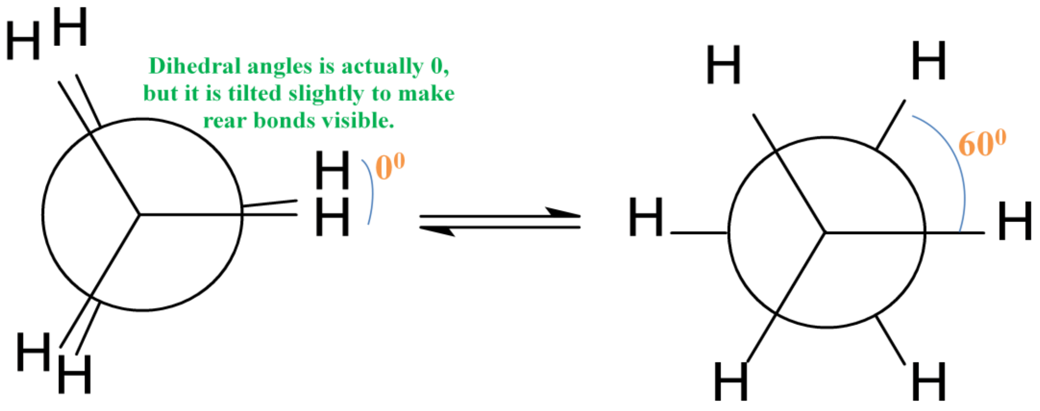


Line wedge representation



Newman projection Modify

While there are an infinite number of conformations about any sigma bond, in ethane two particular conformers are noteworthy and have special names. In the eclipsed conformation, the C-H bonds on the front and back carbons are aligned with each other with dihedral angles of 0 degrees. In the staggered conformation, the C-H bonds on the rear carbon lie between those on the front carbon with dihedral angles of 60 degrees.

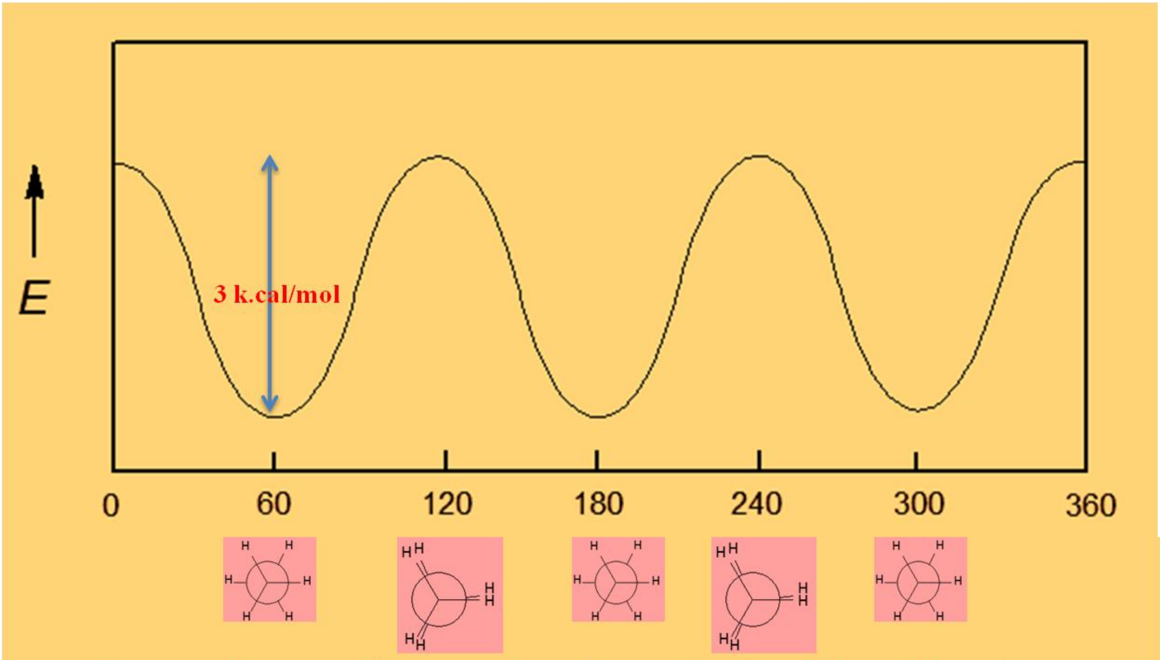


Eclipsed

Staggered

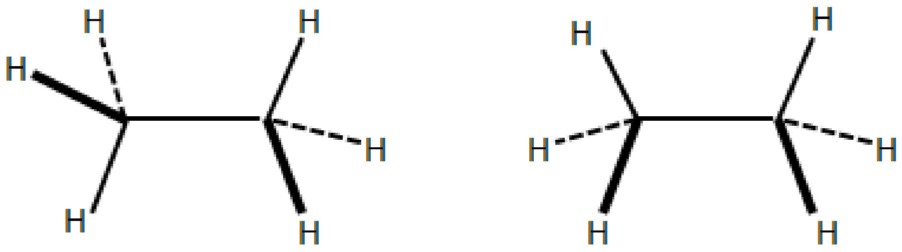
The Eclipsed and Staggered conformation of Ethane

Energetically, not all conformations are equally favoured. The eclipsed conformation of ethane is less stable than the staggered conformation by 3 kcal/mol. The staggered conformation is the most stable of all possible conformations of ethane, since the angles between C-H bonds on the front and rear carbons are maximized at 60 degrees. In t he eclipsed form, the electron densities on the C-H bonds are closer together than they are in the staggered form. When two C-H bonds are brought into a dihedral angle of zero degrees, their electron clouds experience repulsion, which raises the energy of the molecule. The eclipsed conformation of ethane has three such C-H eclipsing interactions.

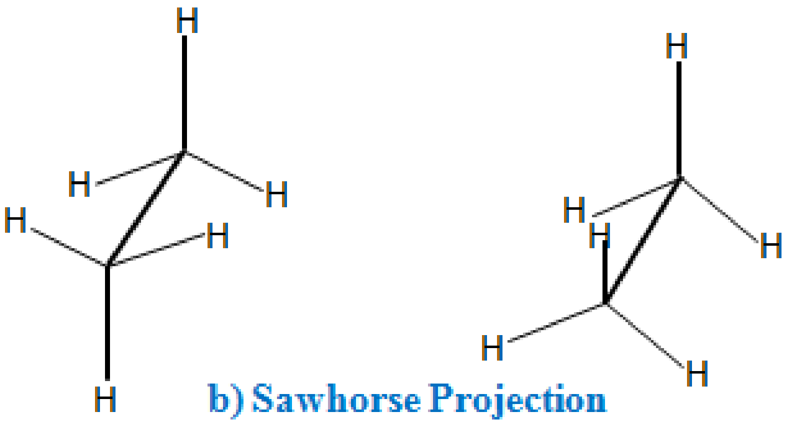


Energy diagram for rotation about the C – C bond in ethane

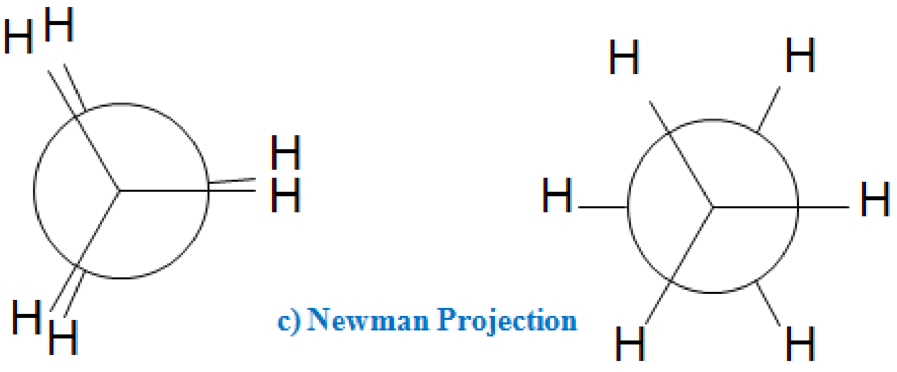
The staggered and eclipsed conformation are interconvertable by rotation. They are three important ways to represent the conformers. They are Wedge-and-dash, sawhorse and Newman projection formulae. They are represented as



a) Wedge and dash Projection



b) Sawhorse Projection



c) Newman Projection

25.4.b Intext questions:

1. Write the Newmann projection formula for ethane.

....

2. Which is the most preferred & least preferred conformation of ethane.

....

3. What is the energy difference between staggered & eclipsed form of ethane ?

....

What you have learnt:

- Conformation of ethane
- Types of representing the conformations
- Potential energy diagram of ethane conformations

Terminal exercise:

1. What are conformations?
2. Write the various types of representation of conformation of ethane?
3. Write the potential energy diagram of conformations of ethane?

25.4.b Answers to Intext questions:

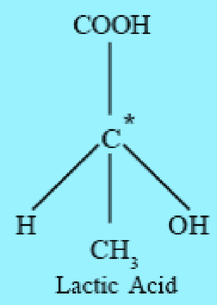
1. 

2. Staggered form, eclipsed form

3. 3 k.cals

25.4.c Asymmetric carbon and elements of symmetry

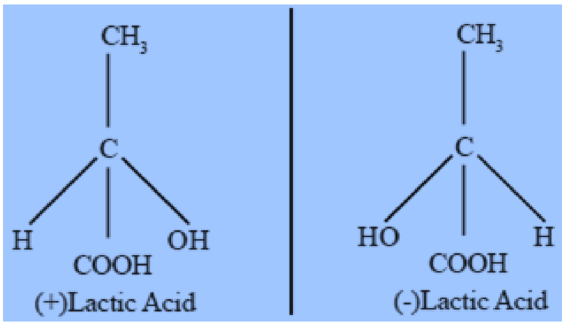
Asymmetric carbon: Carbon whose four valencies are satisfied by different atoms or group of atoms is called asymmetric carbon.



The four valencies of C* are satisfied by H,OH, CH , COOH. So it is called asymmetric carbon

Stereo isomers that have object mirror image relationship and are on-super imposable are called enanliomers. If the isomers are not mirror images, they are called diastereomers.

Eg:



These two are non super imposable mirro images. Hence called enantiomers.

Enantiomers occur only for those compounds whose molecules are chiral. A chiral molecule is defined as the molecule that is not super imposable on its mirror image.

Chire means hand in Greek. The enentiomers are related to each other like the relation between left hand and right hand. Therefore the term chiral is used. To know whether the molecule is chiral or not, the molecule should lack in elements of symmetry.

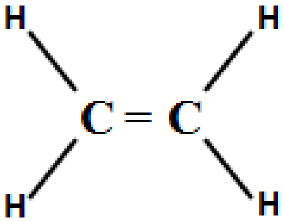
Elements of symmetry:

There are three types of elements of symmetry. They are centre of symmetry, plane of symmetry, axis of symmetry.

1. Centre of symmetry:

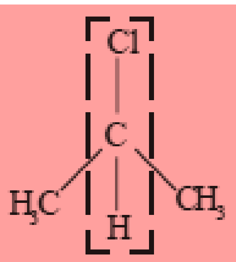
A molecule is said to have centre of symmetry if it has same groups on either side from the centre.

Eg:

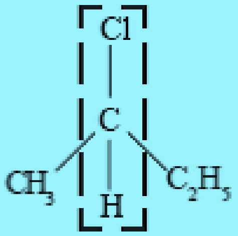


2. Plane of Symmetry:

When an imaginary place bisects a molecule in such a way that the two halves of the molecule are mirror images of each other.



2 - chloro propane
has plane of symmetry

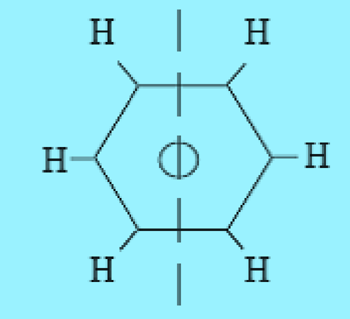


2 - chloro butane
has no plane of symmetry

3. Axis of symmetry:

A molecule is said to have axis of symmetry, if the molecule is rotated about that axis, it gives back the original arrangement of the molecule. If the same structure is repeated twice during 360^0 rotation, it is said to have two fold axis of symmetry. If ‘n’ identical configurations are obtained by rotations thro’ 360^0, then the molecule is said have n-fold axis of symmetry.

Eg:



If benzene is rotated through '360^0' 6 times identical configuration is obtained. Hence it is said to have Six fold axis of symmetry.

25.4.c Intext questions:

1. Give an example of asymmetric carbon.

....

2. What are enantiomers?

....

3. What are different types of elements of symmetry?

....

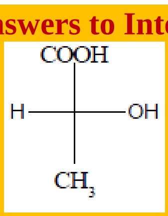
What you have learnt:

- Asymmetric carbon is one whose four valencies are satisfied by different atoms or groups.
- Enantiomers are a pair of optical isomers which have object mirror image relationship is non super imposable.
- Chirality is molecules which are dissymmetric.
- Three types of elements of symmetry. They are centre symmetry, plane of symmetry, axis of symmetry.

Terminal questions:

1. What are enantiomers?
2. Explain the elements of symmetry with suitable example.

25.4.c Answers to Intext questions

1) 

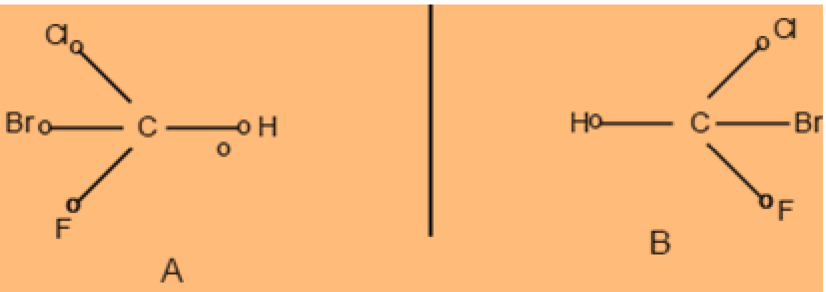
2) The pair of optically active isomers which plane object minor image relationship and are non-super imposable.

3) Centre of symmetry, place of symmetry, axis of symmetry.

25.4.d Compounds containing one chiral centre enantiomers

Geometrical objects like sphere, cube, cone etc. can be superimposed on their mirror images. There are some objects like right hand and left hand which cannot be superimposed on their mirror images. In stereo chemistry such molecules are called dissymmetric or chiral. A molecule which is super imposable on its mirror image is called achiral. According to **Vant Hoff** organic molecule is asymmetric if one of the carbon atoms has four different groups around it. All asymmetric structures are dissymmetric and they cannot be super imposed on their mirror images.

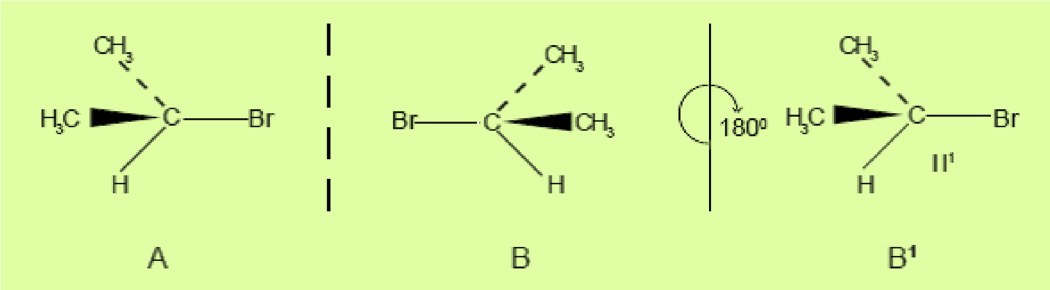
Eg: Bromo Floro chloro methane.



Structures A & B are non – super imposable mirror images. Therefore bromo chloro flour methane is a chiral molecule. The two forms are called **enantiomers**. As they have different arrangement of atoms in space, they are stereo isomers. The stereo isomers that have object image relationship are called enantiomers.

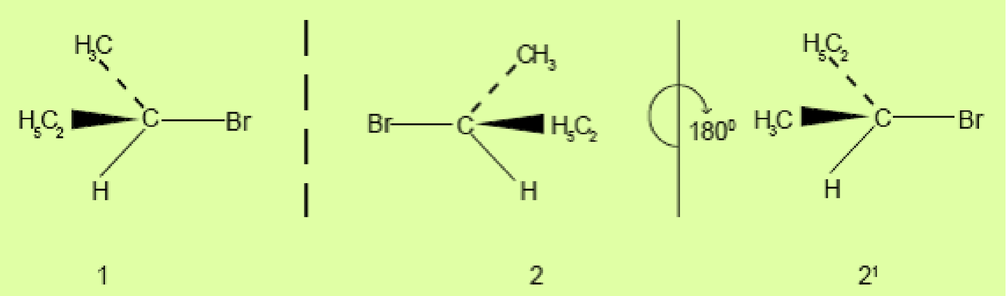
To test super impossibility, reorient B by turning if to 180^0. A & B cannot be super imposed on each other.

For Eg: 2 - bromo propane



A & B are mirror images. If B is rotated through '180^0 B' is super imposable on A. Hence these are not enantiomers.

Eg: 2 - bromo butane



The mirror image of 1 and 2; when 2 rotated through 180^0, 2' is obtained which is not super imposable on 1. Hence 2-bromo butane is a chiral molecule and 1 & 2 are enantiomers.

Enantiomers passers same physical properties like *m.p., b.p.*, refractive index etc. but differ in their action towards plane polarized light.

25.4.d Intext questions:

1. What is dissymmetric?

....

2. How are the properties of enantiomers?

....

What you have learnt:

- Non- super imposable mirror images of stereo isomers are dissymmetric.
- Asymmetric carbon is one whose valencies are satisfied by different groups.
- Super imposable image isomers are said to be a chiral molecules.

Terminal exercise:

1. What are enantiomers? Give an example?
2. What is meant by chirality?
3. What is meant by asymmetric carbon?
4. Explain the elements of symmetry with one example each?
5. What are conformations? Which is the least preferred and which is the most preferred conformations of ethane?
6. Give the energy profile diagram of the conformations of ethane?
7. How do you represent the fisher projection formula? Write the fisher projection formula for glyceraldehydes?

25.4.d Answers to Intext questions:

1. Non super imposable isomers are dissymmetric.
2. Enantiomers have same physical properties.

25.4.e : Racemic forms, Racemisation, R-S nd D-L nomenclature

Resolution of a racemic mixture :

When a racemic mixture is separated into its component isomers, it is called resolution. The resolution of a racemic mixture is carried out by treating the racemix mixture with an enantiomer of some other compounds. This gives a mixture of diastereomers with different melting and boiling points, solubility *etc.*, These are then separated diasteromer is broken down to give pure enantiomers. *Eg :* A racemic mixture of a carboxylic acid (± A) is treated with an amino acid i.e., base (+B). (±)A reacts with (± B) giving (+A) (+B), (-A) (-B) two salts are formed. These diastereomers have different physical properties and also in t he rate of formation. Using one of these differentiating properties the diastereomers.

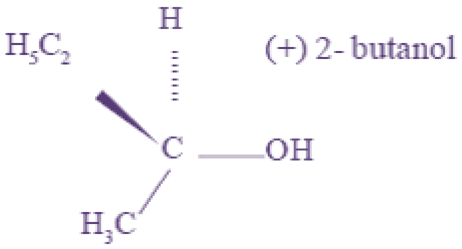
R.S. Notation :

The Cahn–Ingold–Prelog formulated rules to specify the absolute configuration of a stereogenic centre. The rules were developed as sequence rules.

Rules :

1. The substituent on the sterogenic centre are arranged in the decreasing order of the atomic number of the atom directly attached to the stereogenic centre (Priority given as 1,2,3 …)

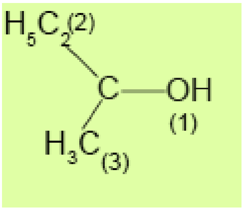
Eg :



$-OH > CH_3CH_2- > -CH_3 > -H$

Highest Atomic no. Lowest Atomic no.

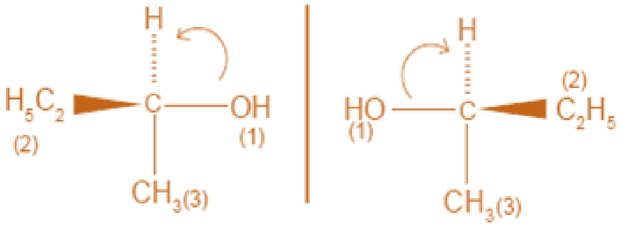
2. The molecule is so oriented such that the least ranked substituent is far away from the given here 'H'.
3. The remaining three ranked substituents are to be written as they appear to the viewer in the molecule.
4. If the priority groups are arranged in clockwise manner (i.e., 1,2,3) then the configuration is assigned 'R' (R in latin means rectors which means right side) and if the priority groups are in anti clockwise direction, the configuration is assigned as 'S' (S in latin stands for sinister means left side) For the above eg.: According to the atomic number of the atom directly attached to stereogenic centre – OH is given (1) priority – C_2H_5 (2) Priority, CH_3(3) priority keeping away the least priority 'H' the molecule is viewed as



1 →2→3 are in anticlockwise direct ion.

This configuration is assigned 'S' configuration.

The mirror image of the molecule is (-)2 but and which as assigned the configuration R.

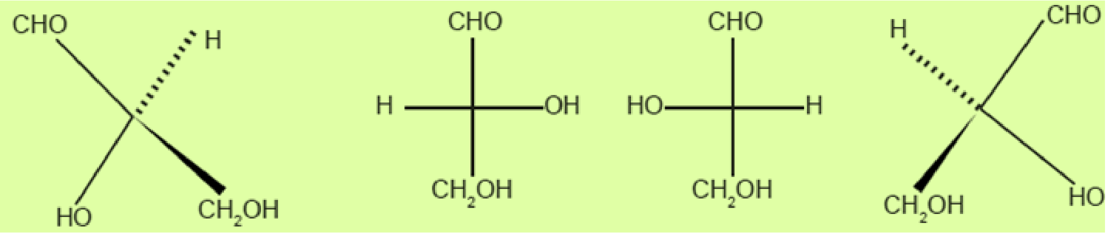


S-(+) 2 butanol R (-) -2- butanol

The racemic mixture is written as (R), (S), 2-butanol. While writing the three dimensional formulae to describe R,S configuration, Fisher projection formulae is written such that the groups having the viewer are on the horizontal line.

D, L notation of configuration :

This method gives the relative configuration with respect to glyceraldehyde. D is assigned to the molecule whose configuration is Similar to D (+) glyseraldyhyde about the chiral carbon. In D(+) glyceraldehyde, in Fisher projection formula –OH is written on the right side to the chiral carbon and for the enantiomer of 'L' configuration. –OH is written to the left.



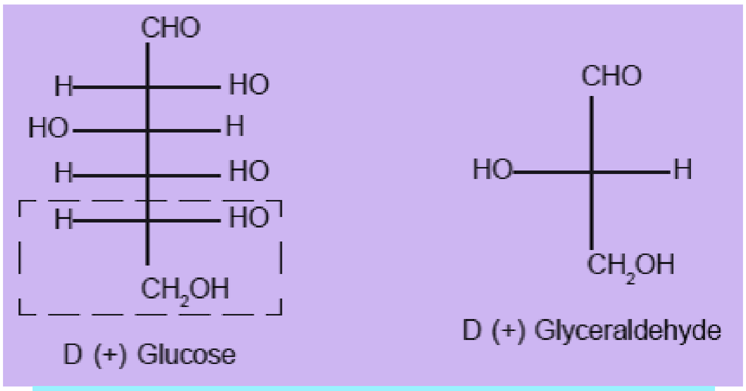
D(+) glyceraldehyde

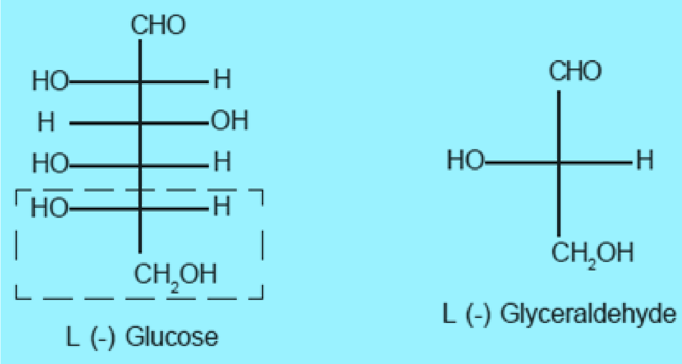
Fisher projection formula for D(+) glyceraldehyde

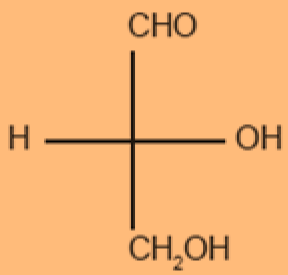
L(-) glyceraldehyde

The substances which have similar configuration with that of D (+) glyceraldehydes belong to D- series, while which have similar configuration that of L(-) glyceraldyhyde belong to L series. It should be noted that there is no relation with D L configurationally relation to d,L or (+) (–) which represent optical activity generally D,L relation is used to represent the stereo chemical aspect of carbohydrates and amino acids.

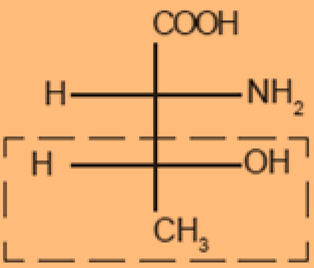
Eg :







D (+) Glyceraldehyde



D - theonin

25.4.e Intext questions :

1. What is notation used for dextro isomer?

....

2. What is meant by resolution?

....

3. What does D, L represent?

....

What you have learnt

- The process of conversion of an enantiomer into a racemic mixture is called racemisation.
- The process of separation of racemic mixture into its components is called resolution.
- R,S notation is used to assign the absolute configuration of e Stereo isomer.
- D, L notation is used to assign the relative configuration of a stereo isomer with respect to glyceraldehydes.

Terminal Exercise :

1. What is meant by racemisation ?
2. What is resolution ?
3. Write the sequence rules for assigning the configuration for stereo isomer in R,S notation.
4. How do you assign D, L configuration of stereo isomer.

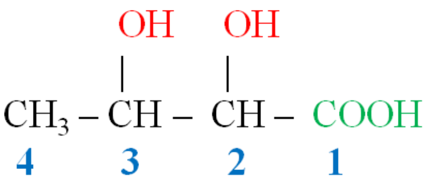
25.4.e Answers to Intext questions :

1. d or (+)
2. Separation of racemic mixture into d, L forms.
3. D, L represent the relative configuration of the stereo isomer with respect to glycerablehyde.

25.4.f Compounds containing two chiral centres, diastereomers, mesoforms, resolution, importance of stereo chemistry.

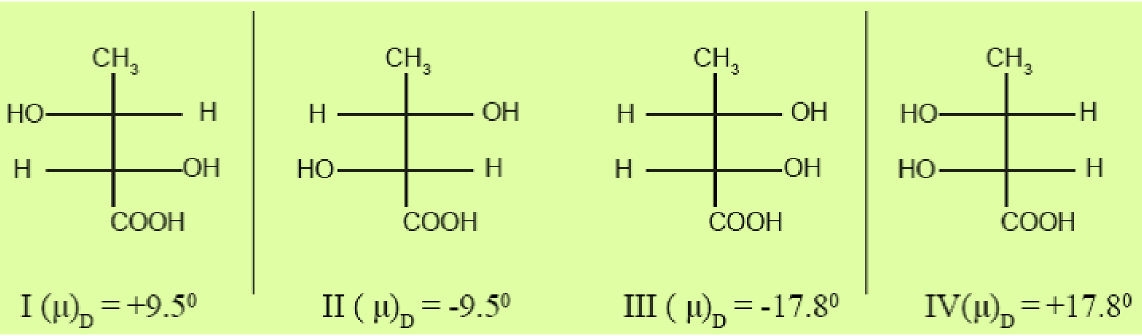
Molecule with one chiral centre, two pairs of enantiomers are possible for molecule with two chiral centres i.e., four enantiomers are possible. For compounds with ‘n’ Chiral centres, generally 2n Stereo isomers are possible and 2n-1 pairs of enantiomers.

For Example : 2,3 di-hydroxy butanoic acid.



$$\begin{array}{cccc} & OH & OH & \\ & | & | & \\ CH_3 - & CH - & CH - & COOH \\ 4 & 3 & 2 & 1 \end{array}$$

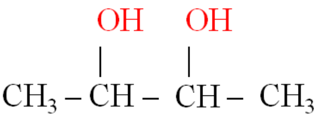
C-2, C-3 are chiral centres i.e., 2, 4 stereo isomers are possible i.e., at c-2 R, or S configuration and at c-3 R & S configuration.



I $(\mu)_D = +9.5^0$ II $(\mu)_D = -9.5^0$ III $(\mu)_D = -17.8^0$ IV$(\mu)_D = +17.8^0$

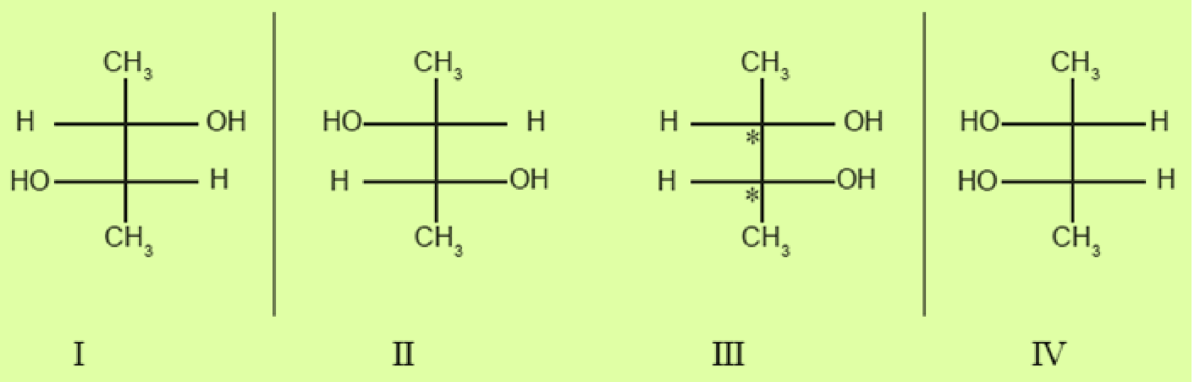
I & II are enantiomers, similarly III & IV are enantiomers. For 'I', III & IV not have object mirror image relationship. II & III and also I & IV are not having object, mirror image relationship. Such molecules which do not have object mirror image relationship are called diastereomers.

Example : 2,3 butanediol



$$\begin{array}{cccc} & OH & OH & \\ & | & | & \\ CH_3 - & CH - & CH - & CH_3 \end{array}$$

They are



Four isomers can be written

I & II are enantiomers but III & IV identical. The III is achiral. It is not optically active. This type of compounds are called meso compounds. When the asymmetric carbons are similar there is plane of symmetry in the molecule. Therefore the molecule is achiral. The optical inactivity is due to internal compensation.

Importance of Stereochemistry :

When two optically inactive compounds react, it leads to product which is optically inactive. But if an optically active compound is used as catalyst, the product may have optical activity using a chiral catalyst preparing a chiral product from achiral reactant is called a symmetric induction. This stereo chemical aspect is useful to know the chemical reactions that are taking place in biological systems.

The properties of the compound with respect to the reactions in biological systems can be known.

Example : (-) Nicotine is harmful than(+) Nicotine.

In the structure of blood vessels (+) adrenaline is more reactive than (-) adrenaline.

25.4.f Intext questions :

1. How many stereo isomers are possible for a molecule having in chiral centres.

....

2. How many enantiomers are possible for a molecule having 2 chiral centres.

....

What you have learnt :

- For a molecule with ‘n’ chiral centres 2n stereo isomers and 2n-1 pairs of enantiomers are possible.
- What two asymmetric centres are similar, than the molecule has only one pair of enantiomers.
- Diastereomers are isomers which do not have object uninor image relationship.

Terminal Exercise :

1. Explain stereo isomerism exhibited by molecule having two different chiral centres.
2. Explain stereo isomerism exhibited by molecule having two similar chiral centres.
3. Given an example of meso compound.

25.4.f Answers to intext questions :

1. 2^n stereo isomers.
2. $2^{2-1} = 2^1$ = two *i.e.*, a pair of enantiomers.

Chapter 26

HYDROCARBONS

You have studied in the previous lesson that hydrocarbons are the compounds containing carbon and hydrogen. You also know that they are classified as aliphatic, alicyclic and aromatic hydrocarbons. They constitute a very important class of organic compounds and are widely used as fuels, lubricants and dry cleaning agents. They are also used as important ingredients in medicines and in dyes. Petroleum and coal are the major sources of various types of hydrocarbons. The products obtained from fractional distillation of petroleum and destructive distillations of coal are used almost in every sphere of life. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with different functional groups. In this lesson, you will study about the preparation, important physical and chemical properties of hydrocarbons.

Objectives

After reading this lesson, you will be able to:

- list different methods of preparation of alkanes;
- explain the reasons for variation in physical properties of alkanes;
- describe different chemical properties of alkanes;
- list different methods of preparation of alkenes;
- explain the physical properties of alkenes;
- describe the chemical properties of alkenes;
- list different methods of preparation of alkynes;
- explain physical and chemical properties of alkynes;
- discuss the cause of greater reactivity of alkenes and alkynes over alkanes;
- distinguish alkanes, alkenes and alkynes;
- list various fractions obtained by destructive distillation of coal;
- explain the stability of various organic compounds using resonance;
- describe methods of preparation, physical properties and chemical properties of benzene, and list various uses of hydrocarbons.

26.1 Alkanes (Paraffins)

Alkanes are saturated hydrocarbons. They are very less reactive towards various reagents; hence, they are also referred to as paraffins (parum means little, affins means affinity).

26.1.1 Methods of Preparation

Some important methods of preparation of alkanes are as follows:

1. From Haloalkanes (Alkyl Halides):

Mono haloalkanes can be converted to alkanes by following three methods:

a) **By reduction of haloalkanes:** The replacement of halogen atom of haloalkanes with hydrogen is called the reduction and can be carried out by the following reagents:

(i) Zinc and dilute HCl

$$CH_3Br + Zn + 2HCl \longrightarrow CH_4 + ZnCl_2 + HBr$$

Bromomethane Methane

(ii) HI in the presence of red phosphorus

$$C_2H_5I + HI \xrightarrow[423K]{\text{red phosphorus}} C_2H_6$$

Iodoethane Ethane

(iii) Catalytic reduction

$$CH_3C1 + H_2 \xrightarrow{\text{Pt (catalyst)}} CH_4 + HCl$$

Chloromethane Methane

b) **By using Grignard's Reagent :** A Grignard reagent is a compound of the type RMgX which is prepared by reacting a haloalkane with magnesium metal in the presence of dry ether.

$$C_2H_5Br + Mg \xrightarrow{\text{dry ether}} C_2H_5MgBr$$

Bromoethane Ethyl Magnesium Bromide

The Grignard's reagents are used to prepare various compounds like hydrocarbons, ethers, alcohols and carboxylic acids. It reacts with the compounds containing active hydrogen and forms alkanes. An easily replaceable hydrogen atom present in the compounds is called active hydrogen. An active hydrogen is present in (i) alcohols and (ii) water and (iii) acids.

$$CH_3MgBr + C_2H_5OH \longrightarrow CH_4 + Mg(OC_2H_5)Br$$

$$C_2H_5MgBr + H_2O \longrightarrow C_2H_6 + Mg(OH)Br$$

c) **By Wurtz Reaction:** In this reaction, an alkyl halide reacts with sodium metal in the presence of dry ether and forms the higher alkanes.

$$CH_3 - Br + 2Na + Br - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaBr$$

Bromoethane Ethane

2. From Unsaturated Hydrocarbons : The unsaturated hydrocarbons (i.e. alkenes and alkynes) can be converted to alkanes by the addition of hydrogen in the presence of a catalyst like nickel, platinum or palladium.

$$CH_2 = CH_2 + H_2 \xrightarrow[573K]{\text{Ni or Pt}} CH_3 - CH_3$$

$$CH \equiv CH + 2H_2 \xrightarrow[573K]{\text{Ni or Pt}} CH_3 - CH_3$$

This reaction is also called hydrogenation and is used to prepare vegetable ghee from edible oils (by converting unsaturated fats to saturated ones.)

3. From Alcohols, Aldehydes and Ketones : Alcohols, aldehydes and ketones on reduction with HI, in presence of red phosphorus, give alkanes. The general reactions are as shown below.

$$\underset{\text{Alcohol}}{ROH} + 2HI \xrightarrow{redP/423K} \underset{\text{Alkane}}{RH} + I_2 + H_2O$$

$$\underset{\text{Aldehyde}}{RCHO} + 4HI \xrightarrow{redP/423K} \underset{\text{Alkane}}{RCH_3} + 2I_2 + H_2O$$

$$\underset{\text{Ketone}}{RCOR'} + 4HI \xrightarrow{redP/423K} \underset{\text{Alkane}}{RCH_2R'} + 21_2 + H_2O$$

4. From Carboxylic Acids : Carboxylic acids can produce alkanes in a number of ways as shown below :

i) Heating with soda lime :

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

In this reaction, an alkane with one carbon less than’ those present in the parent carboxylic acid is obtained.

ii) By Reduction of carboxylic acid :

$$RCOOH + 6\,HI \xrightarrow{redP/423K} RCH_3 + 3I_2 + 2H_2O$$

Here, an alkane with same number of carbon atoms as in the starting carboxylic acid is obtained.

iii) Kolbe’s Electrolysis: Sodium or potassium salt of a carboxylic acid, on electrolysis, gives a higher alkane. The reaction takes place as follows.

$$\underset{\text{Sodium salt of carboxylic acid}}{RCOONa} \xrightarrow{\text{electrolysis}} \underset{\text{Anion}}{RCOO^-} + \underset{\text{Cation}}{Na^+}$$

At Anode:

$$RCOO^{-} \longrightarrow RCOO^{\bullet} + e^{-}$$

$$RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R-R$$

Thus, ethane can be obtained by the electrolysis of sodium ethonate.

$$\underset{\text{Sodium ethanote}}{2\ CH_3COONa} \longrightarrow \underset{\text{Ethane (at anode)}}{CH_3-CH_3}$$

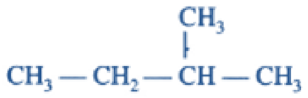
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

26.1.2 Physical Properties of Alkanes

Physical State: The physical state of alkanes depends upon the intermolecular forces of attraction present between molecules which in turn, depend upon the surface area of the molecules. *As the molecular mass of the alkanes increases, their surface area also increases, which in turn, increases the intermolecular forces of attraction, and accordingly, the physical state of alkanes changes from gaseous to liquid and then to solid.* The alkanes containing 1 to 4 carbon atoms are gases, whereas those containing 5 to 17 carbon atoms are liquids, and the still higher ones are solids. In the case of isomeric alkanes, the straight chain alkanes will have maximum surface area and hence, stronger intermolecular force of attraction. As the branching increases, surface area decreases. Hence the intermolecular forces of attraction decrease. Let us consider the isomers of pentane (C_5H_{12}).

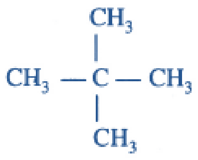
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

n-Pentane



$$CH_3-CH_2-\underset{}{\overset{\overset{\large CH_3}{|}}{CH}}-CH_3$$

2-Methylbutane
(Isopentane)



$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_3$$

2,2-Dimethylpropane
(Neopentane)

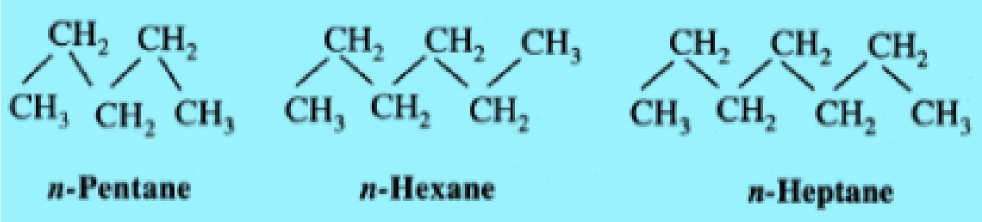
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

Density: *The density of alkanes increases with the increase in molecular mass which increases with the increase in the number of carbon atoms*. All alkanes are lighter than water i.e. their density is less than 1.0 g/cm^3. The maximum density in the case of alkanes is 0.89 g cm^3. The lower density of alkanes than water is due to the absence of strong intermolecular attractions in alkanes.

Boiling Point : *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point of alkanes. Thus, in the above example, isopentane and neopantane have a lower boiling point than pentane.

Melting Point : Similar to the boiling points, the melting points of alkanes also increase with the increase in their molecular mass, but there is no regular variation in melting point. The melting points of alkanes depend not only upon the size and shape of the molecules, but also on the arrangement (*i.e.* the packing) of the molecules in the crystal lattice.

In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of 109°28'. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the interaction between the alkane molecules, with odd number of carbon atoms, is less than the molecule with even number of carbon atoms, in which terminal methyl groups lie on the opposite sides.



(Carbon atoms = 5, m.p.142 K) (Carbon atoms =6, m.p. = 179 K) (carbon atoms = 7, m.p. = 183 K)

In the above structures, we find that alkanes containing even number of carbon atoms are more symmertical and can be more closely packed as compared with alkanes containing odd number of carbon atoms and can be more closely packed. Van der Waal's force of attraction is stronger, due to which they have higher melting points. *Therefore, the alkanes with odd number of carbon atoms have lower melting point than those having even number of carbon atoms.*

26.1.3 Chemical Properties of Alkanes

1. Halogenation reactions: The chemical reactions in which a hydrogen atom of an alkane is replaced by a halogen atom are known as *halogenation*. Alkanes react with chlorine in the following way.

$$CH_4 + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} CH_3Cl$$

Methane Chloromethane

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} CH_2Cl_2$$

Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} CHCl_3$$

Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} CCl_4$$

Tetrachloromethane

Chlorination of methane takes place via the **free radical mechanism**. When the reaction mixture is exposed to sunlight, chlorine molecules absorb energy from sunlight and get converted to free radicals *i.e.* chlorine atoms with an unpaired electron (Cl*). The chlorine radicals then combine with methane and form methyl radial [*CH_3]. The methyl radical further reacts with chlorine molecule and produces chloromethane. This reaction continuously takes place till it is stopped or the reactants completely react to form the products. The free radical mechanism involves the following three steps.

(i) Chain Initiation Step: It involves the formation of free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl^*$$ (h*v* = energy of light)

(ii) Chain Propagation Step: The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \overset{*}{C}l \longrightarrow \overset{*}{C}H_3 + HCl$$

$$C\dot{H}_3 + Cl_2 \longrightarrow CH_3Cl + \dot{C}l$$

(iii) Chain Termination Step : In this step, free radicals combine with one another and the further reaction stops.

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl$$

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3 - CH_3$$

The reactivity of halogens is in the order of **$F_2 > Cl_2 > Br_2 > I_2$**.

2. Oxidation: Alkanes undergo oxidation (combustion) in excess of oxygen and produce carbon dioxide and water. This reaction is highly exothermic in nature. For example:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + 890\ KJ\ mol^{-1}$$

If the combustion is carried out in the presence of an insufficient supply of air or O_2, then *incomplete combustion takes place forming carbon monoxide* instead of carbon dioxide.

$$2C_2H_6 + 5O_2 \xrightarrow{heat} 4CO + 6H_2O$$

3. Cracking or Pyrolysis : At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873K} CH_3CH = CH_2 + H_2 \quad \text{or} \quad CH_2 = CH_2 + CH_4$$

4. Isomerisation : n-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.

$$\underset{n\text{-butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow{AlCl_3/HCl} \underset{\text{isobutane}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

26.1.4 Uses of Alkanes

Alkanes are used as fuel gases, solvents, drycleaning agents, lubricants and in ointments (paraffin wax). Methane is used for illuminating and domestic fuel and also for the production of other organic compounds such as haloalkanes, methanol, formaldehyde and acetylene. Propane is used as a fuel, refrigerant and as raw material in the petrochemical industry. Butane and its isomer-isobutane, are the major constituents of LPG.

Intext Questions 26.1

1. List four important uses of hydrocarbons.

....

2. What is Grignard's reagent in a molecule?

....

3. What is an active hydrogen in a molecule?

....

4. What makes the physical properties of various hydrocarbons different?

....

5. Name two alkanes which are gases and two alkanes which are liquids at room temperature.

....

6. Name three isomers of pentane.

....

7. Which one has higher b.p. n-butane or n-pentane? Explain.

....

8. Write the balanced chemical equation for the complete combustion of propane.

....

26.2 Alkenes

These are unsaturated hydrocarbons containing at least one double bond between two carbon atoms. The hydrocarbons of this class are also called **olefines** (*olefiant* = oil forming).

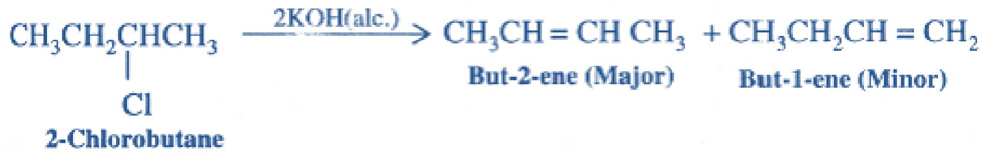
26.2.1 Methods of Preparation

In the laboratory, alkenes are generally prepared either from haloalkanes (alkyl halides) or alcohols.

1. From Haloalkanes : Halaoalkanes are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCI, HBr or HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called *dehydrohalogenation*.

$$CH_3 - CH_2 - Cl + KOH(alc.) \longrightarrow CH_2 = CH_2 + KCl + H_2O$$

Chloroethane Ethene



$$\underset{\underset{\text{Cl}}{|}}{CH_3CH_2CHCH_3} \xrightarrow{2KOH(alc.)} \underset{\text{But-2-ene (Major)}}{CH_3CH=CH\,CH_3} + \underset{\text{But-1-ene (Minor)}}{CH_3CH_2CH=CH_2}$$

2-Chlorobutane

The major product is formed according to the Saytzeff's Rule.

Saytzeff's Rule : *It states that when an alkyl halide reacts with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more substituted, will be the major product*. In the above example, but-2-ene is the major product because it contains two alkyl groups attached to the -C = C- group.

2. From Alcohols: Alkenes can be prepared from alcohols by dehydration in the presence of a suitable dehydrating agent such as (i) Al_2O_3 or (ii) concentrated H_2SO_4.

$$CH_3 - CH_2 - OH \xrightarrow[623-633K]{Al_2O_3} CH_2 = CH_2 + H_2O$$

Ethanol Ethene

$$CH_3-CH_2 - OH \xrightarrow[433K]{conc.H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethanol Ethene

In the dehydration of higher alcohols, the major product obtained is according to the Saytzeff's Rule.

26.2.2 Physical Properties of Alkenes

Some important physical properties of alkanes are as follows:

Physical State: Unbranched alkenes containing upto four carbon atoms are gases and containing five to sixteen carbon atoms are liquids while those with more than 16 carbon atoms are solids.

Boiling Points: The boiling points of alkenes increase with molecular mass as is shown in Table 26.1.

Table 26.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent=1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

The increase in boiling point can be attributed to the ***Van der Waals*** forces which increase with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

Melting Point : In alkenes, there is increase in the melting point with the increase in molecular mass. In the case of isomeric alkenes, the cis and trans isomers have different melting points.

For example

trans-But-2-ene (m.p. 167 K)

cis-But-2-ene (m.p. = 134 K)

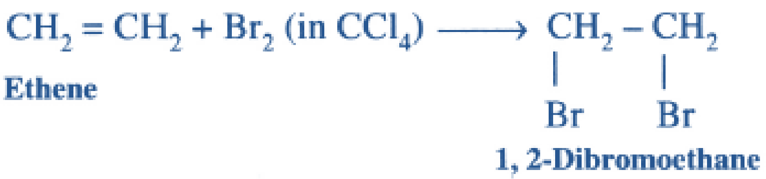
26.2.3 Chemical Properties of Alkenes

1. Addition Reactions : The chemical reactions in which a molecule adds to another molecule are called an *addition reaction*. These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

(i) Addition of Hydrogen : Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2 \xrightarrow[573K]{Ni\ (Pt\ or\ Pd)} \underset{\text{Ethane}}{CH_3 - CH_3}$$

(ii) Addition of Halogens : Halogens on addition to alkenes, form 1,2-dihaloalkanes.



$$\underset{\text{Ethene}}{CH_2 = CH_2} + Br_2\ (\text{in } CCl_4) \longrightarrow \underset{\text{1, 2-Dibromoethane}}{\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}}}$$

As a result of this addition reaction, the reddish-brown colour of Br_2 gets discharged. This reaction is also used as test for unsaturation in hydrocarbons.

(iii) Addition of Halogen Acids (HX) : When halogen acids are added to alkenes , hydrogen adds to one carbon atom whereas halogen atom adds to the second carbon atom of the double bond.

$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2 - Br$$

Ethene Bromoethane

In case of unsymmetrical alkenes (which contain unequal number of H-atoms attached to the carbon atoms of the double bonds), the addition of HX takes place according to the *Markownikoff's rule*. This rule states that in *the addition of halogen acids to unsymmetrical alkenes, the halogen of HX goes to that carbon atom of C = C bond which already has less H-atoms attached to it*. In other words, hydrogen atom of HX goes to the carbon atom with more number of H-atoms attached to it.

$$CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBr\,CH_3$$

Propene 2-Bromopropane

If the addition of HBr is carried out in the presence of peroxides such as benzoyl peroxide, then the reaction takes place contrary to Markownikoff's rule. This is also known as *Anti Markownikoff's addition or peroxide effect*.

$$CH_3CH = CH_2 + HBr \xrightarrow{\text{benzoyl peroxide}} CH_3CH_2 - CH_2 - Br$$

Propene 1 - Bromopropane

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Heat}]{H_2SO_4} CH_3 - CH_2 - OH$$

Ethene Ethanol

(v) Addition of H_2SO_4

$$CH_2 = CH_2 + \text{conc. } H_2SO_4 \longrightarrow CH_3 - CH_2 - HSO_4$$

Ethene Ethyl hydrogen sulphate

(vi) Addition Polymerization: The process in which many molecules of an alkene add together to form a larger molecule is called addition polymerization.

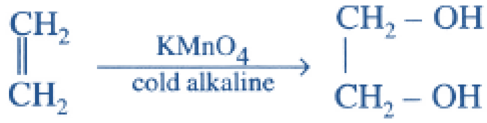
$$n(CH_2 = CH_2) \xrightarrow[\text{heat, pressure}]{} -\!\!\left(CH_2 - CH_2\right)\!\!-_n$$

Ethene Polyethene

2. Oxidation : The oxidation of alkenes can be done by using different oxidizing agents like $KMnO_4$ oxygen and ozone.

(i) Oxidation with $KMnO_4$

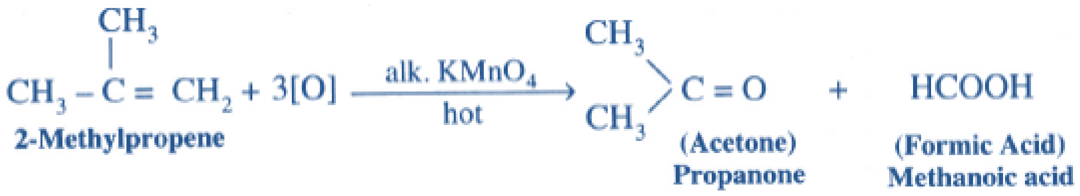
Alkenes are unsaturated hydrocarbons having Pi(π)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



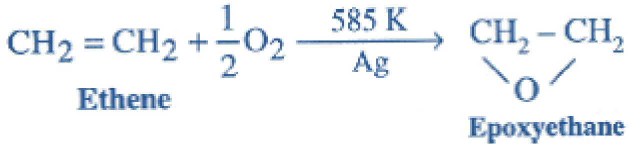
$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow[\text{cold alkaline}]{KMnO_4} \begin{matrix} CH_2 - OH \\ | \\ CH_2 - OH \end{matrix}$$

Ethene **Ethanediol**

When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



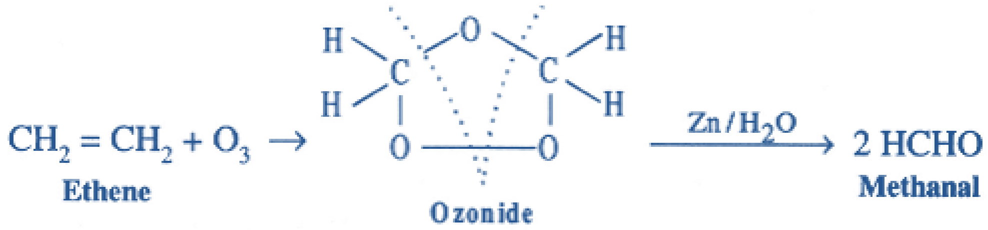
(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called combustion.

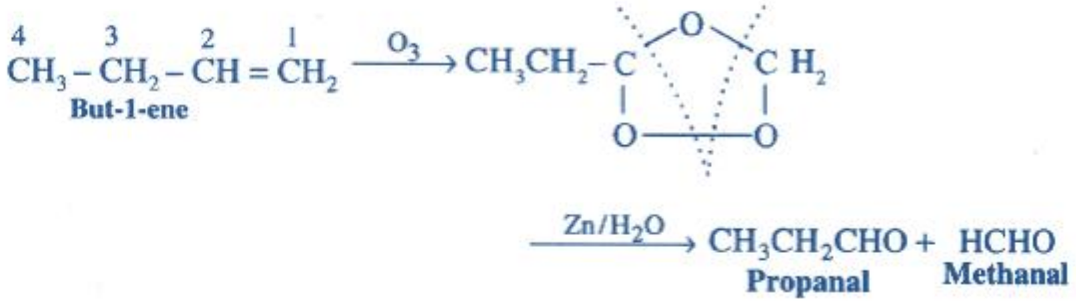
$$CH_2 = CH_2 + 3O_2 \xrightarrow{heat} 2CO_2 + 2H_2O \qquad \Delta H = -1411\ KJ\ mol^{-1}.$$

(iv) Oxidation with Ozone: Ozone adds to the alkene forming ozonide. The is ozonide when further reacted with water in the presence of zinc dust, forms aldehydes or ketones, or both.

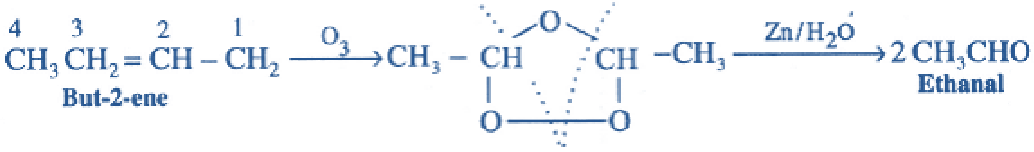


This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis**.

Ozonolysis can be used for the determination of the position of double bonds in alkenes by analysing the products formed i.e. aldehydes and ketones. This is explained below,



When but-l-ene is oxidized with ozone and the ozonide formed is hydrolysed, we get one mole of propanal and one mole of methanal, showing that the double bond is between carbon atom 1 and 2. Whereas but-2-ene on oxidation with ozone, followed by hydrolysis, gives two moles of ethanal, showing that the double bond is present between carbon atoms 2 and 3 as shown below.



26.2.4 Uses of Alkenes

Ethene is used for making mustard gas, which is a poisonous gas used in warfare. It is also used for artificial ripening of fruits, as a general anaesthetic and for producing other useful materials such as polythene, ethanal, ethylene glycol (antifreeze), ethylene oxide (fumigant) etc.

Intext Questions 26.2

1. Which one has higher boiling point: cis but-2-ene or trans but-2-ene?

....

2. Name the products formed when ethene is oxidized with cold alkaline solution of $KMnO_4$.

....

3. Write the conditions for hydrogenation of alkenes.

....

4. What happens when ethene reacts with oxygen at 575 K in presence of Ag?

....

26.3 Alkynes

These are also unsaturated hydrocarbons which contain atleast one triple bond between two carbon atoms. Some examples are as follows :

$CH\equiv CH$,	$CH_3-C\equiv CH$,	$CH_3-C\equiv C-CH_3$
Ethyne	Propyne	But-2-yne

26.3.1 Preparation of Ethyne (Acetylene):

Some important methods for preparation of ethyne are explained below.

1. From Calcium Carbide : Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

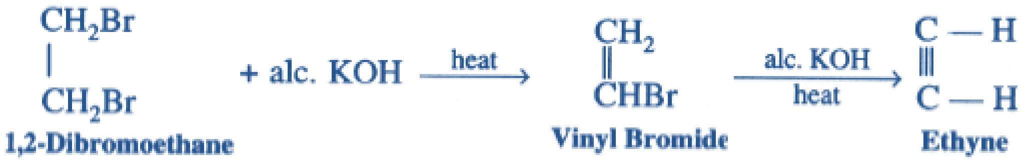
$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Water}}{2H_2O} \longrightarrow \underset{\text{Ethyne}}{H-C\equiv C-H} + Ca(OH)_2$$

Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

2. Preparation of Ethyne from Dihaloalkanes

Ethyne can be prepared by refluxing *geminal* dihaloalkanes (having both halogens attached to the same carbon atom) or *vicinal* dihaloalkanes (having halogen atoms attached to the adjacent carbon atoms) with alcoholic solution of KOH.

Eg.Vicinal dihaloalkane



$$\underset{\text{1,2-Dibromoethane}}{\begin{array}{c}CH_2Br\\|\\CH_2Br\end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\text{Vinyl Bromide}}{\begin{array}{c}CH_2\\\|\\CHBr\end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\text{Ethyne}}{\begin{array}{c}C-H\\|||\\C-H\end{array}}$$

Eg. Geminal dihaloalkane

$$\underset{\text{1,1-Dibromoethane}}{\begin{array}{c}CH_3\\|\\CHBr_2\end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\text{Vinyl Bromide}}{\begin{array}{c}CH_2\\\|\\CHBr\end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\text{Ethyne}}{\begin{array}{c}C-H\\|||\\C-H\end{array}}$$

3. Preparation of higher alkynes : Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R-C\equiv CH + Na \xrightarrow{\text{liq.}NH_3} R–C\equiv C^- Na^+$$

$$R-C\equiv C^- Na^+ + CH_3I \longrightarrow R–C\equiv C–CH_3 + NaI$$

26.3.2 Physical Properties of Alkynes

1. First three members of alkynes are gases, the next eight members are liquids and members having more than twelve carbon atoms are solids.
2. They are colourless and odourless, except ethyne which has a garlic odour.
3. The melting points, boiling points and densities of alkynes increase with the increasing molar mass. In alkynes, there are π(pi)-electrons due to which these molecules are slightly polar. So charge separation takes place in alkynes, and hence dipoles are formed. The presence of dipoles increases the inter molecular force of attraction, and hence the boiling points of alkynes are higher than those of the corresponding alkanes.
4. Alkynes are very slightly soluble in water and soluble in acetone.

26.3.3 Chemical Properties of Alkynes

1. Addition Reactions : Some of the addition reactions of alkynes are as follows.

(i) Addition of Hydrogen : Addition of hydrogen to alkynes takes place in the presence of a catalyst like Ni, Pt or Pd.

$$CH\equiv CH + H_2 \xrightarrow[573K]{Ni\ or\ pt\ or\ Pd} CH_2 = CH_2 \xrightarrow{H_2 + Ni\ or\ Pt\ or\ Pd} CH_3-CH_3$$

(ii) Addition of Halogens : When halogens are added to alkynes, they form 1,2-dihaloalkenes and 1,1,2,2-tetrahaloalkanes.

$$CH\equiv CH \xrightarrow{Br_2\ in CCl_4} CHBr = CHBr \xrightarrow{Br_2\ in CCl_4} CHBr_2 - CHBr_2$$

Ethyne 1, 2 - Dibromoethene 1,1,2,2-Tetrabromoethane

(iii) Addition of Halogen Acids (HX) : Addition of HBr to ethyne is as follows :

$$CH\equiv CH \xrightarrow{HBr} CH_2 = CHBr \xrightarrow{HBr} CH_3 - CHBr_2$$

Ethyne Bromoethene 1,1-Dibromoethane

(iv) Addition of Water : Addition of water takes place in the presence of mineral acids like H_2SO_4 and in the presence of Hg^{2+} as the catalyst.

$$CH\equiv CH + H_2O \xrightarrow[1\%HgSO_4]{40\%H_2SO_4} [CH_2 = CHOH] \xrightleftharpoons{Re\ arrangement} CH_3CHO$$

Ethyne Vinyl Alcohol Ethanal

(Unstable)

(v) Addition of H_2SO_4: Conc. H2SO4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{conc.H_2SO} CH_2 = CHHSO_4 \xrightarrow{H_2SO_4} CH_3 - CH\ (HSO_4)_2$$

Vinyl hydrogen sulphate Ethylidene hydrogen sulphate

2. Oxidation: Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

(i) Oxidation with $KMnO_4$

$$\underset{\textbf{Ethyne}}{CH\equiv CH + 4\,[O]} \xrightarrow{Cold\ alkaline\ KMnO_4} \underset{\textbf{Oxalic acid}}{\begin{array}{c}COOH\\|\\COOH\end{array}}$$

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$R - C \equiv C - R' \xrightarrow[heat]{KMnO_4 + KOH} RCOOH + R'COOH$$

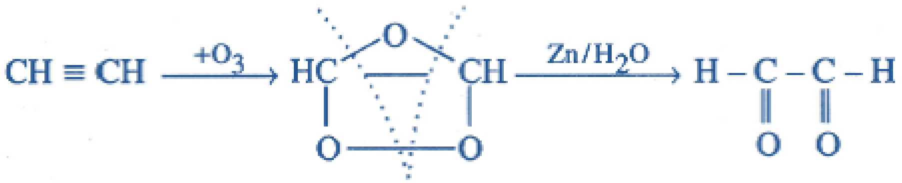
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH\equiv\ CH + 4\ [O] \xrightarrow[heat]{KMnO_4 + KOH} (COOH)_2 \xrightarrow[Heat]{[O]} 2\ CO_2 + H_2O$$

Combustion: Combustion of ethyne in excess of oxygen or air gives carbon dioxide and water as shown below :

$$2\ C_2H_2 + 5\ O_2 \xrightarrow{heat} 4\ CO_2 + 2\ H_2O \qquad \Delta H = -1300\ KJ\ mol^{-1}$$

Ozonolysis: On ozonolysis, alkynes give dicarbonyl compounds at the position of C C without breaking the chain of carbon atoms as shown below :



3. Formation of Acetylides : Ethyne forms precipitates of copper and silver acetylides when passed through ammonical solution of cuprous chloride and ammonical silver nitrate, respectively.

$$CH \equiv CH + 2Cu(NH_3)_2 \longrightarrow CuC \equiv CCu + 2\,NH_4^+ + 2\,NH_3$$

Cuprous acetylide (red)

$$CH \equiv CH + 2Ag(NH_3)_2 \longrightarrow AgC \equiv CAg + 2\,NH_4^+ + 2\,NH_3$$

Silver acetylide (white)

26.3.4 Acidic Nature of Ethyne

The acidic nature of hydrocarbons can be determined with the help of the percentage (%) of s-character of the hydrocarbon. The greater the percentage of s-character of a hydrocarbon, the more will be its acidic nature.

Table 26.2 : % s-Character of hyrid orbitals in Hydrocarbons

Hydrocarbon	Type of hybridization	(%) s-character
Alkanes	sp^3	25%
Alkenes	sp^2	33.3%
Alkynes	sp	50%

As alkynes have 50% *s*-character, they are the most acidic in nature. An sp-hybridized carbon atom is more electronegative than sp^2 or sp^3 carbon atoms. Due to greater electronegativity of sp hybridized carbon atom in ethyne, hydrogen atom is less tightly held by the carbon and hence, it can be removed as a proton (H^+) by a strong base like sodium metal and sodarnide. **The following reactions of ethyne with sodium and sodamide confirm its acidic nature.** In these reactions, disodium acetylide is formed.

$$H - C \equiv C - H + 2\,Na \xrightarrow{\text{Heat}} Na - C \equiv C - Na + H_2$$

Ethyne — Disodium Acetylide

(Acetylene)

$$H - C \equiv C - H + 2\,NaNH_2 \xrightarrow{\text{Heat}} Na - C \equiv C - Na + 2NH_3$$

Ethyne — Sodamide — Disodium Acetylide

26.3.5 Uses of Alkynes

Ethyne (acetylene) is used for producing oxyacetylene flame (2800° C) which is used for welding and cutting of iron and steel. It is also used for artificial ripening of fruits and vegetables. It also finds use in the production of a number of other organic compounds such as ethanal, ethanoic acid, ethanol, synthetic rubbers and synthetic fibre *orlon*.

26.3.6 Distinction Between Alkanes, Alkenes and Alkynes

The following table shows different tests for distinction between alkanes, alkenes and alkynes:

Table 26.3 : Tests for identification of alkanes, alkenes and alkynes

S.No	Test	Alkanes	Alkenes	Alkynes
1	Add bromine dissolved in carbon tetrachloride.	No change	Reddish brown colour of Br_2 is discharged	Reddish brown colour of Br_2 is discharged
2	Add alkaline solution of $KMnO_4$ (Baeyer's reagent)	No change	Purple colour of $KMnO_4$ is discharged	Purple colour $KMnO_4$ is discharged
3	Add ammonical solution of silver nitrate	No change	No change	White ppt. of silver acetylide is formed
4	Add ammonical solution of cuprous chloride (Cu_2Cl_2)	No change	No change	Red ppt. of cuprous acetylide is formed

Intext Questions 26.3

1. How is ethyne prepared from calcium carbide?

....

2. Give one reaction to confirm the acidic nature of ethyne.

....

3. What is the percentage of s-character in ethane, ethene and ethyne?

....

26.4 Aromatic Hydrocarbons

Till now, we have explained various methods of preparation of aliphatic hydrocarbons. Now, we shall deal with an aromatic hydrocarbon (benzene) in detail. It is one of the major components obtained by the destructive distillation of coal as shown in Fig. 26.1

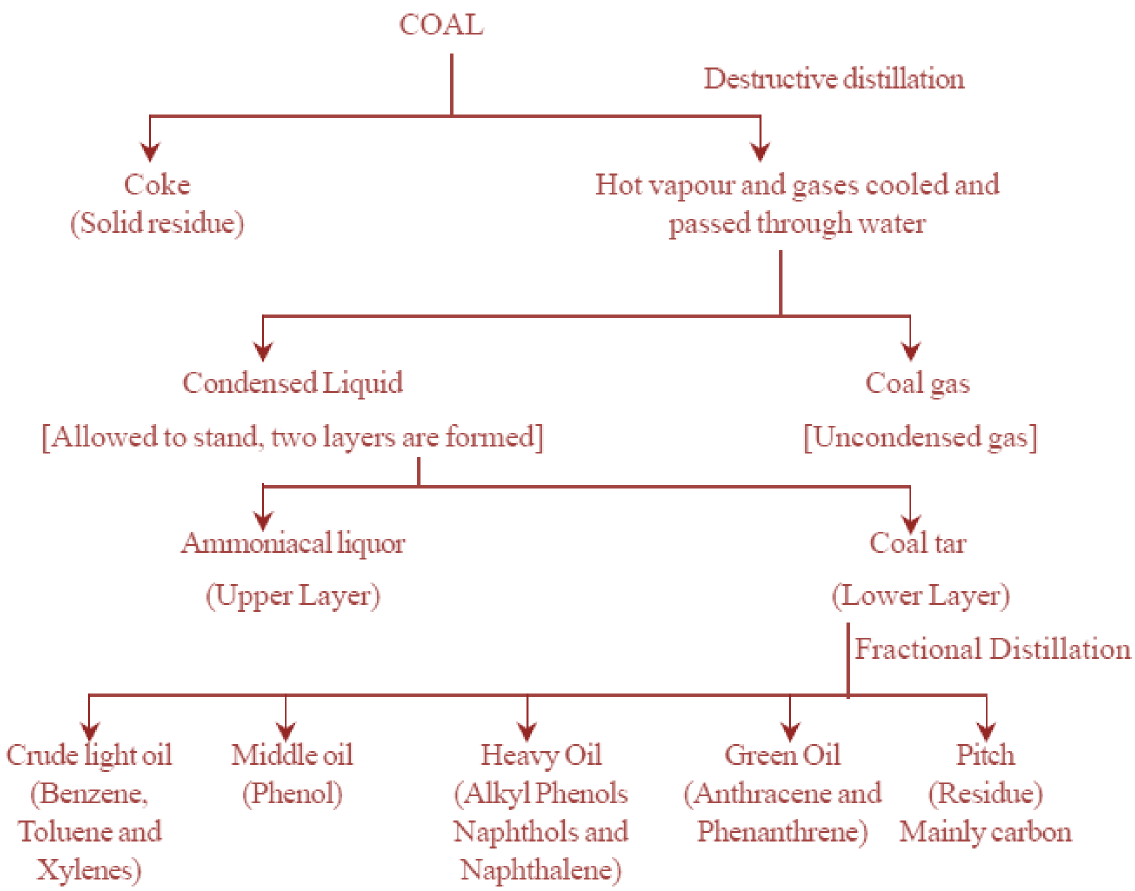


Fig. 26.1 : Destructive Distillation of coal

26.4.1 Structure of Benzene

The molecular formula of benzene is C_6H_6 which indicates that benzene is an unsaturated hydrocarbon. The unsaturation in benzene can be verified by the following reactions.

(i) Benzene undergoes the addition of H_2 in the presence of Ni or Pt as catalyst.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Cyclohexane}}{C_6H_{12}}$$

(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

$$\underset{\text{Benzene}}{C_6H_6} + 3Cl_2 \xrightarrow{h\nu} \underset{\text{Benzene hexachloride (B.H.C.)}}{C_6H_6Cl_6}$$

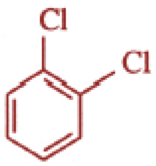
Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes ie., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions. e.g.

$$\underset{\text{Benzene}}{C_6H_6} + Br_2 \xrightarrow{\text{Fe or FeCl}_3} \underset{\text{Bromobenzene}}{C_6H_5Br} + HBr$$

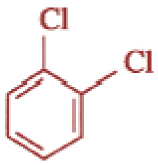
Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.

As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 and all the carbon-carbon bond lengths are equal i.e. 139 pm.

If Kekule's structure is to be taken as a true structure, then benzene should form only one monosubstitution product and two ortho distubstitution products, shown below as (a) and (b).



(a)



(b)

In structure (a), the two halogen atoms are on the doubly bonded carbon atoms, whereas in structure (b), the two halogen atoms are on singly bonded carbon atoms. As per the Kekule's structure these two isomers (a and b) should exist and show different properties. But, in reality, only one ortho disubstituted product exists. In order to explain this, Kekule proposed a dynamic equilibrium between the two structures.

Kekule's structure does not explain the stability of benzene and its some unusual reactions. Resonance can explain the unusual behaviour of benzene. Let us now study about resonance.

Resonance : *The phenomenon by virtue of which a single molecule can be represented in two or more structures is called resonance.* The actual structure is the resonance hybrid of all the canonical or resonating structure. (see lesson 25)

Heat of hydrogenation data provides proof for resonance stabalization in benzene. The heat of hydrogenation is the amount of heat liberated when hydrogen is added to a one mole of an unsaturated compound in the presence of a catalyst.

$$\text{Cyclohexene} \quad + H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5\ \text{KJ mol}^{-1}$$

$$(\text{One - C = C- bond})$$

If the three double bonds in benzene do not interact, then it should behave like cyclohexatriene and the amount of heat liberated on adding there molecules of hydrogen should be 358.5 KJ mol^{-1}. But, the actual heat of hydrogenation of benzene is 208.2 KJ mol^{-1}.

$$\text{Benzene} + 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2\ \text{KJ mol}^{-1}$$

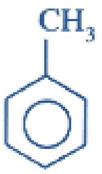
(Three - C = C- bond)

This difference of (358.5 - 208.2) 150.3 KJ mol^{-1} in the heat of hydrogenation is the measure of stability of benzene. Benzene acquires stability due to resonance and hence, this energy is called ***resonance energy*** of benzene.

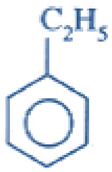
26.4.2 Physical Properties of Aromatic Hydrocarbons

1. Benzene and its homologues are colourless liquids having a characteristic odour.
2. They are immiscible in water but are miscible in all proportions with organic solvents such as alcohol, ether, petrol, etc. They dissolve fats and many other organic substances.
3. Most of the aromatic hydrocarbons are lighter than water.
4. Their boiling points show a gradual increase with increasing molecular mass e.g. benzene (b.p. 353 K), toluene (b.p. 383 K) and ethylbenzene (b.p. 409 K) and so on.

Benzene
(b.p. 353 K)



Toluene
(b.p. 383 K)



Ethylbenzene
(b.p. 409 K)

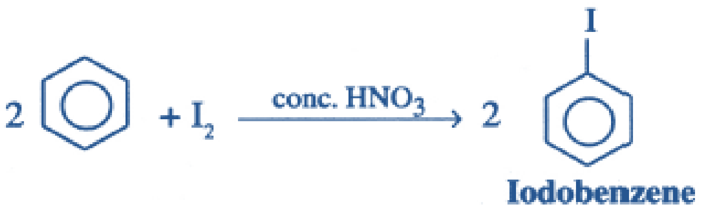
26.4.3 Chemical Properties of Aromatic Hydrocarbons

Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(i) Halogenation: The reaction in which a hydrogen atom of benzene is replaced by a halogen atom is called halogenation of benzene. Halogenation takes place in the presence of iron, or ferric halides (FeX_3 , where X = Cl or Br).

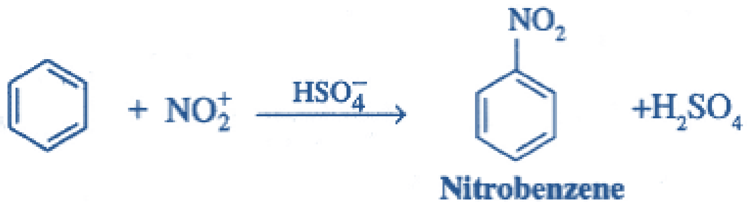
Halobenzene

In case of iodination the product iodobenzene can be reduce back to benzene which is prevented by carrying out this reaction in the presence of HNO_3 or HIO_3. These acids react with HI as soon as it is formed.

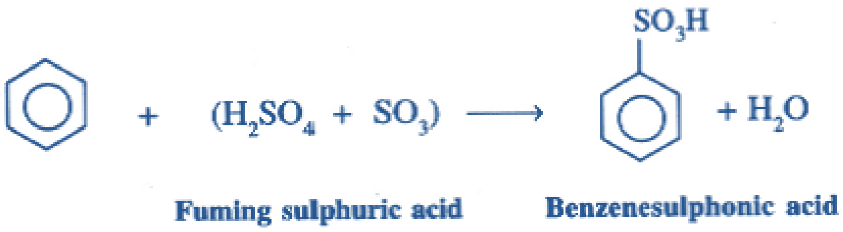


(ii) Nitration: the chemical reaction, in which a hydrogen atom of benzene ring is replaced by -NO_2 group, is called nitration. It is carried out in the presence of nitrating mixture, i.e. a mixture of conc. HNO_3 and conc. H_2SO_4. Nitronium ion (NO_2^+) so formed acts as an electrophile.

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^- + NO_2^+ + H_3O^+$$



(iii) Sulphonation: The chemical reaction in which the hydrogen atom of benzene is replaced by -SO_3H group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.



(iv) Friedel-Craft's Reactions: In Friedel-Craft's reaction, benzene is heated either with alkyl halide (alkylation) or acyl halide (acylation) in the presence of a catalyst (anhydrous $AlCl_3$). The products formed are alkyl or acyl derivatives of benzene.

Alkylation:

Acylation:

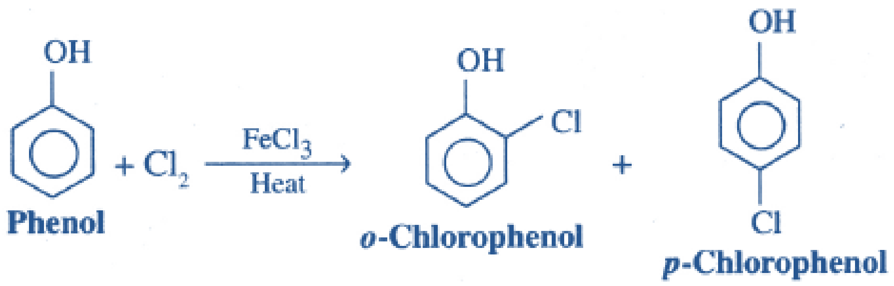
26.4.4 Directive Influence of Functional Groups

In case of substituted aromatic compounds, the functional group(s) already present directs the next incoming group to a particular position in the aromatic ring. It is called directive influence of the group already attached to the benzene ring. For example, phenol on chlorination gives a mixture of *ortho* - chlorophenol and *para*- chlorophenol as - OH groups is an *ortho* and *para* directing group.

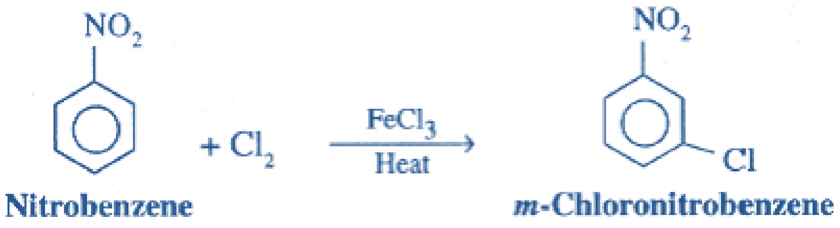
Hint:

(i) Groups directly attached to aromatic ring when situated are *ortho, para* directing groups.
Eg. -NH_2, -OH, -R, -Cl - Ortho, Para directing groups (ring activating groups)

(ii) Groups directly attached to aromatic ring when unsaturated are *Meta* directing groups.
Eg: -NO_2, -C(=O)R, -COOH, -CN, -Meta directing groups (ring deactivating groups)



In case of nitrobenzene, we find that –NO_2 group is a *meta* directing group and hence, the product obtained on chlorination is *meta-chloronitrobenzene*.



26.4.5 Uses of Aromatic Hydrocarbons

Benzene is used as a solvent for several organic compounds and thus, acts as a medium for carrying out synthetic reactions. It is the basic aromatic hydrocarbon and can be converted to other organic compounds by carrying out substitution in the benzene ring. Toluene, a higher homologue of the benzene, finds its uses for dry-cleaning, as a solvent, and as a starting material for the manufacture of dyes, drugs, explosive (trinitrotoluene, T.N.T.), benzaldehyde, benzoic acid etc.

Intext Questions 26.4

1. What is the value of resonance energy of benzene?

....

2. Name the product formed when:
   (i) benzene reacts with chlorine in the presence of light.

   ....

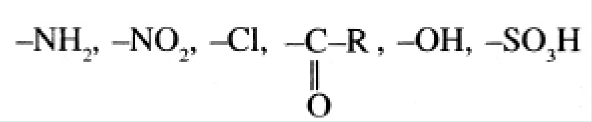
   (ii) phenol reacts with chlorine in the presence of FeCl .

   ....

   (iii) nitrobenzene reacts with chlorine in the presence of FeCl .

   ....

3. Classify the following into o-and p- or m-directing groups:



$-NH_2,\ -NO_2,\ -Cl,\ -\underset{\underset{O}{\|}}{C}-R,\ -OH,\ -SO_3H$

....

What You Have Learnt

- Alkanes can be prepared by (i) the reduction of haloalkanes, (ii) action of water or alcohol on Grignard's reagent, (iii) Wurtz reaction and (iv) hydrogenation of unsaturated hydrocarbons.
- Physical properties of hydrocarbons depend on the intermolecular forces of attraction. Which in turn depend upon the shapes of molecules and their surface area.
- The melting points of hydrocarbons depends upon the symmetry of the molecules i.e. hydrocarbons with even number of carbon atoms are more symmetrical and have higher melting points.
- Alkenes can be prepared by dehydrohalogenation of alkyl halides and by dehydration of alcohols.
- Alkenes and alkynes undergo addition reaction e.g. addition of hydrogen, halogens, halogen acids, water, sulphuric acid etc. due to the presence of carbon-carbon double or triple bonds.
- Addition of halogen acids and other unsymmetrical reagents to unsymmetrical alkenes and alkynes takes place according to the Markownikoff's rule.
- Alkenes undergo polymerization on heating under pressure.
- All hydrocarbons (saturated as well as unsaturated) form CO_2 and H_2O on combustion and liberate energy.
- An alkaline solution of $KMnO_4$ can oxidize alkenes and alkynes forming different products such as carboxylic acids, aldehydes and/or ketones and carbon dioxide.
- Ozone can oxidize unsaturated hydrocarbons (alkenes and alkynes) forming ozonides which when further reacted with water in the presence of zinc dust either form aldehydes or ketones or both.
- Reaction of ozone with alkcnes can be used to determine the position of double bond.
- Ethyne can be prepared by the action of water on calcium carbide and by dehydrogenation of dihaloalkanes.

- Alkynes are acidic in nature due to sp-hybridization of carbon atoms. Because sp hybridized carbon atoms are more electronegative than sp2 and sp3, and the bond between C-H is weakened. Hence, hydrogen atoms in alkynes can be replaced by certain metal atoms.
- Alkanes, alkenes and alkynes can be distinguished by using:
  a) Br_2 dissolved in carbon tetrachloride. b) Ammoniacal solution of $AgNO_3$
  c) Ammoniacal solution of Cu_2Cl_2 d) Alkaline solution of $KMnO_4$
- Benzene is obtained by destructive distillation of coal.
- A ring structure of benzene was suggested by Kekule. Actual structure of benzene is the resonance hybrid of the canonical structures.
- Aromatic hydrocarbons undergo substitution reactions i.e. the reactions in which hydrogen atom of hydrocarbons is replaced by another atom or group of atoms. Halogenation, sulphonation, nitration and Friedel Craft's reaction are substitution reactions of benzene.
- The position of second substituent on a benzene ring depends upon the nature of the group already present.

Terminal Exercise

1. What happens when: (Write chemical equations)
   (i) Iodoethane is heated with HI in the presence of red phosphorus.
   (ii) 2-Chlorobutane reacts with sodium metal.
   (iii) Ethyl magnesium bromide is reacted with methyl alcohol (methanol).
   (iv) 2-Chloropropane reacts with alcoholic solution of KOH.
   (v) l, l-Dichloroethane reacts with alcoholic solution of KOH.
2. Give reasons for the following:
   (i) The boiling point of neopentane is less than that of n-pentane.
   (ii) Stability of benzene ring
   (iii) Boiling points of hydrocarbons decrease with the increase in branching.
3. How will you prepare the following?
   (i) Ethane from ethene
   (ii) Ethene from ethanol
   (iii) Cyclohexane from benzene
   (iv) Methane from sodium acetate
   (v) Butane from bromoethane
4. What happens when (write balanced chemical equations):
   (i) Hydrochloric acid is added to ethene.
   (ii) Hydrobromic acid (HBr) is added to propene in the presence of benzoyl peroxide.
   (iii) Benzene reacts with chloromethane in the presence of anhydrous $AlCl_3$.
   (iv) Br_2 is added to ethyne.
   (v) Methane is oxidized with oxygen in the presence of copper at 475K and a high pressure of 120 atm.
5. How are the following conversions carried out?
   (i) Ethyne to ethane
   (ii) Benzene to nitrobenzene

(iii) Ethyl alcohol (ethanol) to ethene
(iv) Ethyne to ethanedioic acid
(v) Benzene to O-nitrochlorobenzene.

6. You are provided with three gas jars containing ethane, ethene and ethyne. Give the suitable chemical tests to identify the three hydrocarbons.

7. What is ozonolysis? How is it used to determine the position of a double bond?

8. Give reasons for the following:
   (i) Alkanes do not undergo addition reactions like alkenes and alkynes.
   (ii) Ethyne is more acidic than ethane.
   (iii) Ethene undergoes polymerization but not ethane.
   (iv) Benzene undergoes electrophilic substitution reactions.

Answers to Intext Questions

26.1

1. They are used as fuels and to prepare detergents, dyes, drugs, explosives etc. Hydrocarbons are used to prepare some important organic compounds like alcohols, aldehydes, carboxylic acids etc.
2. The alkyl magnesium halides (R-MgX) are called Grignard's reagent.
3. Easily replaceable hydrogen present in a molecule is called active hydrogen.
4. The physical properties of hydrocarbons differ from one another due to difference in molecular mass, surface area, intermolecular force of attraction.
5. Methane and ethane are gases, pentane and hexane are liquids.
6. Three isomers of pentane are : n-pentane, isopentane and neopentane.
7. n-pentane has higher boiling point than n-butane.
8. $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

26.2

1. Trans-2-butene has higher boiling point than cis-isomer.
2. Ethane-1, 2-diol
3. Hydrogen in presence of catalist Ni, Pt or Pd
4. Epoxyethane is produced.

26.3

1. Calcium carbide is reacted with water to prepare ethyne.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

2. Reaction with sodium metal confirms the acidic nature of ethyne.

$$H-C \equiv C-H + 2\,Na \longrightarrow Na-C \equiv C-Na + H_2$$

3. The s-character in : Ethane = 25%, Ethene = 33%, Ethyne = 50%

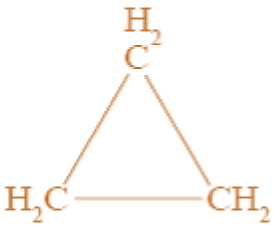
26.4

1. The resonance energy of benzene is 150.3 KJ mol-I.
2. (i) Benzene hexachloride (BHC).
   (ii) *o*-Chlorophenol and *p*-chlorophenol.
   (iii) *m*-Chloronitrobenzene.
3. o - and p - directing groups: $-NH_2$, -Cl, - OH
   m-directing groups: NO_2, -C(=O)R, SO_3H

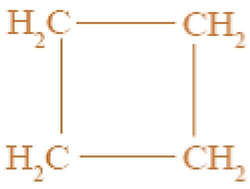
26.1.4.a Cycloalkenes

Alkenes are the simplest class of hydrocarbons with general molecular formula C_nH_{2n+2}. They are acyclic, saturated molecules. All the carbons are sp^3 hybridized. Cycloalkenes are hydrocarbons with carbon atoms joined in ring. Like alkenes, they also have C-C single bonds with sp^3 carbons and general molecular formula C_nH_{2n}. the simplest cycloalkane is cyclopropane.

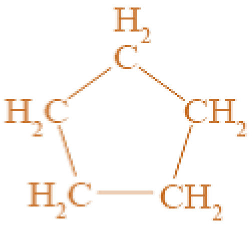
Cycloalkenes are monocyclic hydrocarbon. The first member is cyclo propane. Molecular formula C_3H_6. Next higher homologues are C_4H_8, C_5H_{10}, C_6H_{12} and so on.



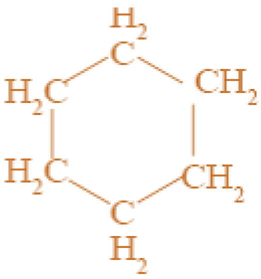
Cyclopropane



Cyclobutane



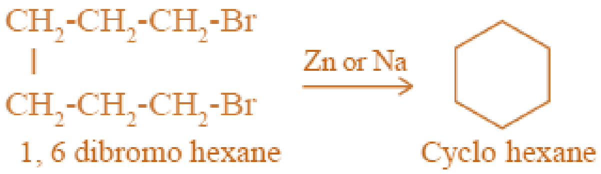
Cyclopentane



Cyclohexane

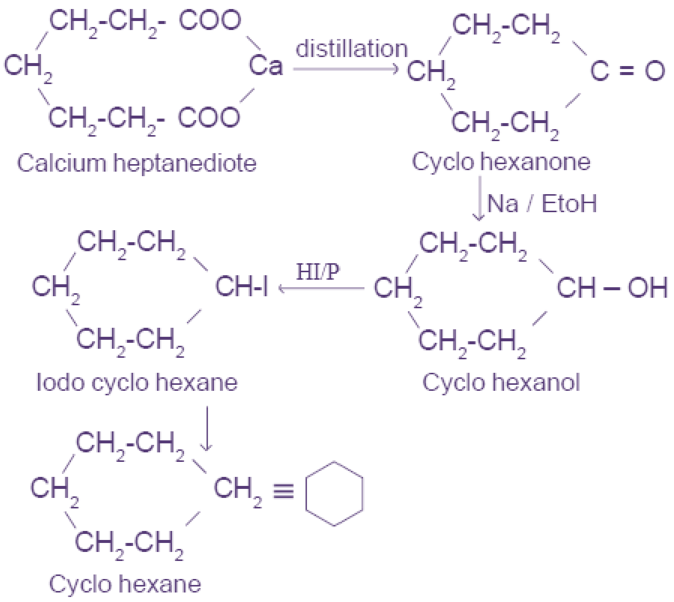
Cyclohexane: Methods of preparation:

1. Freund's method: From (a, w) – dihalo alkenes. When 1,6 dibromo hexane is treated with metallic sodium or zinc, internal **Wurtz reaction** takes place to form cyclo hexane.

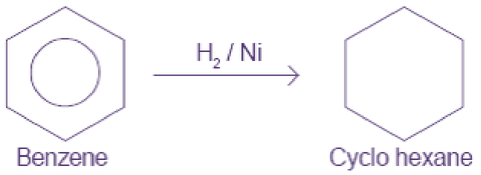


2. Wislicenus method: Calcium or barium salts of dicarbonylic acids on distillation give the corresponding cycloketone.

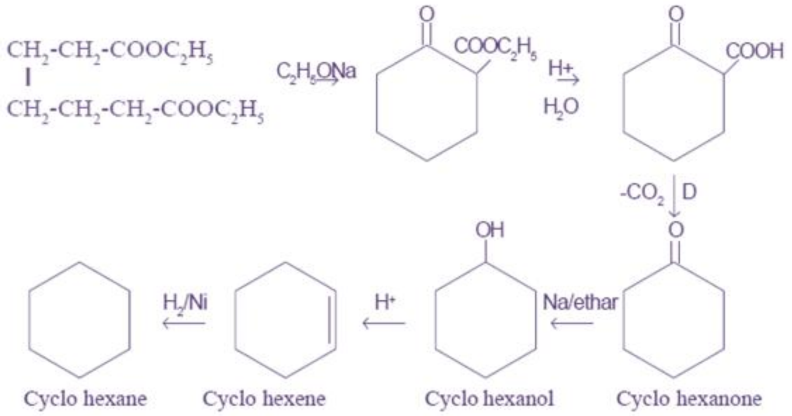
For Eg: when calcium heptanes diote is distilled, cyclo hexanone is formed which when reduced with sodium in ethanol forms cyclo hexanol. This on treatment with HI gives do cyclo hexane on reduction gives cyclo hexane.



3. By reduction of benzene with Hydrogen / Nickel: By catalytic reduction of benzene cyclo hexane is prepared.



4. Dieckmann Condensation: It is intra molecular condensation esters of dicarboxylic acids using Sodium ethoxide.



5. Diel's Alder reaction: This reaction is addition of a mono ene called dienophile to a conjugated dienes. Two new sigma bonds are formed at the cost of two '=' bonds.
Eg:

Properties:

Cyclohexane is a liquid, non-polar, insoluble in water but soluble in organic solvents. Cyclo hexane is as stable as hexane due to minimum angle, strain. Cyclo propane and cyclo butane are more reactive due to angle strain. Like alkenes, cyclohexane is inert towards chemical reactions. Halogenations of cyclo hexane in free radical substitution, similar to alkenes.

26.1.4.a Intext Questions:

1. What are cyclo alkenes?

....

2. What are the reactants of Diel's Alder reaction?

....

3. Write the general molecular formula of Cyclo alkenes.

....

What you have learnt:

1. Cyclo alkenes are monocyclic hydrocarbons with general molecular formula C H .
2. Methods of preparation of cyclo alkenes.
3. Diel's Alder reaction is by addition of dienophite to diens.
4. Cyclo alkenes also give rise to substitution reactions like alkenes.

Terminal exercise:

1. Discuss any three methods of preparation of cyclo hexane.
2. Explain Dieckmann condensation.
3. What is meant by die's Alder reaction? Give an example.

26.1.4.a Answers to intext questions:

1. Cyclo alkenes are monocyclic hydrocarbons.
2. Diene & dienophile
3. C_nH_{2n}

26.2.a Alkenes

Alkenes also known as olefins are open chain hydrocarbons containing atleast one C=C. Hence they are also known as a unsaturated compounds. General molecular formula of alkenes is C_nH_{2n}.

Nomenclature:

In the IUPAC nomenclature of these compounds suffix used is '*ene*'. This class of compounds start from n=2. For the root word '*ene*' is suffixed to name the compound.

For Eg: When n=2 alkene is C_2H_2 root word is eth, ene, is the suffix. Therefore C_2H_2 is called ethane.

'n' Value	Mol. formula	Root Word	IUPAC Name	Common Name
2	C_2H_4	eth	Ethene	Ethylene
3	C_3H_6	Prop	Propene	Propylene
4	C_4H_8	But	Butene	Butylene

For n=4 onwards different strictures are possible. Molecules with same molecular formula are called isomers. For naming the isomers, the position of the double bond is prefixed to the name of the alkene. If substituent is present, it is also prefixed along with its position to the name of the alkene.

Eg: C_4H_8

$CH_2=CH-CH_2-CH_3$

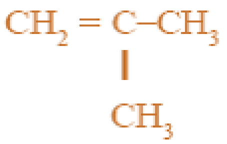
1-Butene or But-1-ene

I

$CH_3-CH=CH-CH_3$

2-butene or But – 2 – ene

II



$$CH_2=C(CH_3)-CH_3$$

2-methyl propene

III

Three isomers are possible for C_4H_8, I & III, II & III are chain isomers, I & II are position isomers. For C_5H_{10} five (05) structures are possible.

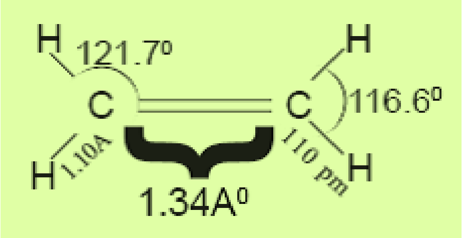
Activity:

Students should be asked to write the five possible structures for C_5H_{10} and name the isomers.

Structure of the double bond:

In alkenes we have atleast one C = C. in C = C one is s bond formed by end on end overlap of sp^2 hybrid orbital of one carbon with sp^2 hybrid orbital of the other carbon. The pi-bond is formed by later overlap of P_z orbital of the two carbons containing one unpaired election each. It is a weak bond having bond enthalpy 284 K.J/mol. The sigma bond is a strong bond having bond enthalpy 397 KJ/mol. The C=C bond length is $1.34A^0$ which is shorter than C-C ($1.54A^0$). As p bond is weak bond, these elections attract electrophiles. Hence alkenes are more reactive than alkanes and the characteristic reactions are electrophilic addition reactions.

The structure of ethylene can be represented as

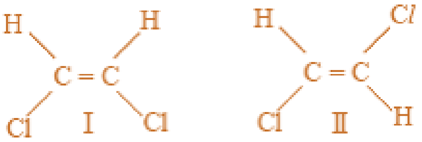


Geometrical Isomerism:

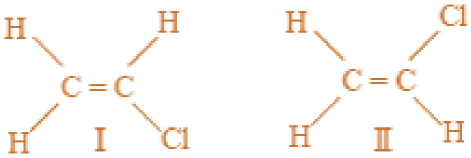
The phenomenon of existence of more than one compound with same structure but cliffering in spatial arrangements of atoms or groups due to restricted rotation about C=C is called geometrical isomerism. These are stereo isomers. The formula should be baC = Cab.

Eg: 1) ClHC=CHCl

Two spatial arrangements are possible due to planar configuration.



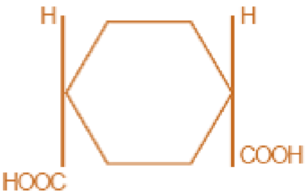
In structure I both Cl atoms are on one side of the double bond. This is designated as '*cis*'. In structure II the 'Cl' atoms are on opposite side of the double bond. This is designated as *trans*. So I is called as 1,2-dichloro ethane & Ii is called trans – 1,2 – dichloro ethane.



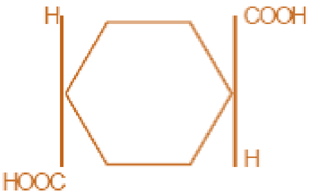
I & II are identical. So they are not isomers.

If there are 'n' number of conjugated or is dated double bonds. There will be 2^n geometrical isomers provided all substituents are different.

Geometrical isomerism is also observed in ring compounds due to restricted rotation.



Cis-1, 4- cyclo hexane dicarboxylic acid



Trans -1, 4- cyclo hexane dicarboxylic acid

As geometrical isomers are not mirror images, they are called diasteromers. They have different properties.

Physical properties of geometrical isomers:

Trans isomers are more symmetrical than cis-isomers. Steric hindrance due to bulk groups present on same side, make the cis-isomer non symmetrical. Therefore, trans isomers have generally more melting points and lower solubilities in inert solvents. The cis-isomer has higher density, refractive index, dipole moment, heat of combustion than its trans isomer. As they contain same functional group, their chemical properties are same except in stereo specific reactions.

26.2.a Intext questions:

1 What is the general molecular formula of alkenes?

....

2 Write the IUPAC name of Ethylene?

....

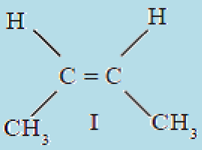
3 What is the hybridization of carbon in ethane?

....

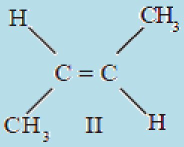
4 In *cis*-isomer the identical group are on which side of the double bond?

....

5 Name the isomers given here under.



I



II

....

What you have learnt:

- Alkenes have general molecular formula C_nH_{2n}
- In alkenes ‘C’ is sp^2 hybridized
- In alkenes C = C one is s bond and the other is p bond.
- cyeometric isomerism arises due to restricted rotation about C=C.

- If similar groups are on one side of the double bond it is called cis while if they are on opposite sides it is trans.
- Generally trans isomer has higher melting point and less solubility than cis isomer.

Terminal exercise:

1) What is meant by geometri isomerism? Give example.
2) Write the formation of ethylene.
3) Explain cis-trans isomerism with an example.

26.2.a Answers to Intext questions:

1) C_nH_{2n} 2) Ethene 3) sp^2
4) On the same side of double bond
5) I is *cis*-2-butane, II is *trans*-2-butane.

26.3.a Alkynes

In the IUPAC nomenclature of these compounds '*yne*' is suffixed to the root word. The class of compounds start from n=2.

For eg: n=2, HC ≡ CH 'Eth'-rootword 'yne'suffix.

Therefore name of HC ≡ CH is Ethyne common name is acetylene.

'n' Value	Mol. formula	Root Word	IUPAC Name	Common Name
2	C_2H_2	eth	Ethyne	Acetylene
3	C_3H_4	prop	Propyne	Methyl acetylene
4	C_4H_6	but	Butyne	Ethyl acetylene

For n = 4 we have two structural isomers. They are

$CH \equiv C - CH_2 - CH_3$ $CH_3 - C \equiv C - CH_3$

1- Butyne 2-Butyne

These are position isomers. The position of the triple bond should be prefixed to the name of the alkyne. For n=5 we have 3 isomers & For n = 6, 7 isomers are possible.

Activity: Students should be asked to draw the structures for n=5, & n=6 alkynes and name them.

Structure of the triple bond:

The first molecule of alkynes is Ethyne or acetylene. In ethyne each carbon undergoes SP hybridization in its excited state leaving behind two unhybridised *p*-orbits which are perpendicular to each other containing an unpaired electron each. In the formation of ethyne, one *sp* hybrid orbital of first carbon overlaps end on end with SP hybrid orbital of second carbon forming a '*s*' bond. The other *sp* hybrid orbital on each carbon is then overlapped by is orbital of hydrogen. Forming two -C-H s bonds, one each carbon. The P_y-P_y , P_z-P_z on both carbons which are perpendicular to each other, overlap laterally forming two p bonds. The strength of C≡C is 823 K.J/mol and C≡C bond length is $1.20A^0$ shorter than C-C ($1.54A^0$) or C=C ($1.34A^0$). The bonded electron cloud between two carbon atoms is cylindrically symmetrical about the inter nuclear axis. Due to this ethyne is a linear molecule. With H - C ≡ C bond angle 180^0.

$H - C \equiv C - H$

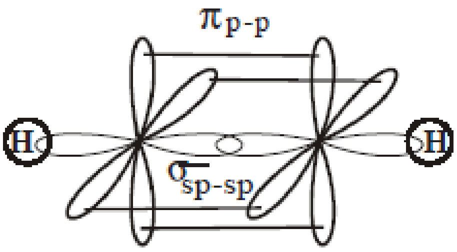


Fig. 26.3.a Orbital overlapping in Ethyne / Acetylene

26.3.a Intext questions:

1. What is the IUPAC name of acetylene?

....

2. What is the hybridization of carbon in ethyne?

....

3. What is the bond length of -C≡C- in acetylene?

....

What you have learnt:

- The IURAC name of alkynes is suffix ‘*yne*’ to root word.
- In alkynes at -C≡C- carbon is *sp* hybrilised.
- The shape of acetylene is linear, bond angle 180^0.

Terminal Exercise:

1. Write the possible isomers for the molecular formula C_nH_{2n-2}, when n=5 and name them.
2. Draw the orbital diagram of acetylene.

26.3.a Answers to Intext questions

1. Ethyne 2. *sp* 3. $1.20A^0$

Chapter 27

COMPOUNDS OF CARBON CONTAINING HALOGENS (HALOALKANES AND HALOARENES)

You have studied about the hydrocarbons in the previous lesson. When a hydrogen attached to a carbon atom in the hydrocarbons is replaced by a halogen atom (i.e. F,C I ,Br or I), the compounds formed are called haloalkanes or haloarenes. The halogen derivatives do not occur in nature and they are synthesized in the laboratory. These compounds have wide applications in industry and domestic uses. They are used as industrial solvents, in the manufacture of pharmaceuticals, as dry cleaning agents, as pesticides, as anesthetics in medicine, as refrigerants, as fire extinguishers and as antiseptics. In this lesson, you will study the nomenclature, methods of preparation and properties of this important class of carbon compounds.

Objectives

After reading this lesson, you will be able to :

- define haloalkanes and haloarenes;
- name haloalkanes and haloarenes according to IUPAC rules;
- explain methods of preparation, physical properties, chemical properties and uses of haloalkanes and haloarenes;
- distinguish between haloalkanes and haloarenes, and explain the preparation, properties and uses of some important poly halogen compounds.

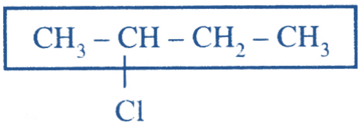
27.1 Nomenclature of Haloalkanes and Haloarenes

You have learnt the nomenclature of hydrocarbons in lesson 25. In this section, you will learn the nomenclature of halogen derivatives of both aliphatic and aromatic hydrocarbons i.e. haloalkanes and haloarenes.

Nomenclature of Haloalkanes

The following rules are used for naming haloalkanes according to the IUPAC system.

1. The longest chain of the carbon atoms bearing the halogen atom is selected.

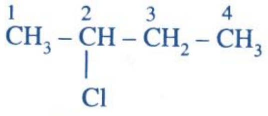


$$\boxed{CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3}$$

The longest chain of carbon atoms in the above example is shown in the box.

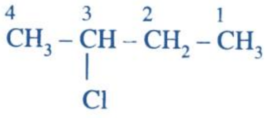
2. Numbering of the carbon atoms in the chain is done in such a way that the carbon atom bearing the halogen atom gets the lowest number.

For example.



$$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

(Correct) I

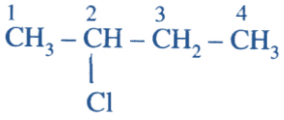


$$\overset{4}{CH_3}-\underset{\underset{Cl}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

(Incorrect) II

In the above example, numbering shown in (I) is correct while in (II), it is incorrect since the carbon atom bearing halogen atom gets lower number in 1 than in ll.

3. The word chloro, is prefixed to the parent hydrocarbon name. So, the correct name for the above halo compound is

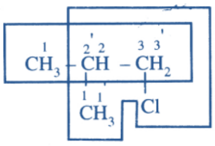


$$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

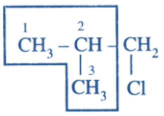
2- Chlorobutane

4. In case of alkyl substituted haloalkanes, the longest chain containing halogen atom is selected for numbering.

For example:



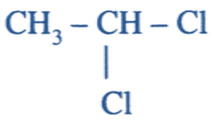
I



II

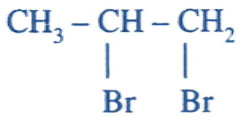
In structure I, the selection of chain is shown by two different ways. Both the ways of selection are correct since they include chloro group. In structure II numbering shown is not correct since it does not include chloro group.

5. When two or more halogen atoms are present in a compound, the longest chain selected must contain the maximum number of halogen atoms. The multiplicative prefixes (di, tri, tetra, etc.) are added before the name of halogen atom to indicate the number of halogen atoms. The following examples illustrate this rule.



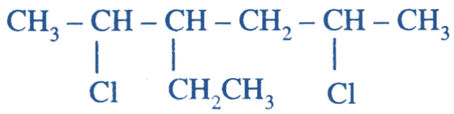
$$CH_3-\underset{\underset{Cl}{|}}{CH}-Cl$$

1, 1 - Dichloroethane



$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$$

1, 2 - Dibromopropane

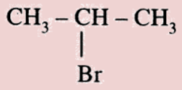
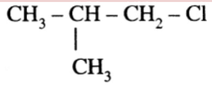
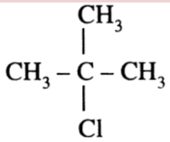


$$CH_3-\underset{Cl}{CH}-\underset{CH_2CH_3}{CH}-CH_2-\underset{Cl}{CH}-CH_3$$

2,5 - Dichloro - 3 - etylhexane

Some more examples are given in Table 27.1 to illustrate the above rules.

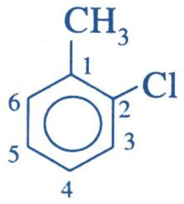
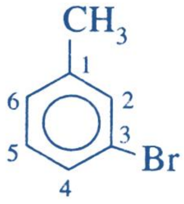
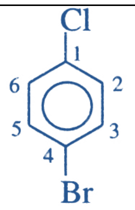
Table 27.1: Names of Some Haloalkanes

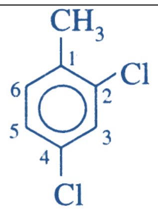
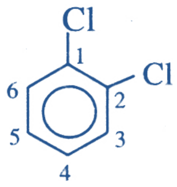
Compound	IUPAC name	Common name
CH_3CH_2Br	Bromoethane	Ethyl bromide
$CH_3CH_2CH_2Br$	l-Bromopropane	*n*-Propyl bromide
 $CH_3-\underset{Br}{CH}-CH_3$	2-Bromopropane	*iso*-Propyl bromide
 $CH_3-\underset{CH_3}{CH}-CH_2-Cl$	l-Chloro- 2- methylpropane	*iso-Butyl* chloride
 $CH_3-\underset{Cl}{CH}-CH_2-CH_3$	2-Chlorobutane	*sec*- Butyl chloride
 $CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_3$	2-Chloro- 2-methylpropane	*tert*-Butyl chloride

* All compounds essentially do not have common names.

Nomenclature of Haloarenes

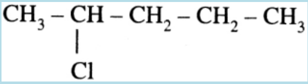
Haloarenes are those aromatic halogen compounds in which the halogen atom is directly linked to an aromatic ring. Their general formula is Ar-X where Ar- represents an aromatic ring and X denotes the halogen. In naming a haloarene, the prefix chloro, bromo-or iodo- *etc*. is/are added to name of arene according to halogen(s) present. The relative positions of halogen atoms are indicated by appropriate numbers. The prefixes *ortho (o-), meta(m-) and para (p-)* are also commonly used respectively to indicate the relative positions i.e. 1,2- ; 1,3 - and 1,4- of substituents in a benzene ring. Following examples illustrate the nomenclature of some haloarenes.

			
Chlorobenzene	**2-Chlorotoluene (*o*-Chlorotoluene)**	**3-Bromotoluene (*m*-Bromotoluene)**	**4-Bromochlorobenzene (*p*-Bromochlorobenzene)**

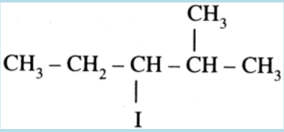
		
2,4-Dichlorotoluene	**1,2-Dichlorobenzene *o*-Dichlorobenzene**	**1,4-Dichlorobenzene *p*-Dichlorobenzene**

Intext Questions 27.1

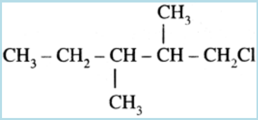
1. Write the IUPAC names of each of the following compounds:

(i) 

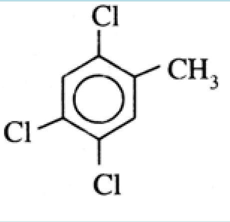
$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-CH_3$ ....

(ii) 

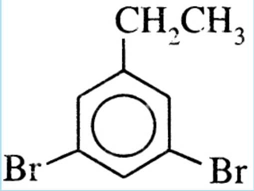
$CH_3-CH_2-\underset{\underset{I}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$ ....

(iii) 

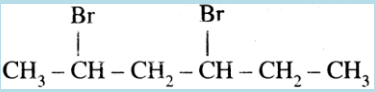
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl$ ....

(iv) 

....

(v) 

....

(vi) 

$CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-\overset{\overset{Br}{|}}{CH}-CH_2-CH_3$ ....

2. Draw structural formulae of the following compounds:

(i) 2-Bromo-3-methylbutane

....

(ii) 3-Chloro-4-methylhexane:

....

(iii) 3- Bromochlorobenzene

....

(iv) 2,4-Dibromotoluene

....

27.2 Preparation of- Haloalkanes and Haloarenes

27.2.1 Preparation of Haloalkanes

(i) From Hydrocarbons : Direct halogenation of hydrocarbons takes place in the presence of sunlight or at high temperature in dark. For example, chloroethane is prepared by monochlorination of ethane.

$$\underset{\text{Ethane}}{CH_3 - CH_3} + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{Chloroethane}}{CH_3 - CH_2Cl} + HCl$$

This reaction follows a free radical mechanism. You have already learnt the mechanism of chlorination of methane in lesson 26.

Bromo derivatives of alkanes are also prepared by direct bromination.

$$\underset{\text{Ethane}}{CH_3 - CH_3} + Br_2 \xrightarrow{\text{Sunlight}} \underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} + HBr$$

Direct iodination is not possible with iodine as the reaction is reversible. Direct fluorination is also not possible because due to the high reactivity of the fluorine, the reaction cannot be controlled.

(ii) From Alcohols : Alcohols are converted into halo alkanes by treating with (a) hydrogen halides (b) phosphorus halides or (c) thionyl chloride.

(a) Reaction with Hydrogen Halides : Hydrogen halides react with an alcohol in presence of a dehydrating agent such as anhydrous zinc chloride to produce a haloalkane.

Chloroethane is conveniently prepared by the reaction of ethanol with concentrated hydrochloric acid in presence of anhydrous zinc chloride.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + HCl \xrightarrow{\text{anhy.}ZnCl_2} \underset{\text{Chloroethane}}{CH_3 - CH_2\,Cl} + H_2O$$

Zinc chloride absorbs water from the reaction mixture and thus prevents the reverse reaction. Bromoethane is obtained by refluxing ethanol with HBr in presence of little concentrated H_2SO_4 as the catalyst.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + HBr \xrightarrow[\Delta]{\text{conc.}H_2SO_4} \underset{\text{Bromoethane}}{CH_3CH_2Br} + H_2O$$

(b) Reaction with Phosphorus Halides: Haloalkanes are conveniently prepared by the reaction of an alcohol with a phosphorus halide (PCl_3), PCl_5 or PBr_3 according to the following equations.

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3C_2H_5OH + PBr_3 \longrightarrow 3C_2H_5Br + H_3PO_3$$

(c) Reaction with Thionyl Chloride : Thionyl chloride ($SOCl_2$) is another reagent which reacts with an alcohol to yield a chloroalkane.

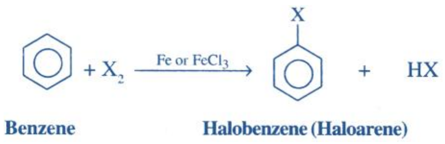
$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2\uparrow + HCl\uparrow$$

Ethanol Chloroethane

As both the byproducts, SO_2 and HCl are gases, the purification of final product is not required.

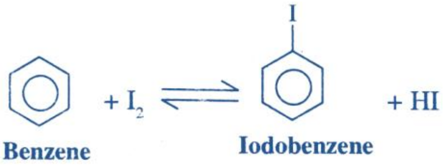
27.2.2 Preparation of Haloarenes

(i) From Aromatic Hydrocarbons : Haloarenes are obtained by direct halogenation of aromatic hydrocarbons in the presence of a catalyst. Usually iron filings or iron (III) halide is used as the catalyst.



where X = CI or Br

The direct iodination of aromatic hydrocarbons is not a useful reaction since the HI produced reduces the aryl iodide back to the aromatic hydrocarbon.

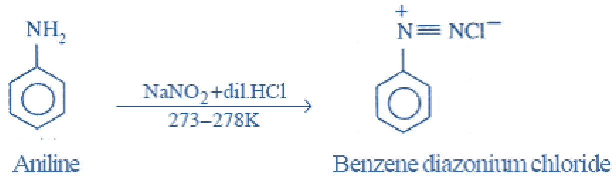


However, in the presence of an oxidizing agent such as nitric acid, iodic acid (HIO_3), mercury oxide, the HI produced is either oxidized to iodine or is eliminated as mercuric iodide and, thus, iodobenzene is obtained.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

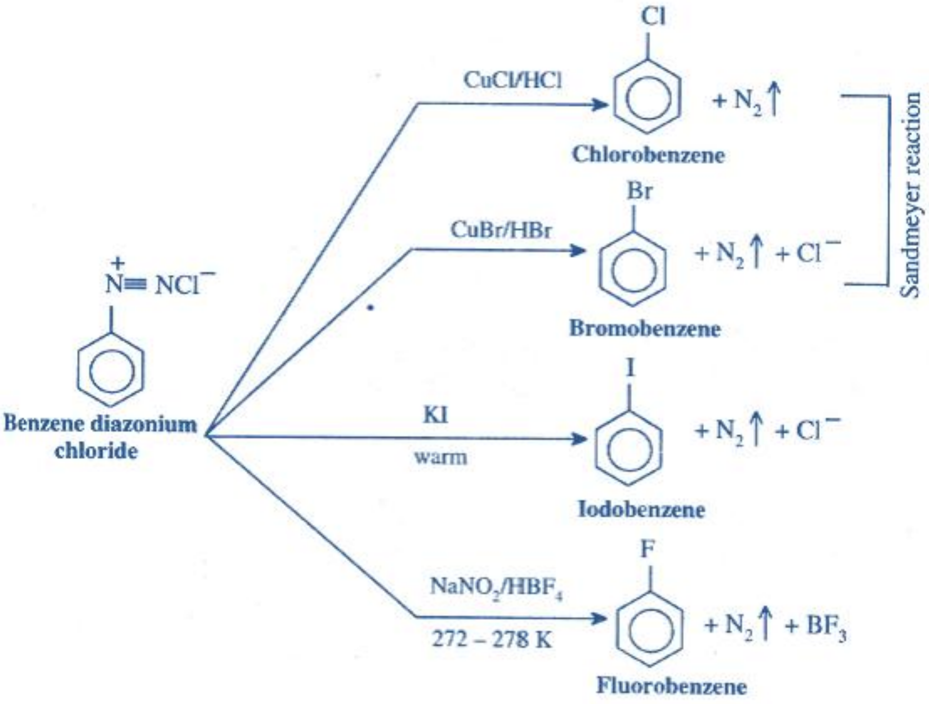
Fluorobenzene cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be controlled.

(ii) From Diazonium Salts: Benzene diazonium salt is formed by treating an aromatic primary amine with $NaNO_2$ and dil. HCl at low temperature. The process is known as diazotisation.

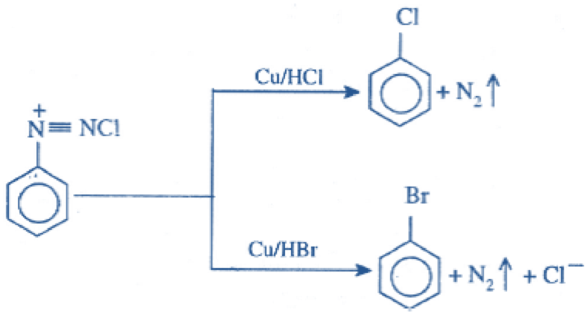


Diazonium salts are highly reactive compounds. They are used in the preparation of a large number of arene derivatives. When a diazonium salt is treated with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2), the corresponding haloarene is formed.

This reaction is known as **Sandmeyer reaction**. It is used for introducing a chloro or bromo group in the benzene ring.



Haloarenes can also be prepared by reacting benzene diazonium chloride with copper powder in presence of corresponding halogen acid. This reaction is called Gattermann reaction and is shown below :



Intext Questions 27.2

1. Write the structure of the main product obtained by treating 1-propanol with excess of hydrogen chloride in the presence of anhydrous zinc chloride.

....

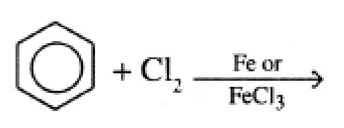
2. What will be the product obtained on treatment of 1-propanol with thionyl chloride?

....

3. Give one example of preparation of chlorbenzene using Sandmeyer reaction?

....

4. Complete the following reaction:



……

27.3 Properties of Haloalkanes and Haloarenes

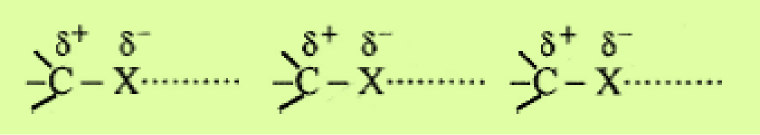
The important physical and chemical properties of alkylhalides and aryl halides are discussed below:

27.3.1 Physical Properties

1. The lower alkyl halides (CH_3F, CH_3Cl, CH_3Br, C_2H_5Cl) are gases at room temperature. The other alkyl halides containing upto CI8 are liquids having high boiling points.

2. Haloalkanes and haloarenes are moderately polar molecules $(\overset{\delta+}{\geq C}-\overset{\delta-}{X})$. Still they are immiscible in water. It is due to their inability to form hydrogen bonds with water molecules.

3. The melting and boiling points of haloalkanes and haloarenes are higher than those of their parent hydrocarbons (Table 27.2) This is due to **(i)** the greater molecular mass and hence greater magnitude of van der Waals forces of attraction in halocompounds than in the parent hydrocarbons and **(ii)** the existence of intermolecular dipole-dipole interaction, as shown below:

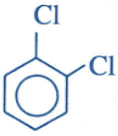


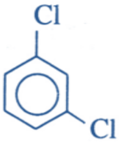
For a given alkyl or aryl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 27.2 to show this variation.

Table 27.2: Boiling Points of Haloalkanes and Haloarenes

Compound	Boiling Point(K)				
	X=H	X=F	X=O	X=Br	X=I
CH_3-X	111.5	194.6	248.8	276.6	315.4
C_2H_5-X	184.3	241	285	311.4	345
C_6H_5-X	351	358	405	429	461

4. All monohalobenzenes are liquids at room temperature. Among dihalobenzenes, the *para* isomers have the highest melting points. It is due to the greater symmetry that causes a better packing of molecule in the *para* isomer.

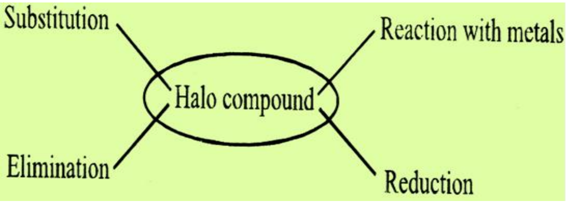




m.p. 256k 249k 325k

27.3.2 Chemical Properties

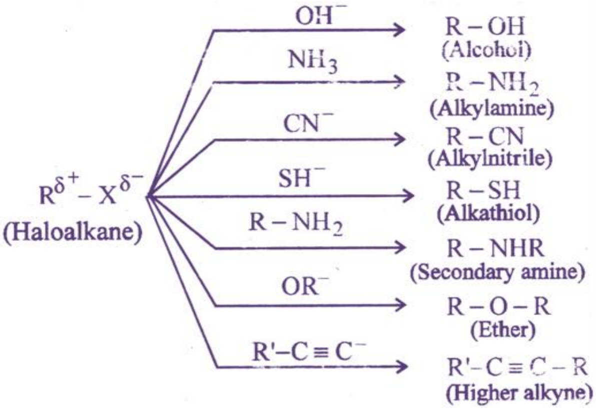
Halo compounds can undergo the following types of reactions:



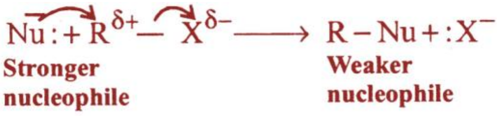
1. Substitution: Substitution reactions are those in which an atom or a group of atoms from the reactant molecule is displaced by another atom or a group of atoms. For example, on treating chloro ethane with sodium hydroxide, the chlorine atom of chloroethane is substituted by the hydroxyl group and ethanol is formed as the reaction product.

$$C_2H_5 - Cl + OH^- \longrightarrow C_2H_5OH + Cl^-$$

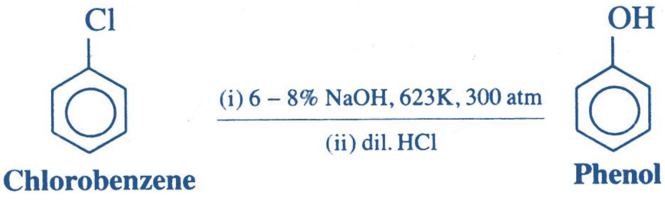
In this reaction, it is to be noted that the hydroxide ion (nucleophile) displaces the chlorine atom from C_2H_5Cl as chloride ion (another nucleophile). Such reaction which are initiated by the attack of a nucleophile are known as nucleophilic reactions. In haloalkanes, the carbon atom carrying the halogen atom is electron deficient due to - I effect of halogen atom. This electron deficient carbon atom is susceptible to attack by a nucleophile. Thus, you may conclude that haloalkanes undergonuclephillic substitution reactions. Following are a few examples of nucleophilic substitution reactions of halo alkanes.



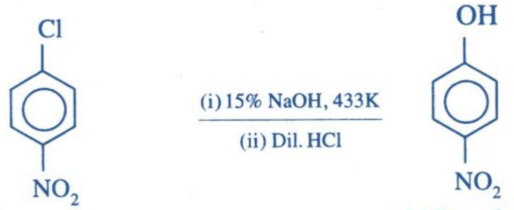
In all the above reactions, the stronger nucleophile (HO^-, $C_2H_5O^-$, CN^- or NH_3 etc.) displaces a weaker nucleophile X.



Haloarenes are almost unreactive to reagents such as NaOH, C_2H_5ONa, NaCN and NH_3 under ordinary laboratory conditions but can show nucleophillic substitution reactions under drastic conditions.

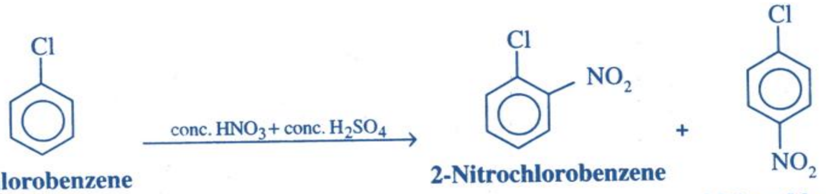


It is also observed that the presence of electron withdrawing groups such as NO groups at o- and p-position (but not a m-position) with respect to halogen activates the halogens towards nucleophillic displacement. For example:



4-Nitrochlorobenzene 4-Nitrophenol

Haloarenes can also readily undergo substitution reactions in benzene ring. The benzene ring is an electron rich species. Therefore, it is attacked by an electron deficient species such as NO. As *ortho* and *para* positions in haloarenes are electron rich due to resonance (Fig. 27.1), the electrophilic substitution takes place mainly at these positions. For example, the nitration of chlorobenzene, with a mixture of concentrated HNO_3 and H_2SO_4, gives a mixture of 2-nitrochlorobenzene and 4-nitrochlorobenzene.



Chlorobenzene 2-Nitrochlorobenzene 4-Nitrochlorobenzene

Haloalkanes are highly reactive compounds due to the presence of a polar carbon-halogen bond in their molecules. The bond energy values of C-X bonds in haloalkanes and haloarenes are given in Table 27.3.

Table 27.3 : C-X bond energy Values

Bond	C-F	C-Cl	C-Br	C-I
Energy/KJ mol−1	485	339	284	213

These bond energy values show that C-I bond is the weakest bond and C-F bond is the ,strongest bond. Therefore, the order of reactivity of halo alkanes is iodoalkane >bromoalkane > chloroalkane> fluoroalkane.

Comparing the haloalkanes and haloarenes, haloalkanes are found to more reactive than haloarenes in reactions involving the breaking of C-X bond (X =F,Cl,Br, or I). It is due to the existence of the phenomenon of resonance which cause carbon-halogen bond to acquire double bond character in haloarenes. The resonating structures of chlorobenzene are shown below :

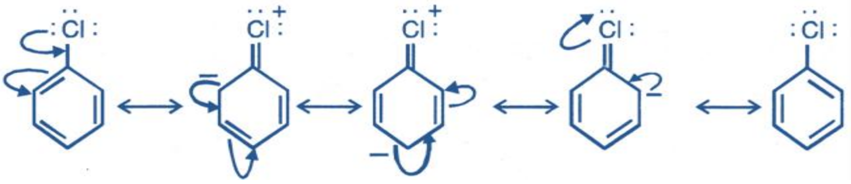


Fig. 27.1 : Resonance Structures of Chlorobenzene

2. Elimination reactions: Haloalkanes, when heated with aqueous solution of potassium or sodium hydroxide, the major product formed is the alcohol, produced by nucleophilic displacement of the halogen atom by HO^-.

$$C_2H_5Cl \xrightarrow{aq.KOH} C_2H_5OH + Cl^-$$

Chloroethane Ethanol

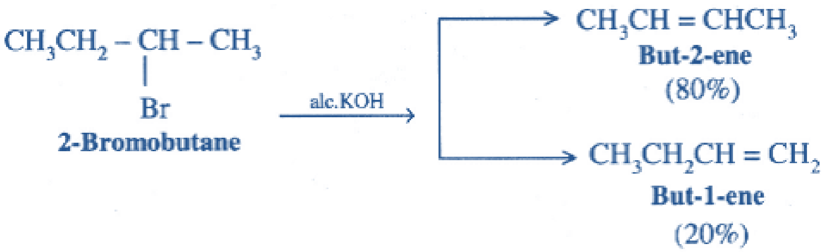
If a haloalkane is heated with concentrated alcoholic potassium hydroxide, the major product formed is an alkene due to the elimination of hydrogen halide. This is called α,β-elimination or dehydrohalogenation.

$$C_2H_5Cl \xrightarrow{aq.KOH} CH_2 = CH_2$$

Chloroethane Ethene

In this reaction, the OH ion acts and a base removes a proton from the molecule.

If the structure of alkyl halide is such that it can undergo elimination in two different ways, then the more highly substituted alkene (i.e. having lesser number of hydrogen atoms on the doubly bonded carbon atoms) is the major product of elimination. This is known as **Saytzeff's rule**. For example, elimination reaction of 2-bromobutane gives 2-butene as major product according to the Saytzeffs rule, (refer lesson 26).



$$CH_3CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{alc.KOH} CH_3CH=CHCH_3 \text{ (80\%)} + CH_3CH_2CH=CH_2 \text{ (20\%)}$$

3. Reactions with metals : Haloalkanes and haloarenes react with a variety of metals (zinc, magnesium and lithium). The compounds so obtained have a metal atom directly bonded to a carbon atom. Such compounds in which the metal atom is directly bonded to a carbon atom are known as **organometallic compounds**. The organometallic compounds of magnesium with alkyl and aryl halides are known as **Grignard reagents**.

$$C_2H_5-Cl + Mg \xrightarrow{dry\ ether} C_2H_5-Mg-Cl$$

Chloroethane Ethyl magnesium chloride

These are named after the French chemist Victor Grignard.

Alkyl halides react with metallic sodium in presence of dry ether to form symmetrical higher alkanes. This reaction is called **Wurtz reaction.**

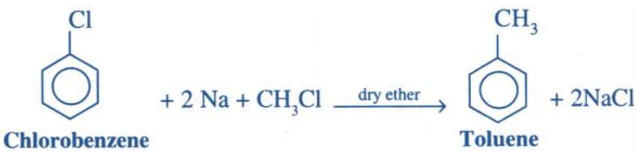
$$2\,R-X + 2\,Na \xrightarrow{dry\ ether} R\text{-}R + 2\,Na^+X^-$$

Ethyl bromide can react with lead in presence of dry ether to form tetraethyl lead (TEL) which is used as antiknocking agent in gasoline used for running automobiles.

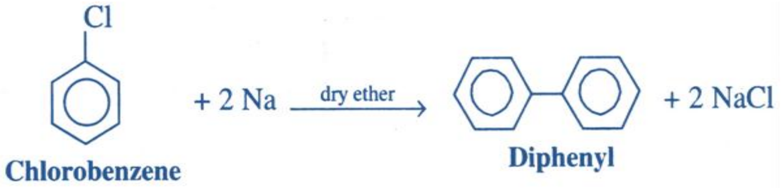
$$4CH_3CH_2Br + 4Pb \xrightarrow{dry\ ether} (CH_3CH_2)_4Pb$$

Bromethane Tetraethyl lead

When haloarenes react with alkyl halides in presence of sodium and dry ether, the alkyl derivatives of benzene are formed. This reaction is called Wurtz-Fittig reaction.



When haloarenes are treated with sodium, diaryls are produced. This reaction is called **Fittig reaction.**



4. Reduction : Haloalkanes can be reduced to the corresponding alkanes. For example, bromoethane can be reduced to ethane by using metal catalyst such as nickel or palladium or platinum or by using hydroiodic acid (HI) in presence of red phosphorus.

$$CH_3CH_2Br + H_2 \xrightarrow[\text{or Pd}]{\text{Ni or Pt}} CH_3 - CH_3 + HBr$$

Bromethane Ethane

$$CH_3CH_21{+}H1 \xrightarrow{\text{red P}} CH_3 - CH_3 + I_2$$

Iodoethane Ethane

Distinction between haloalkanes and haloarene

Haloalkane and haloarenes can be distinguished by silver nitrate ($AgNO_3$). Haloalkanes react with $AgNO_3$ to give white precipitate of AgCl while haloarene do not react.

$$RCl + NaOH \longrightarrow NaCl + ROH$$
$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow + NaNO_3$$

Intext Questions 27.3

1. Although haloalkanes are polar in nature, they are immiscible in water. Explain.

....

2. Which one of the following isomers has the higher boiling point and why? (i) *o*-dichlorobenzene (ii) *p*-dichlorobenzene

....

3. What will be the products of nitration of chlorobenzene?

....

4. What products will obtained when ethylbromide reacts with
(i) aq. KOH and (ii) alc. KOH

....

5. What is the major product of elimination reactions of 2- bromobutane?

....

27.4 Some Useful Poly Halogen Compounds

A large number of poly halogen aliphatic and aromatic halogen compounds are known. These are extensively used as solvents, pesticides, anaesthetics etc. Some of the important compounds are chloroform ($CHCl_3$), iodoform (CHI_3), carbon tetrachloride (CCl_4), benzene hexachloride (BHC), DDT, etc.

Let us now study some of these compounds.

27.4.1 Chloroform

Chloroform is a derivative of the simplest hydrocarbon, methane. Its IUPAC name is trichloromethane. In the laboratory, it is prepared from ethanol or propanone as given below:

1. From Ethanol

Chloroform is prepared in the laboratory by treating ethanol or propanone with chlorine gas in the presence of an alkali. Following is the reaction sequence in this process:

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{(Chloral)}}{\underset{\text{Trichloroethanal}}{Cl_3CCHO}}$$

$$Ca(OH)_2 + 2Cl_3C-CHO \longrightarrow \underset{\text{formate}}{\underset{\text{Calcium}}{(HCOO)_2Ca}} + \underset{\text{Chloroform}}{2CHCl_3}$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[-3HCl]{3Cl_2} Cl_3C-CO-CH_3$$

$$Ca\,(OH)_2 + 2\,CCI_3CO-CH_3 \longrightarrow \underset{\text{acetate}}{\underset{\text{Calcium}}{(CH_3COO)_2\,Ca}} + \underset{\text{chloroform}}{2\,CHCI_3}$$

Chloroform is a colourless sweet smelling liquid (b.p. 334K). It is slowly oxidized by air in the presence of light to a poisonous gas, phosgene. Chemically phosgene is carbonyl chloride, ($COCl_2$). Therefore, chloroform is stored in dark coloured bottles to protect it from light. The bottle are completely filled so that the air is kept out. A small amount of ethanol is added to chloroform to convert toxic phosgene, if formed, into a nontoxic compound, ethyl carbonate.

$$CHCI_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{COCl_2} + 2\,HCI$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCI$$

Chloroform is used in isocyanide test for the detection of primary amines. In this test, a mixture of amine and chloroform is heated with alcoholic NaOH. A foul smelling isocyanide is obtained. This test is also known as **carbylamine test**. It can be used to test aliphatic and aromatic primary amines.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + CHCI_3 + 3\,NaOH \longrightarrow \underset{\text{Ethyl isocynanide}}{C_2H_5NC} + 3\,NaCl + 3\,H_2O$$

27.4.2 Iodoform

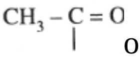
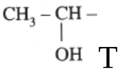
Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

Preparation

Iodoform is prepared by heating ethanol or acetone with iodine in the presence of alkali.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3CONa + 3NaI + 3H_2O$$

Yellow crystals of iodoform can easily be recognized by the characteristic smell. Formation of iodoform is used to test compounds containing  $CH_3-\underset{|}{C}=O$ or  $CH_3-\underset{OH}{\underset{|}{CH}}-$ This test is known as **iodoform test**. Iodoform is used as an antiseptic.

27.4.3 Dichlorodiphenyltrichloroethane (DDT)

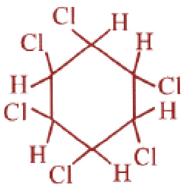
It is available in several different forms : powder, aerosols, granules, etc.

DDT

Uses: It is used mainly to control mosquito-borne malaria. It is also used as an agricultural insecticide. The use of DDT has been banned in many countries because being non-biodegradable, it accumulates in environment. It is toxic to other living organisms such as: mammals, birds, fishes, etc.

27.4.4 Benzene hexachloride (BHC)

It is sold under the name gammexane, lindane or 666 and has the formula $C_6H_6Cl_6$.



Gammexane

(1, 2, 3, 4, 5, 6-hexachloro cyclohexane)

Uses : It is used as a pesticide in agriculture.

Intext Questions 27.4

1. Write IUPAC names of chloroform and iodoform.

....

2. Why is chloroform stored in dark coloured bottles?

....

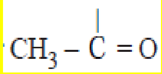
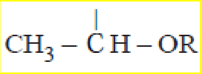
3. What type of compounds will give a positive iodoform test?

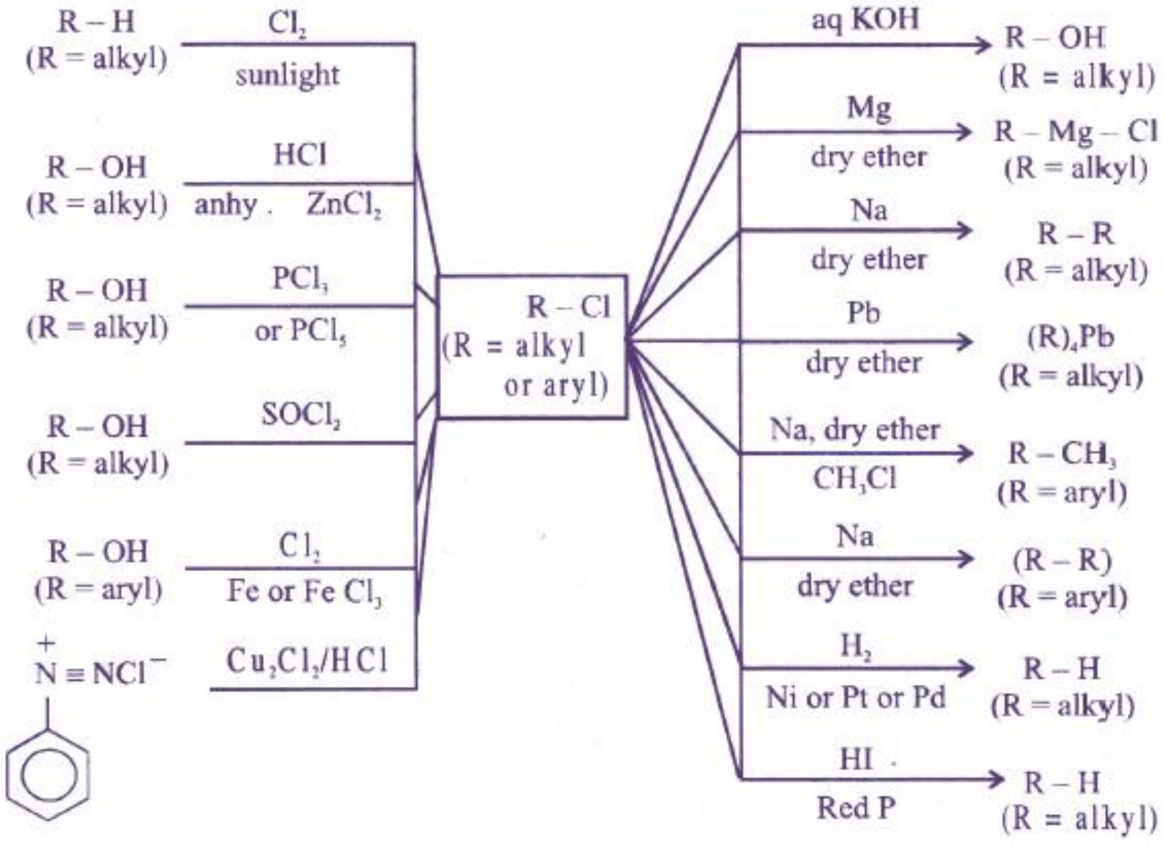
....

4. Name two commonly used polyhalogen compounds.

....

What You Have Learnt

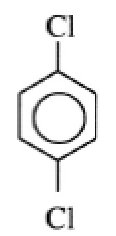
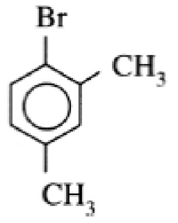
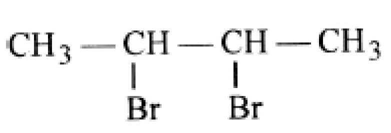
- Haloalkanes and haloarenes are important organic compounds having wide industrial and household applications.
- Various rules for IUPAC naming of haloalkanes and haloarenes.
- Due to the polar nature, halo compounds have higher melting and boiling points than the corresponding hydrocarbons.
- Chemically, fluoro compounds are comparatively least reactive and iodo compounds are the most reactive. Also, haloalkanes are more reactive than haloarenes in reactions involving cleavage of C-X bond.
- Haloalkanes undergo nucleophilic substitution reactions. But in haloarenes, the substitution in the benzene ring is an electrophilic substitution reaction.
- Grignard reagents are produced by the reaction of a haloarene or haloalkane with magnesium metal.
- Chloroform and idoform are useful trihalo derivatives of methane. Chloroform is prepared in the laboratory from ethanol or propanone by reacting with chlorine in presence of alkali.
- Iodoform test is given by compounds containing either  $CH_3-C=O$ or  $CH_3-CH-OR$ group.
- Methods of preparation and chemical properties of haloalkanes and haloarenes which are summarized below:



Terminal Exercise

1. Give IUPAC names of the following compounds:

(i) *sec*-butyl chloride (ii) *iso*- propyl bromide

(iii)  (iv)  (v) 

$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$$

2. Name the product obtained by treating 2-propanol with hydrogen chloride in presence of anhydrous zinc chloride. Also write reaction involved.

3. Alkyl halides are more reactive towards nucleophilic reagents than aryl halides. Discuss briefly.

4. Write chemical equations for the reactions of :
   - (i) n-propanol with PCl_5.
   - (ii) chlorine gas with benzene in presence of $FeCl_3$ as catalyst.
   - (iii) bromoethane with aqueous KOH solution.
   - (iv) nitrous acid with aniline at 278 K.
   - (v) chlorobenzene with magnesium.
   - (vi) chlorobenzene with a mixture of conc. $HNO_3$and H_2SO_4.

5. Give reason for the following:
   - (i) Haloalkanes undergo nucleophilic substitution reactions.
   - (ii) Haloarenes undergo electrophilic substitution reactions.

6. What is a Grignard reagent? How is it prepared?

7. Discuss briefly the following:
   - (i) Iodoform test (ii) Carbylamine test (iii) Diazotization
   - (iv) Relative reactivities of chloroethane and bromoethane

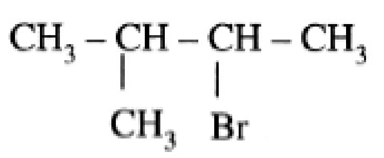
8. How is chloroform prepared in the laboratory? Write the reaction for its preparation from ethanal.

Answers to Intext Questions

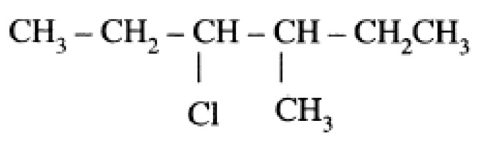
27.1

1.
   - (i) 2-Chloropentane (ii) 3-Iodo-2-methylpentane
   - (iii) I-Chloro-2,3-dimethylpentane
   - (iv) 1,3,4- Trichloro-6-methylbenzene or 2,4,5 - Trichlorotoluene
   - (v) 1,3-Dibromo-5-ethylbenzene
   - (vi) 2,4-Dibromohexane

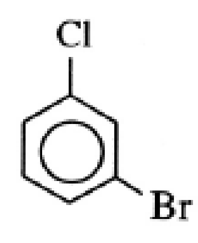
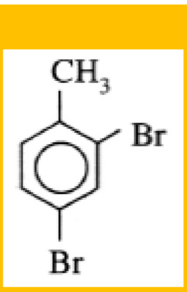
2.

(i) 

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$$

(ii) 

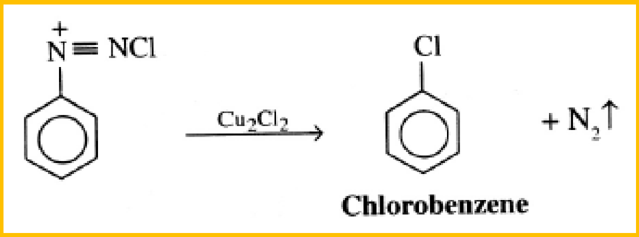
$$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$$

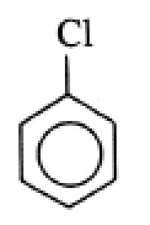
(iii)  (iv) 

27.2

1. $CH_3CH_2CH_2Cl$ 2. l-chloropropane

3. The Diazonium salt on treatment with copper(I)chloride Cu_2Cl_2 gives chlorobenzene.



4. 

27.3

1. Due to their inability to form hydrogen bonds.

2. *Para* dichlorobenzene; due to greater symmetry and hence a better packing.

3. 

4.

$$\text{(i) } C_2H_5Cl \xrightarrow{\text{aq.KOH}} C_2H_5OH$$

$$\text{(ii) } C_2H_5Cl \xrightarrow{\text{aq.KOH}} CH_2 = CH_2$$

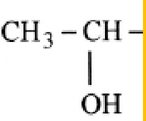
5. 

$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc.KOH}} \underset{\textbf{major product}}{CH_3CH = CHCH_3}$$

27.4

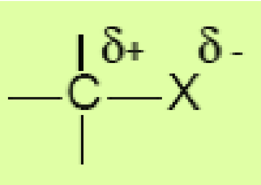
1. (i) Trichloromethane (ii) Triodomethane
2. Chloroform oxidises to phosgene in the presence of air and sunlight. Dark coloured bottles reduce formation of poisionous phosgene

$$CHCl_3 + O_2 \xrightarrow{\text{sunlight}} COCl_2 + HCl$$

3. Compounds having  $CH_3-\underset{|}{C}=O$ or  $CH_3-\underset{\underset{OH}{|}}{CH}-$ units in their structure.
   Dark coloured bottles reduce formation of poisonous phosgene.
4. DDT, BHC, $CHCl_3$ and CHI_3.

27.2.1.a Compounds of Carbon containing Halogens (Haloalkanes)

The bond between carbon and halogen of alkyl halide is polarized with partial positive charge on carbon atom and partial negative charge on halogen atom.



Alkyl halides undergo substitution and elimination reactions. In alkyl halides substitution reactions takes place with the help of nucleophile. This type of nucleophile substitution reactions are of two types. They are 1) S_N^2 2) S_N^1.

S_N^2 (Nucleophilic substitution bi molecular reaction):

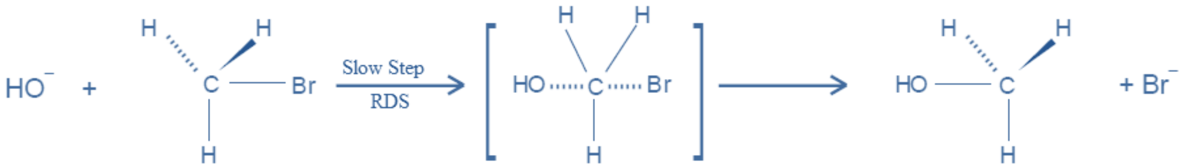
In this reaction the rate of the reaction depends on both the reactants concentration. So, it is a second order reaction. Here the rate depends on alkyl halide concentration and nucleophile concentration.

Rate α [Alkyl halide] [Nucleophile]

Eg: $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

The above reaction takes place in two steps.

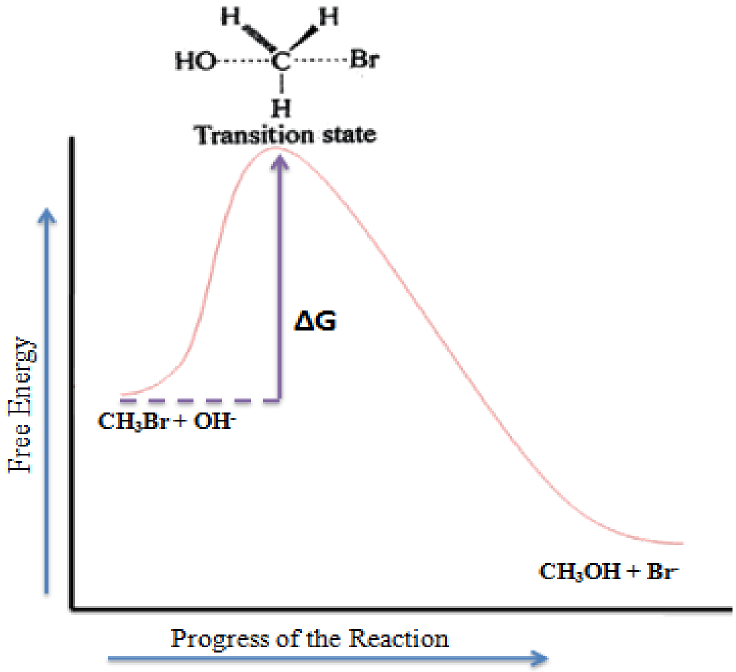
In the first step of S_N^2 reaction the nucleophile attacks from back side of the carbon of alkyl halide forming a weak bond with the carbon and a transition state is formed.



In the transition state both the nucleophile and the halogen of the halide form weak bonds with carbon atom.

In the second step halide is removed from the transition state and the products are formed.

In S_N^2 reaction the first step both the reactants alkyl halide and nucleophile are involved so the rate of the reaction depends on the concentration of both reactants.



If asymmetric alkyl halide is involved in SN^2 reaction, we can observe inversion of configuration in the products formed. This inversion of configuration is known as **Walden Inversion**.

The reactivity order of SN^1 in alkyl halides is

$$CH_3\,X \sim 1^0R\text{-}X > 2^0R\text{-}X > 3^0R\text{-}X.$$

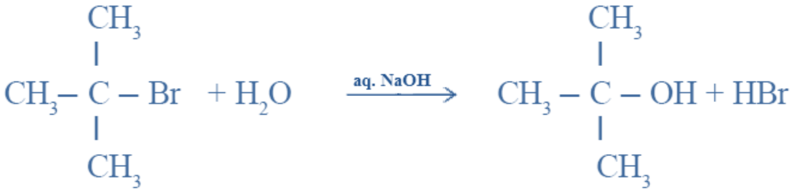
If the basicity difference between releasing group and nucleophile increases the rate of a reaction also increases in SN^2 reaction.

$S_N{}^1$ (nucleophilic substitution unimolecular):

In this type of reaction the rate of the reaction depends on the concentration of only one reactant. So it is $S_N{}^1$ reaction.

Here the rate depends on the concentration of alkyl halide.

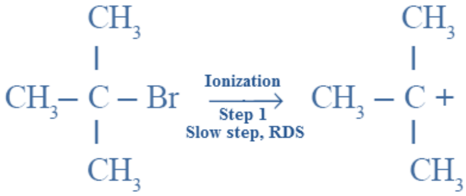
Rate of the reaction α [alkyl halide]



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \;+ H_2O \xrightarrow{\text{aq. NaOH}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HBr$$

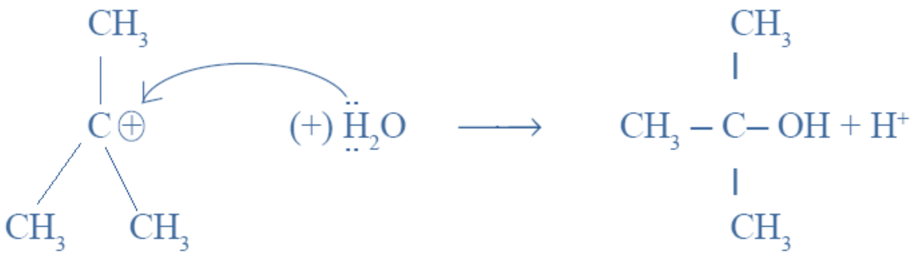
The above $S_N{}^1$ reaction takes place in two steps.

In the first step of $S_N{}^1$ reaction alkyl halide undergoes ionization and carbonium ion is formed.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\substack{\text{Step 1}\\ \text{Slow step, RDS}}]{\text{Ionization}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}\,+$$

In the second step nucleophile attacks on this carbonium ion and the products are formed.



In both steps the first step i.e., carbonium ion formation step takes place slowly. So it is the rate determining step. In this step (rate determining) only one reactant alkyl halide is involved. So the rate depends on concentration of alkyl halide.

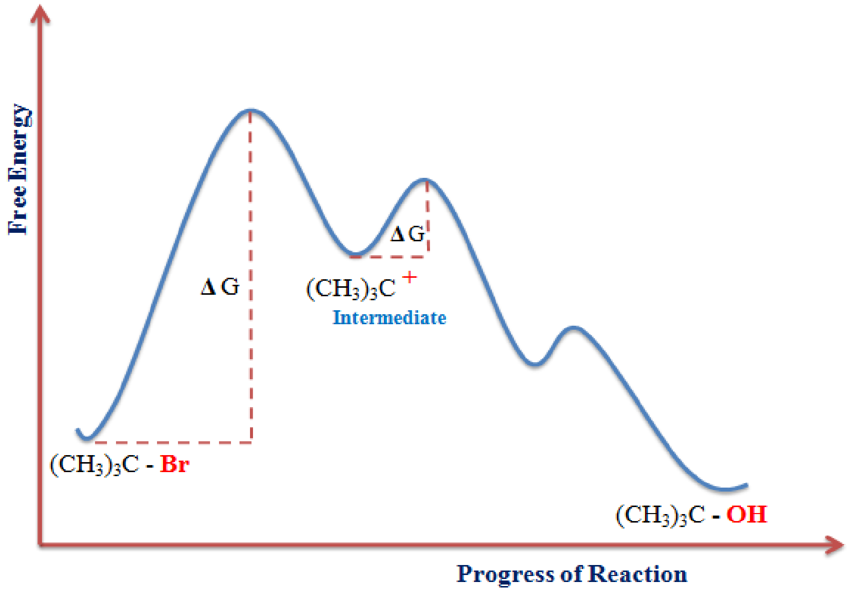
In S_N^1 reaction if asymmetric alkyl halide is involved racemic mixture is formed in the reaction. The reactivity order in alkyl halides is

$3^0R\text{-}X > 2^0R\text{-}X > 1^0R\text{-}X \sim CH_3\text{-}X$.

Due to the resonance in allyl and benzyl halides stabilized carbonium ion is formed. So in this halides S_N^1 reaction takes place more i.e., they have higher reactivity towards S_N^1 reaction.

$$[CH_2{=}CH - {}^{+}CH_2 \leftrightarrow {}^{+}CH_2 - CH = CH_2]$$

Allyl carbo cation



Energy diagram for SN1 reaction between $(CH_3)_3C - Br + H_2O$

27.2.1.a Intext questions:

1. Write the order of reactions. In S_N^1 and S_N^2 reactions?

....

2. What is rate determination step in SN^2 reaction?

....

27.2.1.a Answers to Intext Questions:

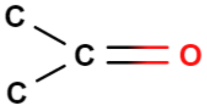
1. SN^1 first order reaction SN^2 second order reaction
2. The first step formation of Transition state is rate determination step in SN^2 reaction.

Chapter 28

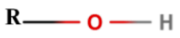
ALCOHOLS, PHENOLS AND ETHERS

So far you have learnt the chemistry of hydrocarbons which serve as basic skeleton for the attachment of various functional groups to give a large number of their derivatives. In the last lesson, we discussed one such class of compounds viz. halogen derivatives of hydrocarbons. Another very useful and important category of hydrocarbon derivatives is that of compounds containing functional groups in which the carbon atom is linked to an oxygen atom.

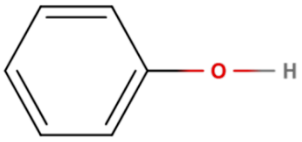
We have devoted two lessons for the study of these compounds. In this lesson, you will study about compounds containing carbon-oxygen single bond (-C-O-) whereas the next lesson deals with compounds containing carbon-oxygen double-bond



Among the compounds with carbon-oxygen single bond are the classes of alcohols, phenols and ethers having the following general structures.



Alcohol



Phenol

Ether
R/R' can also be aromatic

These are very important categories of compounds both in the industry and in the synthesis of other organic compounds. You will study each of these classes of compounds in this Lesson.

Objectives:

After reading this lesson, you should be able to

- Classify alcohols as primary, secondary or tertiary;
- Name simple alcohols according to IUPAC system of nomenclature;
- List general methods of preparation of alcohols;
- Discuss the properties of alcohols in the light of their structure;
- Explain various reactions exhibited by alcohols to give other categories of organic compounds;

- Give the names of common phenolic compounds;
- Describe the laboratory and industrial methods of preparation of phenols;
- Explain the greater acidity of phenols as compared to alcohols;
- Discuss the reactions of phenols;
- Name ethers according to the IUPAC system of nomenclature;
- Describe the general methods of preparation of ethers and
- Explain the important reactions of ethers.

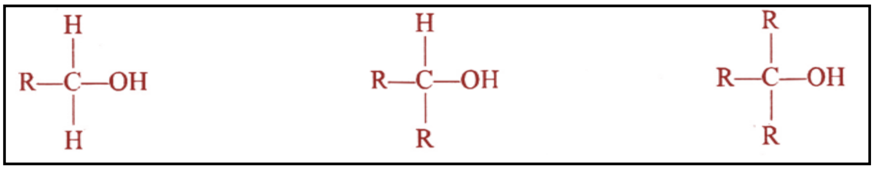
28.1 Alcohols

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded to the *carbon atoms in aliphatic compounds*. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methanol and ethanol are two industrially important alcohols.

Formula	IUPAC Name	Common Name
CH_3 - OH	Methanol	(Methyl Alcohol)
CH_3 - CH_2 - OH	Ethanol	(Ethyl Alcohol)

28.1.1 Classification and Nomenclature of Alcohols

Alcohols are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°) depending upon whether the number of alkyl groups bonded to the carbon atom bearing the hydroxy group is one, two or three, respectively.



primary alcohol **secondary alcohol** **tertiary alcohol**

According to the IUPAC system of nomenclature, alcohols are called alkanols. They are named as the derivatives of the corresponding alkane in which the *-e* of the alkane is replaced by *-ol*.

The procedure for nomenclature involves the following steps:

Step 1: Select the longest carbon chain which contains the carbon atom bearing the -OH group. Count the number of carbon atoms and identify the corresponding alkane. From the name of this alkane, drop the final e and suffix *-ol* in its place. This gives the root name or the parent name.

Step 2: Number the carbon chain starting from the end nearest to the hydroxy group. The number of the carbon atom bearing the hydroxy group is indicated before *-ol* in the name.

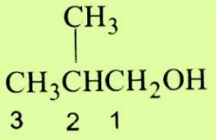
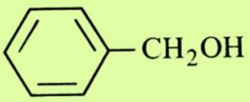
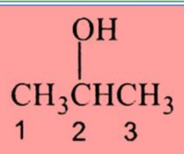
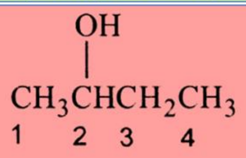
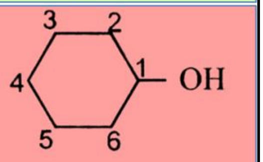
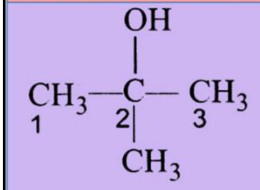
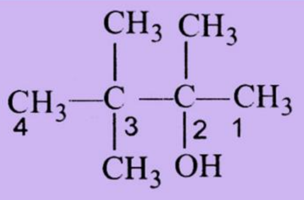
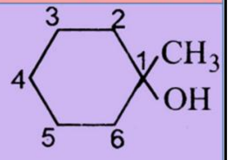
Step 3: Number the other substituents according to their position on the chain.

Step 4: Write the name of the alcohol by listing the substituents in the alphabetical order along with their position.

Recap from Lesson 25:
that the hydroxyl group takes precedence over double and triple bonds.

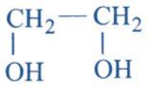
Table 28.1 illustrates some common alcohols and their IUPAC and common names. Go through them in light of the steps given above for nomenclature.

Table 28.1 : Some common Alcohols and their Names

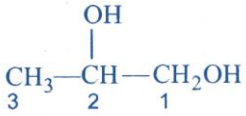
Primary Alcohols	 **2-Methylpropan-1-ol** **(Isobutyl alcohol)***	 **Phenylmethanol** **(Benzyl alcohol)**	$\underset{3}{CH_3}\underset{2}{CH}\underset{1}{CH_2}OH$ **1-Propanol** **(*n*-Propyl alcohol)** $\underset{3}{H_2C}=\underset{2}{CH}\underset{1}{CH_2}OH$ **Prop-2-en-1-ol**
Secondary Alcohols	 **Propan-2-ol** **(*Iso*propyl alcohol)**	 **Butan-2-ol** **(*sec* Butyl alcohol)**	 **Cyclohexanol** **(Cyclohexyl alcohol)**
Tertiary Alcohols	 **2-Methylpropan-2-ol** **(*tert*-Butyl alcohol)**	 **2,3,3-Trimethylbutan-2-ol**	 **1-Methylcyclohex-1-ol**

* The names given in the brackets are common names.

In the above examples, only one -OR group is present in the molecule. These alcohols are called monohydric alcohols. Alcohols having two hydroxyl groups in a molecule are known as dihydric alcohols or diols or glycols. Examples of some diols are shown below:



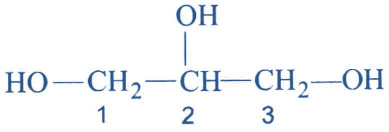
Ethane-1,2-diol
(Ethylene glycol)



Propane-1,2-diol
(Propylene glycol)

Note that the term glycol generally means 1,2-diol or a vicinal diol. In these diols, the two hydroxyl groups are present on the adjacent carbon atoms.

Similarly, alcohols having three hydroxyl groups are called trihydric alcohols. 1,2,3-propanetriol which is commonly known as glycerol, is a trihydric alcohol.



$HO-\underset{1}{CH_2}-\underset{2}{\overset{OH}{CH}}-\underset{3}{CH_2}-OH$

1,2,3-Propanetriol
(Glycerol)

28.1.2 General Methods of Preparation

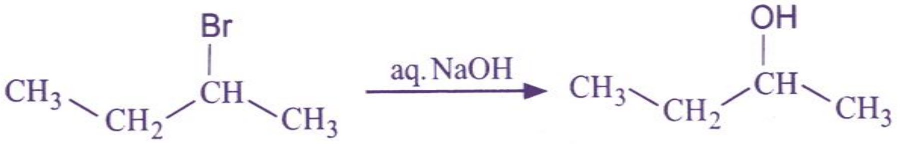
Alcohols are synthesized by the following general methods. You might have come across some of these methods in previous lessons. Let us now study these methods.

1. Hydrolysis of Haloalkanes

Haloalkanes can be converted to corresponding alcohols using aqueous sodium or potassium hydroxide or water as nucleophiles.

$$CH_3CH_2Cl + NaOH(aq.) \longrightarrow CH_3CH_2OH + NaCl$$

Chloroethane Ethanol



2-Bromobutane

Butan-2-ol (90%)

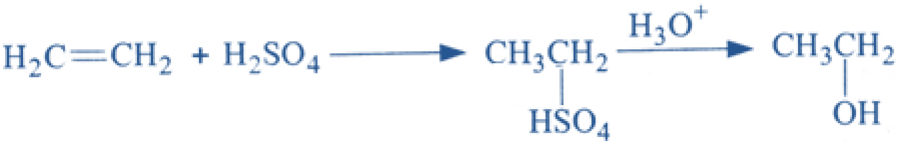
2. From hydration of Alkenes

Hydration means addition of water molecule. In case of alkenes, hydration is the addition of H+ and OH- across the double bond to give alcohols.

Alkenes can be hydrated by the following methods:

(i) Acid-catalysed Hydration

Alkenes can be hydrated to yield alcohols in the presence of acid catalysts.

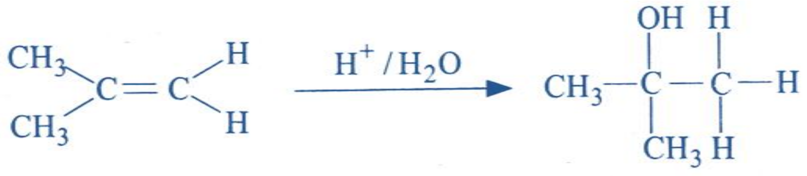


$$H_2C{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2HSO_4 \xrightarrow{H_3O^+} CH_3CH_2OH$$

Ethene **Ethyl hydrogen sulphate** **Ethanol**

The reaction proceeds via alkyl hydrogen sulphate and this method is used for the industrial preparation of ethanol.

In case of unsymmetric alkenes, the addition follows Markovniokov's rule.



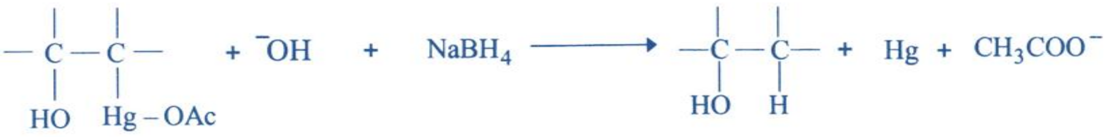
2-Methylpropene **2-Methyl-2-propanol**

(ii) Oxymercuration demercuration

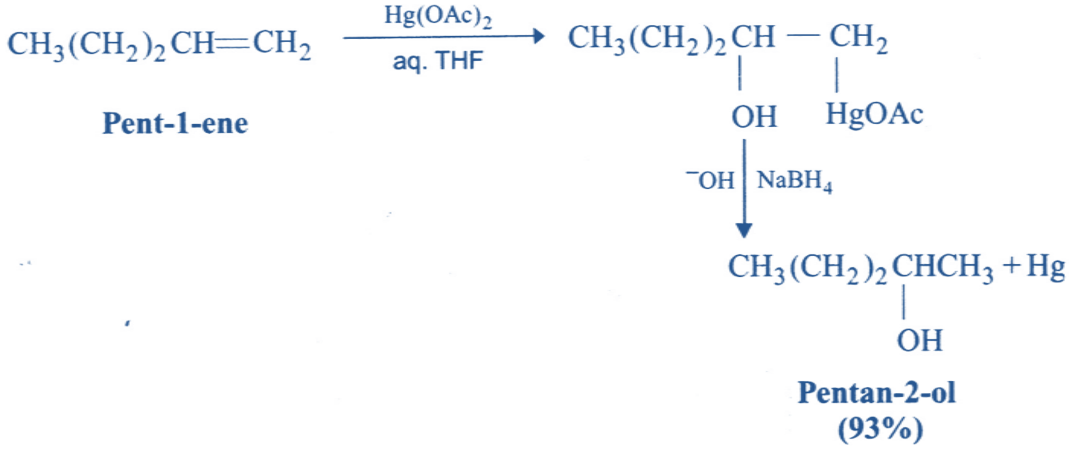
Alkenes react with mercury (II) acetate, i.e. mercuric acetate also represented as [Hg(OAc)] in aqueous tetrahydrofuran (THF) solvent to give hydroxyalkyl mercury compounds which are reduced to alcohols by sodium borohydride.

Step 1: Oxymercuration

Step 2: Demercuration

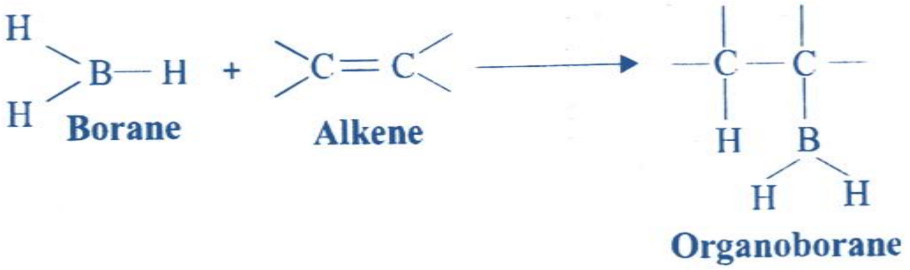


This method gives very good yield of alcohols and here also, the addition takes place in Markovnikov's fashion.

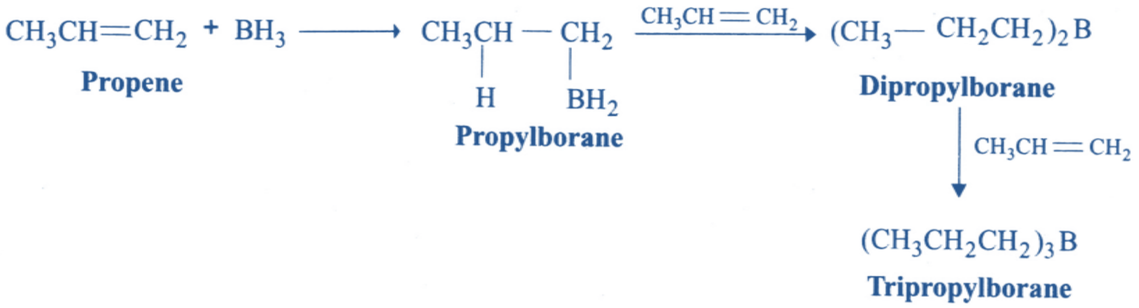


(iii) Hydroboration - Oxidation

When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained.



Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane (R_3B). This is shown below for propene.



The trialkylborane so obtained is oxidised using alkaline hydrogen peroxide solution to give three molecules of alcohols and boric acid.

$$(CH_3\text{-}CH_2\text{-}CH_2)_3\text{-}B \xrightarrow{H_2O_2\,/\,OH} 3\,CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + B(OH)_3$$

Tripropylborane Propanol Boric acid

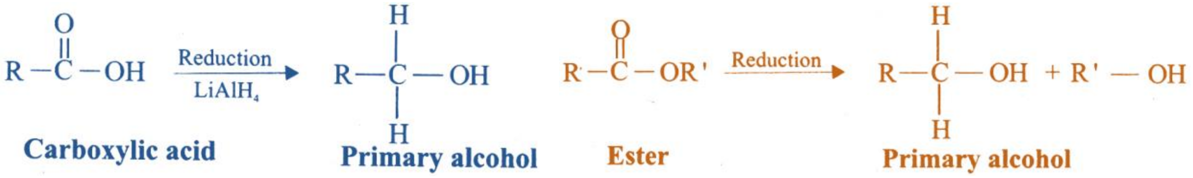
Note that hydroboration-oxidation yields the anti-Markovnikov addition of water although the reaction proceeds according to Markonikov's rule.

3. Reduction of Carbonyl Compounds

Carbonyl compounds (which contain $\overset{O}{\overset{\|}{-C-}}$ group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols.

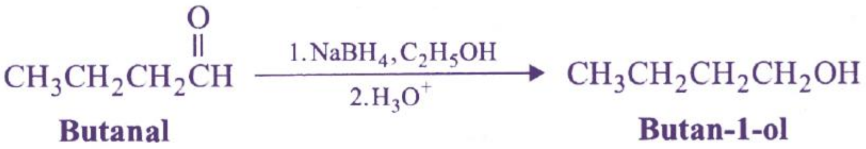
Aldehydes give primary alcohols while ketones yield secondary alcohols on reduction.

Carboxylic acids and esters also give primary alcohols on reduction.

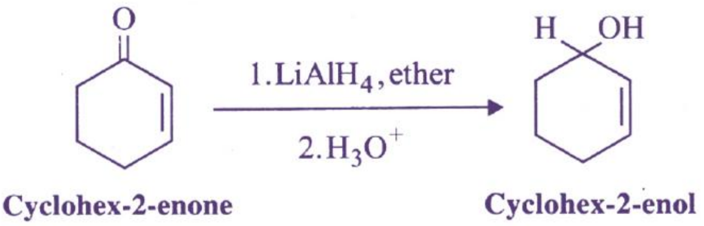


The reduction is carried out using hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). $LiAlH_4$ is stronger and reacts explosively with water while $NaBH_4$ is convenient to handle and reacts slowly.

Lithium aluminium hydride reduces all of the above classes of compounds while sodium borohydride reduces only aldehydes and ketones and does not reduce carboxylic acids and esters. Hence, it can be used to selectively reduce aldehydic / ketonic carbonyl group in presence of carboxylic acid/ester function. Some examples below illustrate the use of these reagents.

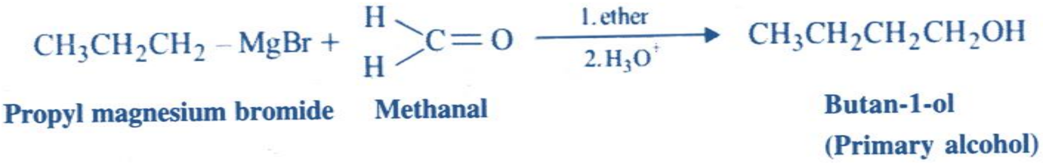


$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow[2.H_3O^+]{1.NaBH_4,C_2H_5OH} CH_3CH_2CH_2CH_2OH$$



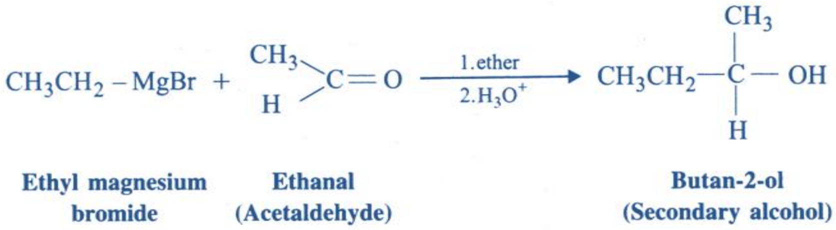
4. From Aldehydes and Ketones using Grignard Regents

Grignard reagents react with methanal (or formaldehyde) to give a *primary alcohol*.



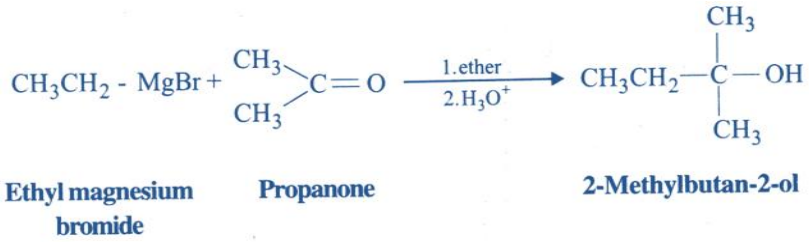
$$CH_3CH_2CH_2-MgBr + \begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow[2.H_3O^+]{1.ether} CH_3CH_2CH_2CH_2OH$$

All other aldehydes yield secondary alcohols on reaction with Grignard reagents.



$$CH_3CH_2-MgBr + \begin{matrix}CH_3\\H\end{matrix}\!\!>C=O \xrightarrow[2.H_3O^+]{1.ether} CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-OH$$

With ketones, Grignard reagents give tertiary alcohols.



5. Diazotization of Primary Aliphatic Amines

This reaction also yields alchols and will be discussed in **Lesson 30**.

6. Fermentation

Ethanol is prepared on a large scale using fermentation. It involves breaking down large molecules into simpler ones using enzymes. Usually, yeast is added as a source of enzymes. The fermentation of sugar is shown below :

$$\underset{\textbf{Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Investase}} \underset{\textbf{Glucose}}{C_6H_{12}O_6} + \underset{\textbf{Fructose}}{C_6H_{12}O_6}$$

$$\big\downarrow \textbf{Zymase}$$

$$\underset{\textbf{Ethanol}}{2\,C_2H_5OH + 2\,CO_2}$$

28.1.3 Structure and Physical Properties

The structure of alcohols is similar to that of water. The structures of water and methanol molecules are shown in Fig. 28.1.

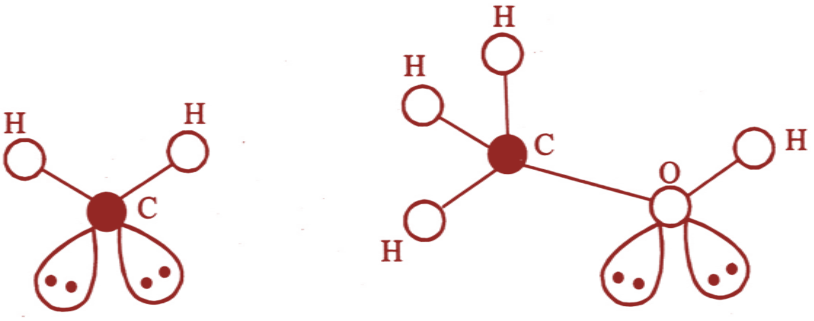


Fig. 28.1: Water and Methanol molecule

You know that the electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the OH bond is polar in nature. In other words, oxygen has a slight negative charge on it whereas hydrogen has a slight positive charge. This bond polarity alone cannot explain the higher boiling points of alcohols as compared to hydrocarbons or similar haloalkanes, as listed in Table 28.2.

Normally, hydrogen bonding is responsible for higher boiling points of alcohols. Hydrogen bonding amongst alcohol molecules is depicted in Fig. 28.2.

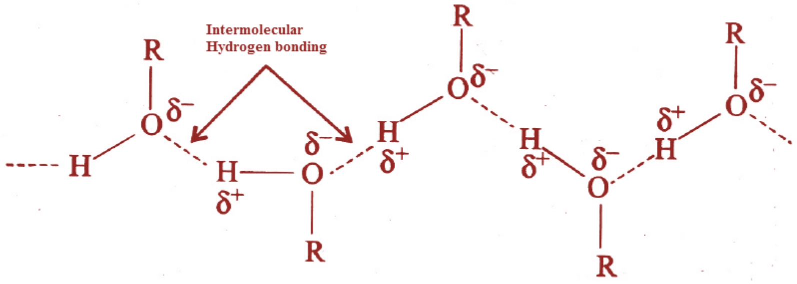
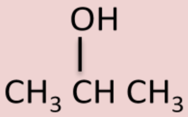
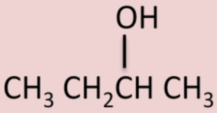


Fig. 28.2: Hydrogen bonding in alcohol molecules

You can see that the negatively polarised oxygen atom of one alcohol molecule attracts• the positively polarised hydrogen atom of the other molecule forming intermolecular H-bonding. Thus, alcohol molecules are associated or are held together. This force of attraction is to be overcome before a molecule is set free from the liquid state and vaporises. Thus, more heat energy is required to break the hydrogen bonds and hence, the boiling points of alcohols are higher than alkanes and haloalkanes of comparable molecular mass.

Table 28.2: Physical Properties of some Alcohols, Hydrocarbons and related Haloalkanes

Compound	IUPAC Name	Melting Point (K)	Boiling Point (K)	Solubility g/100 m of water
CH_3OH	Methanol	175.2	322.8	∞
CH_4	Methane	90.5	181.13	-
CH_3Cl	Chloromethane	175.3	248.8	-
$CH_3\ CH_2OH$	Ethanol	158.3	351.5	∞
$CH_3\ CH_3$	Ethane	189.7	184.4	-
$CH_3\ CH_2Cl$	Chloroethane	136.6	285.3	-
$CH_3\ CH_2\ CH_2OH$	Propan-1-ol	-	378.04	∞
$CH_3\ CH_2\ CH_3$	Propane	85.3	230.9	-
 $CH_3\ \overset{\overset{OH}{\vert}}{C}H\ CH_3$	Propan-2-ol	184	355	∞
$CH_3\ CH_2\ CH_2\ CH_2\ OH$	Butan-1-ol	183	391	83
 $CH_3\ CH_2\overset{\overset{OH}{\vert}}{C}H\ CH_3$	Butan-2-o1	159	373	10

From the last column of Table 28.2, you must have noticed that alcohols have high solubilities in water. The lower alcohols are completely miscible and their solubilities decrease as the hydrocarbon portion of the molecule becomes larger. The higher solubility of alcohols can be again attributed to the hydrogen bonding. In this case, hydrogen bonding takes place between the alcohol and water molecules as is shown below in Fig. 28.3.

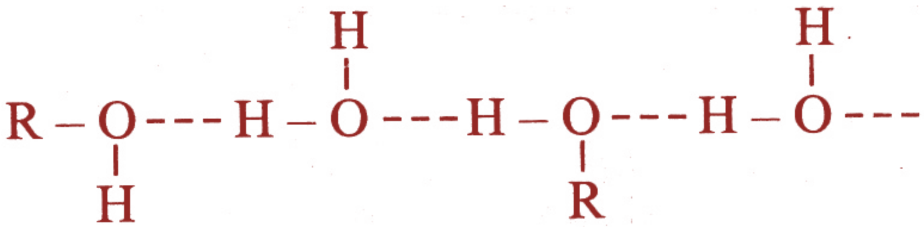


Fig. 28.3: Hydrogen bonding in a solution of methanol and water

28.1.4 Reactions of Alcohols

Alcohols exhibit the following reactions:

1. Acidic and Basic behaviour

Alcohols behave both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H) in sodium hydride (NaH), can remove the proton from the alcohol molecule and an alkoxide ion results.

When water is used as a base, the *acid dissociation constant (K)* and *pK* can be written as follows:

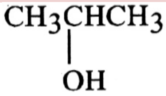
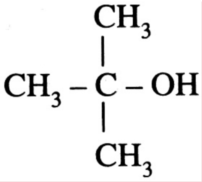
$$R-O-H+H_2O \xrightleftharpoons{K_a} R-O^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][RO^-]}{[ROH]}$$

$$pK_a = -\log K_a$$

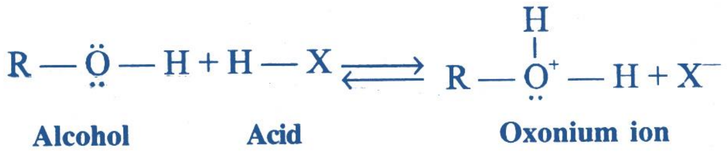
Some pK values are listed in Table 28.3.

Table 28.3: pK$_a$ values of some compounds

Compound	pK$_a$
CH_3OH	15.5
H_2O	15.74
CH_3CH_2OH	15.9
 $CH_3CH(OH)CH_3$	16.5
 $CH_3-C(CH_3)_2-OH$	18.0

Remember that the lower the pK value, higher is the acidity of the compound.

Alcohols can behave as weak bases also. They have lone pair of electrons on oxygen atom and hence they can be protonated by strong acids to give oxonium ions as shown below:



2. Formation of Alkoxides

Alcohols react with sodium or potassium metals to give the respective alkoxides.

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2O^-Na^+ + \frac{1}{2}H_2(g)$$

Ethanol　Sodium metal　Sodium ethoxide

$$(CH_3)_3C-OH + K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

tert-Butyl alcohol　Potassium metal　Potassium *tert-butoxide*

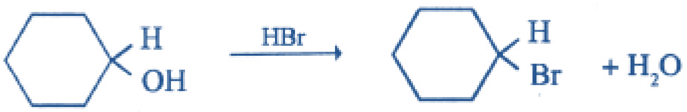
Alkoxides are used in the synthesis of organic compounds.

3. Conversion to Alkyl Halides

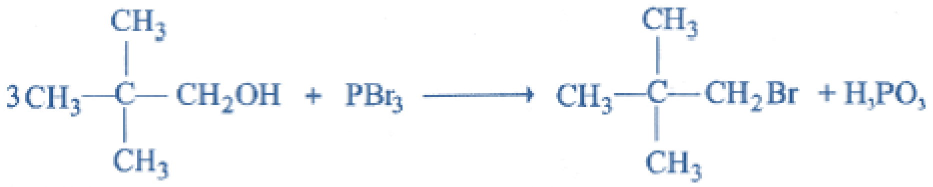
You have already studied in Lesson 27 that alcohols react with a variety of reagents to form alkyl halides. These are hydrogen halides (such as HCI, HBr or HI), phosphorus tribromide (PBr_3) and thionyl chloride ($SOCl_2$). The reaction involves the breaking of R - OH bond of alcohol molecule.

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HCl\,(conc.) \xrightarrow{298\,K} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + H_2O$$

2-Methyl propan-2-ol　**2-chloro-2-methyl propane**



Cyclohexanol　**Bromocyclohexane**



$$3\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + PBr_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br + H_3PO_3$$

2, 2-Dimethylpropan-1-ol　**1-Bromo-2, 2-Dimethylpropane**

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_{2(g)} + HCl_{(g)}$$

Propan-1-ol　1-chloropropane

Tertiary alcohols are readily converted to alkyl halides by HCl or HBr while the best method with primary and secondary alcohols is by using PBr_3 or $SOCl_2$ as the reagents. Another advantage of using $SOCl_2$is that both the by-products in this reaction, *i.e.* SO_2 and HCl are gases and hence can be easily eliminated to yield pure alkyl halide.

Lucas Test

The formation of alkyl halides from alcohols is the basis of this test. In involves the reaction of the alcohol with Lucas reagent (*i.e.* anhyd. $ZnCl_2$+conc.HCI). Since the reactivity of alcohols is in the following order.

primary alcohols < secondary alcohols < tertiary alcohols

With primary alcohols turbidity does not appear. In case of secondary alcohols, turbidity appears within 5 mintues whereas it appears immediately with tertiary alcohols. The turbidity is due to the formation of alkyl chlorides from the corresponding alcohols.

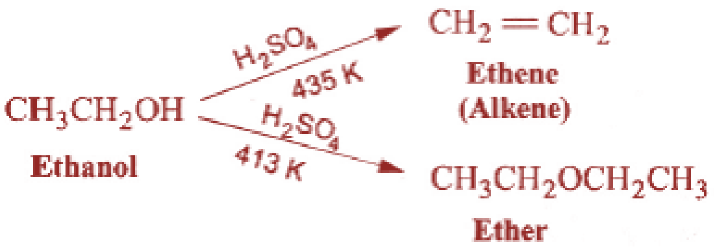
4. Formation of Alkenes

Alcohols can be dehydrated to alkenes. This reaction requires an acidic catalyst and is favoured at higher temperatures. Usually sulphuric and phosphoric acid are used as acidic catalysts. You have come across this reaction in Lesson 26 also. The ease of dehydration follows the following order amongst alcohols.

tertiary alcohols > secondary alcohols > primary alcohols

5. Dehydration to form Ethers

Intermolecular dehydration of alcohols yields ethers. This reaction takes place at a lower temperature than that for dehydration to give alkenes.



The formation of ethers by dehydration is a substitution type of reaction and gives only symmetrical ethers. You will study a better method of synthesis of ethers later under the section of ethers in this lesson.

6. Oxidation

Alcohols can be oxidised to carbonyl compounds. Primary alcohols give aldehydes or carboxylic acids on oxidation while secondary alcohols yield ketones. The tertiary alcohols do not usually undergo oxidation. Normally $KMnO_4$, Cr_2O_3 and $Na_2Cr_2O_7$ or $K_2Cr_2O_7$ are used as oxidising agents.

$$CH_3CH_2CH_2OH \xrightarrow[H_2O]{K_2Cr_2O_7,\ H_2SO_4} CH_3CH_2CHO \xrightarrow{\text{Further oxidation}} CH_3CH_2COOH$$

Propanal-1-ol Propanal Propanoic acid

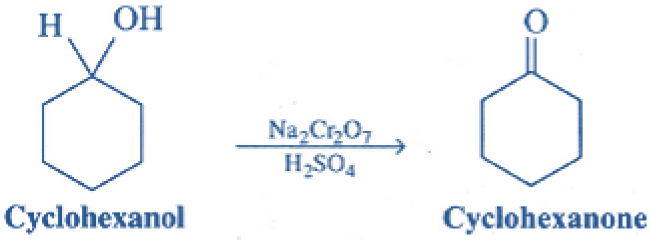
The aldehydes obtained by oxidation of the primary alcohols get further oxidised to carboxylic acids as shown above. You will study more about these classes of compounds in the next lesson.

The oxidation can be controlled and aldehydes are obtained as the products by using pyridium chlorochromate (PCC) which is a mild reagent.

$$CH_3(CH_2)_8CH_2OH \xrightarrow{PCC} CH_3(CH_2)_8CHO$$

Decanol Decanal

Secondary alcohols can be oxidised to ketones as shown below:



7. Formation of Esters

Alcohols react with carboxylic acids to form esters. This reaction is discussed in the next lesson.

$$CH_3COOH + CH_3CH_2OH \xrightleftharpoons{H+} CH_3COOCH_2CH_3 + H_2O$$

Ethanoic acid Ethanol Ethyl ethanoate Water

This reaction is called esterification reaction and is reversible in nature.

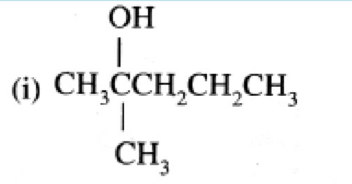
Uses:

Alcohols find a large variety of uses as follows :

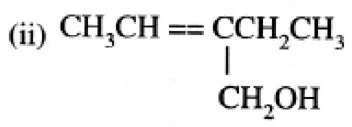
1. As solvents
2. As laboratory reagents
3. In medicines
4. As thinners in paints, varnishes, etc.

Intext Questions 28.1

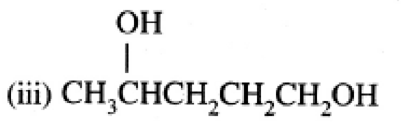
1. Give the IUPAC names of the following alcohols:



$$\text{(i) } CH_3\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$$



$$\text{(ii) } CH_3CH{=\!=}\underset{\underset{CH_2OH}{|}}{C}CH_2CH_3$$



$$\text{(iii) } CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2OH$$

....

2. How Will you prepare propan-l-o1 from propanal?

....

3. Give the synthesis of 2-methylpropan-2-o1 using Grignard reagent.

....

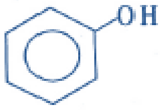
4. Give the product of the following reactions:

$$\text{(i) Hexan-l-ol} \xrightarrow[H_2O,\ H^+]{CrO_3}$$

$$\text{(ii) Hexan-l-ol} \xrightarrow[\text{Chlorochromate}]{\text{Pyridium}}$$

28.2 Phenols

The name phenol is specifically used for the following compound (hydroxybenzene) in which one hydroxyl group is attached to the benzene ring.

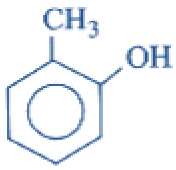


Phenol

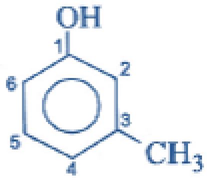
It is also used as a general name for the class of compounds derived from the above compound. Phenol is a disinfactant. Phenols are widely distributed in nature. They are also important in the synthesis of organic compounds such as aspirin and in the preparation of dyes. Phenol is also used in the manufacture of bakelite which is a very useful polymer.

28.2.1 Nomenclature of Phenols

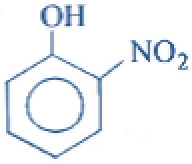
Some representative examples of phenolic compounds are given below:



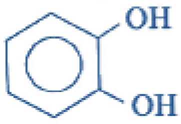
2-Methylphenol
(*o*-Cresol)



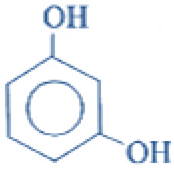
3-Methylphenol
(*m*-Cresol)



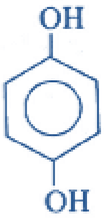
2-Nitrophenol
(*o*-Nitrophenol)



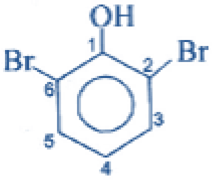
1,2-Benzenediol
(Catechol)



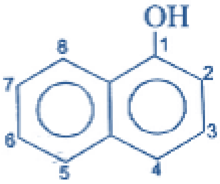
1,3-Benzenediol
(Resorcinol)



1,4-Benzenediol
(Hydroquinone)



2,6-Dibromophenol



1-Naphthol
(α – Naphthol)

Note that the term *phenol* is used as a parent name and the other substituents present in the compound are given a specific number according to their position on the aromatic ring. As done before the common names of the above compounds are given in the brackets below their IUPAC names.

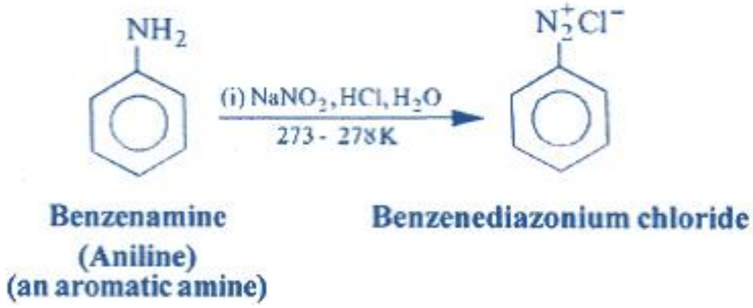
28.2.2 General Methods of Preparation

We can categorise the methods of preparation as methods of *laboratory synthesis and industrial synthesis* of phenols.

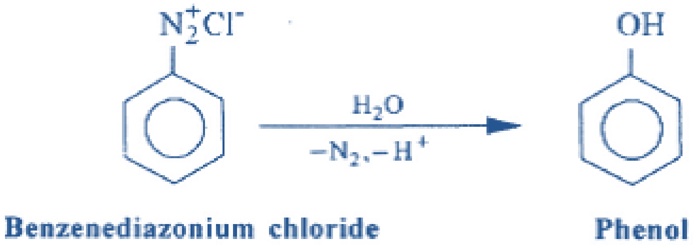
A. Laboratory Synthesis of Phenols

1. From Arenediazonium Salts

It is the most general method of preparation of phenols and requires mild conditions. Arenediazonium salts or aromatic diazonium salts are obtained by the *diazotization* of primary aromatic amines as given below:



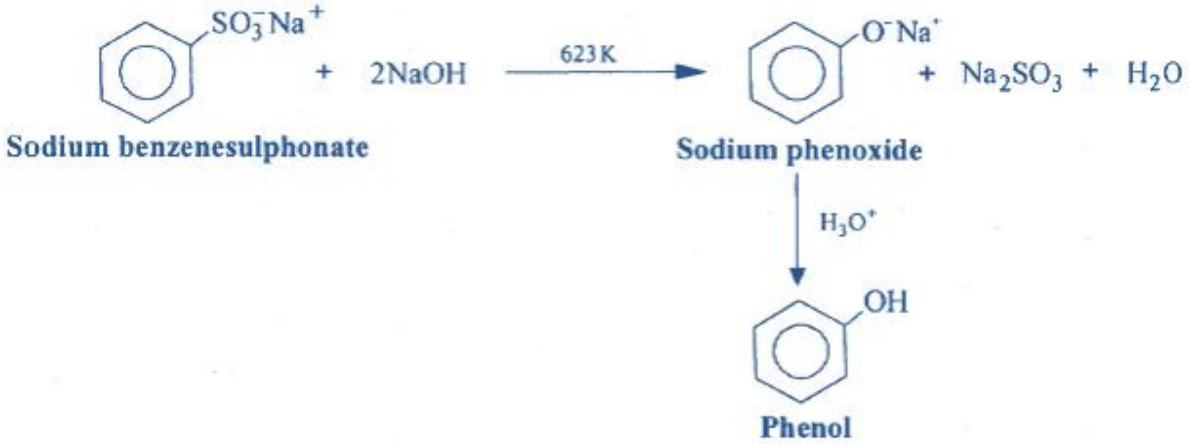
The arenediazonium salt on hydrolysis yields phenol.



2. Alkali Fusion of Sodium Benzenesulphonate

This was the first commercial synthesis of phenol developed in Germany in 1890. It can also be used as a laboratory method for synthesis of phenol.

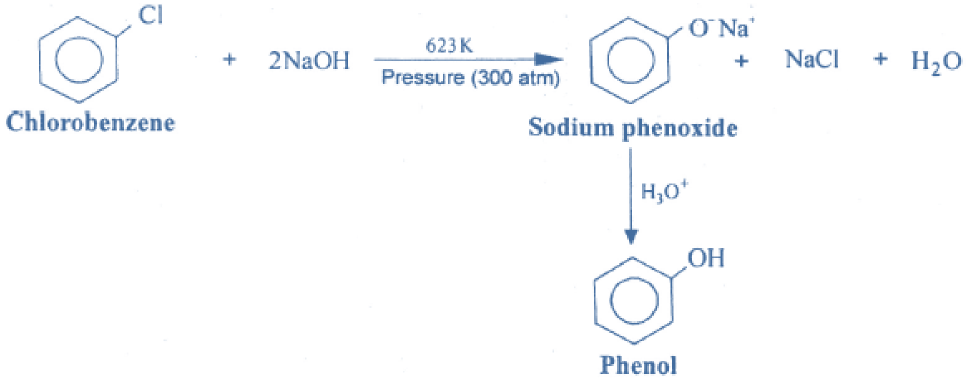
Sodium benzenesulphonate is fused with sodium hydroxide to give sodium phenoxide which on acidification yields phenol.



B. Industrial Synthesis of Phenols

1. Dow Process

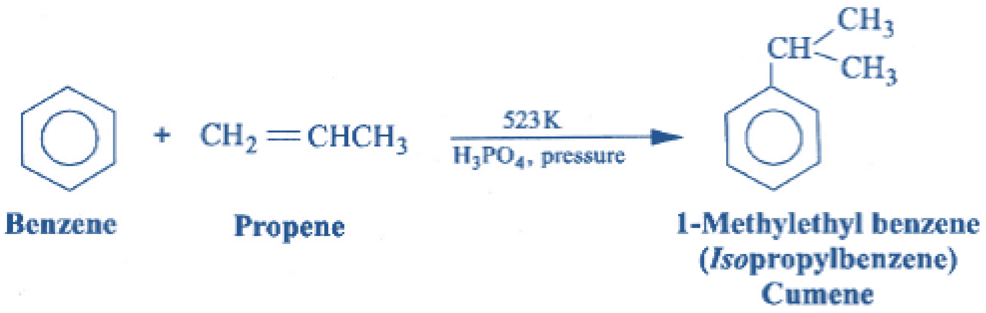
In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.



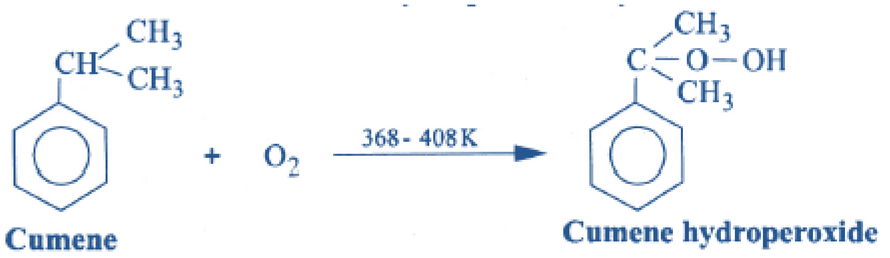
This method was in use for many years but now phenol is synthesised via cumene hydroperoxide which is discussed below.

2. From Cumene Hydroperoxide

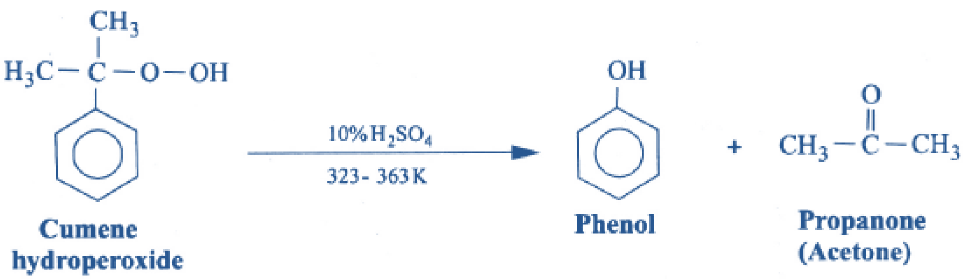
The reaction between benzene and propene in presence of phosphoric acid yields cumene.



Cumene is then oxidised to cumene hydroperoxide by air.



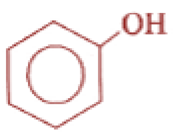
In the final step, cumene hydroperoxide is treated with 10% sulphuric acid to give phenol and acetone on hydrolytic rearrangement.



Note that propanone is obtained as a valuable byproduct in this reaction.

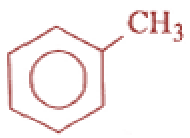
28.2.3 Physical Properties

Similar to alcohols, phenols also have hydrogen atom linked to the electronegative oxygen atom. Thus, phenols also exhibit hydrogen bonding and hence have higher boiling points as compared to the hydrocarbons of similar molecular weight.



b.p. = 454.7K

Phenol



b.p. = 383.6K

Methylbenzene

(Toluene)

Due to their ability to form hydrogen bonds, phends show some water solubility. For example, the solubility of phenol is 9.3 g per 100 ml of water.

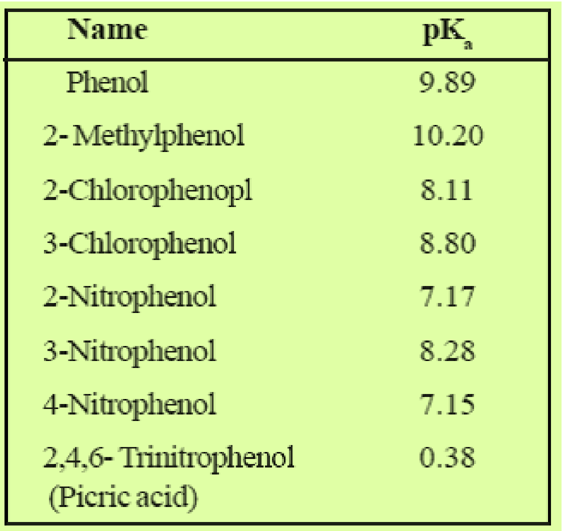
28.2.4 Reactions of Phenols

Let us now study the reactions exhibited by phenols.

1. Acidic and Basic Nature

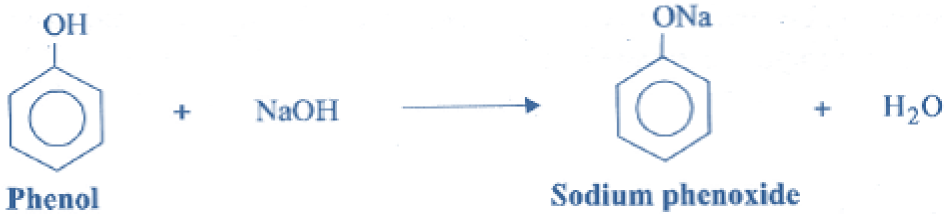
Phenols are much more acidic than alcohols. pKa values of some phenols are listed in Table 28.4.

Table 28.4: *pKa* values of phenols



Name	pK_a
Phenol	9.89
2- Methylphenol	10.20
2-Chlorophenopl	8.11
3-Chlorophenol	8.80
2-Nitrophenol	7.17
3-Nitrophenol	8.28
4-Nitrophenol	7.15
2,4,6- Trinitrophenol (Picric acid)	0.38

Since phenols are acidic in nature, they are soluble in dilute sodium hydroxide.



The greater acidity of phenols can be attributed to the resonance stablisation of the phenoxide ion. The resonance structures of phenoxide ion are shown in Fig. 28.4.

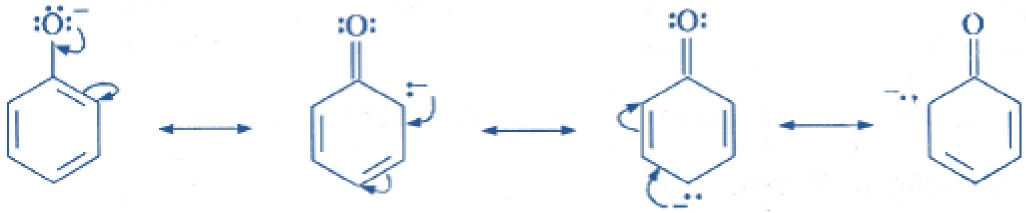


Fig. 28.4: Resonance structures of phenoxide ion

The delocalisation of the negative charge over the benzene ring stabilises the phenoxide ion. No such stabilisation is possible, in case of alkoxide ions.

Similar resonance is also shown in phenol itself, see Fig 28.5. But the resonance structures of phenol are less stable as compared to those of phenoxide ion as they involve the separation of charge.

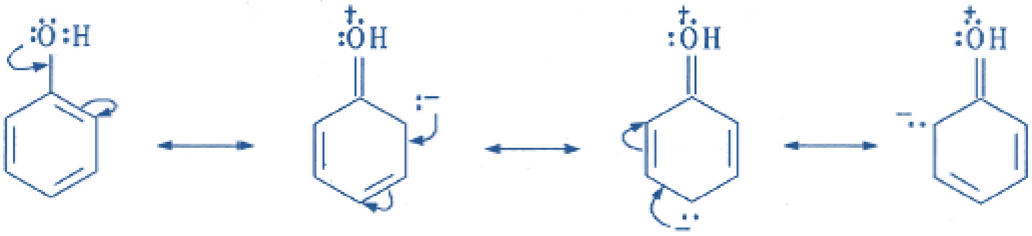
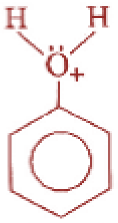


Fig. 28.5 : Resonance structures of phenol

If you carefully go through the pKa values given in Table 28.4, you would see that, **the electron donating substituents such as methyl group decrease the acidity of phenol** and hence alkylphenols have greater pKa values as compared to phenol itself. On the other hand, **electron withdrawing substituents increase the acidity and phenols having these substituents** (-Cl, -NO_2, etc.) have lower pKa values than phenol. In fact, 2,4,6-trinitrophenol is more acidic than many carboxylic acids.

Phenols behave as weak bases also. Similar to alcohols, they can also be protonated to give phenyloxonium ion.

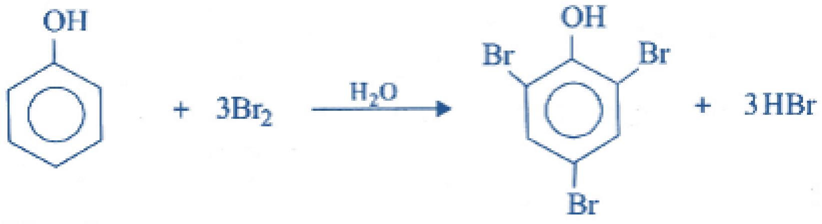


Phenyloxonium ion

2. Electrophilic Substitution Reactions

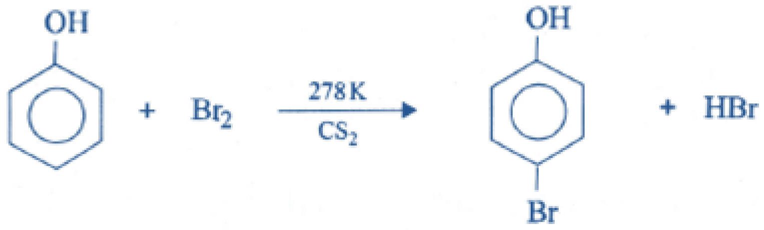
The hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. In this reaction, an electrophile (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho and para* positions of the phenol are electron rich, the substitution takes place at these positions. Two such reactions are halogenation and nitration reactions. Let us now study them in details.

(i) Halogenation: Phenol reacts with bromine in aqueous solution to give 2,4,6-tribromophenol in about 100% yield.



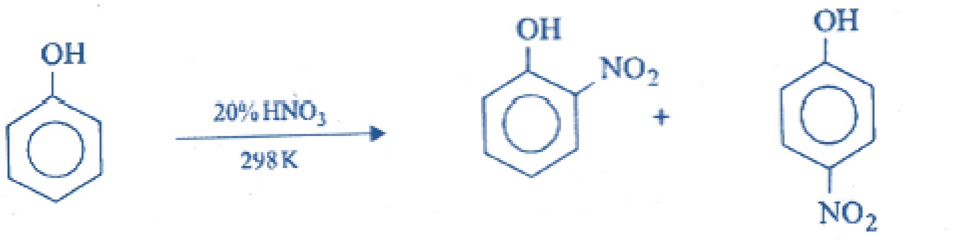
Phenol **2,4,6-Tribromophenol**

Bromination can be limited to monobromination to give mainly 4-bromophenol using low temperature and less polar solvent such as carbon disulphide. The other product is formed in minor quantity is 2-bromophenol.



Phenol **4-Bromophenol**

(ii) Nitration: Phenol gives a mixture of 2-nitro and 4-nitrophenols on nitration with dilute nitric acid.

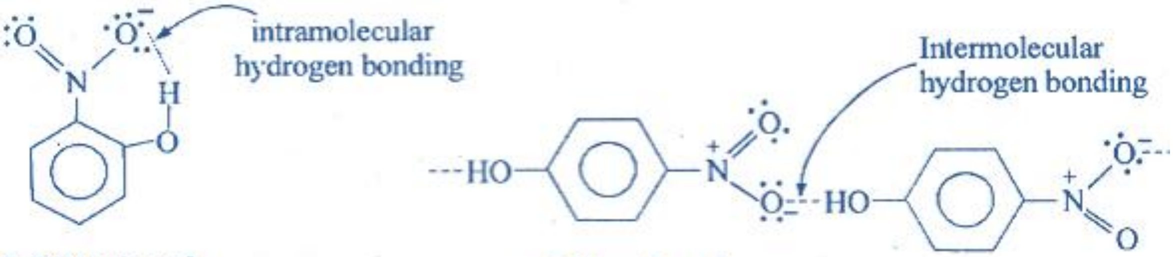


Phenol

2-Nitrophenol (*o*-Nitrophenol) (30-40%)

4-Nitrophenol (*p*-Nitrophenol) (15%)

The mixture of nitro phenols so obtained is separated using steam distillation. Both these products show hydrogen bonding. In case of 2-nitrophenol, the hydrogen bonding is intramolecular (in the same molecule) whereas in case of 4-nitrophenol, it is intermolecular (between different molecules). These are depicted in Fig. 28.5.



2-Nitrophenol **4-Nitrophenol**

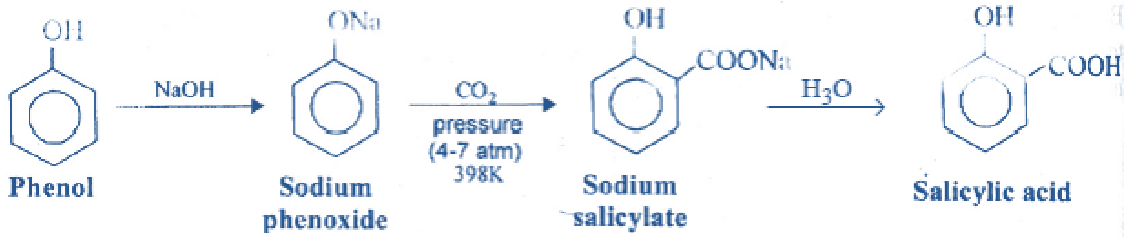
Fig. 28.5: Intramolecular and intermolecular hydrogen bonding in nitrophenols

2-Nitrophenol is steam volatile and distills out on passing steam whereas 4-nitrophenol is less volatile due to intermolecular hydrogen bonding.

Treatment of phenol with a mixture of cone. nitric acid and cone. sulphuric acid at 323K yields 2,4,6-trinitrophenol also known as picric acid.

3. Kolbe Reaction

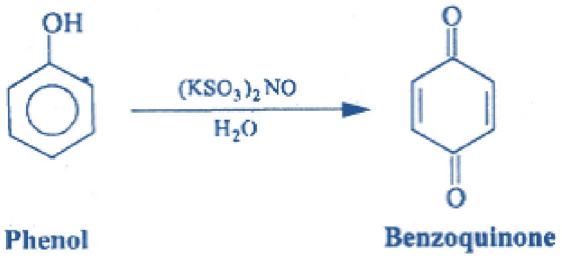
It involves sodium phenoxide which is allowed to absorb carbon dioxide and then heated under a pressure of CO_2 to 398K. Sodium salicylate so obtained on acidification yields salicylic acid.



By reaction with acetic anhydride, salicylic acid yields asprin, which is the common pain reliever.

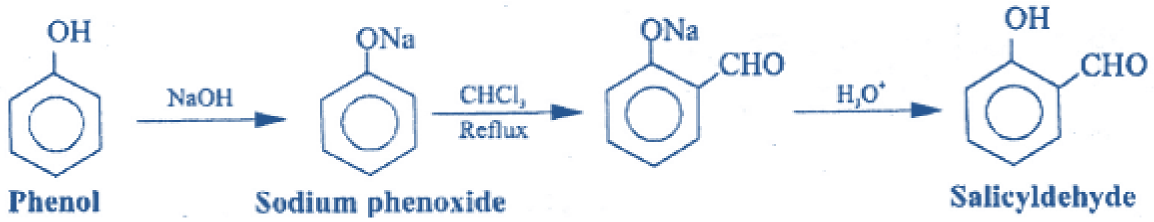
4. Oxidation

Phenols undergo oxidation reactions to give products which are different from those obtained by alcohols. They can be oxidised using a variety of oxidising agents such as sodium dichromate or silver oxide to give quinones. These days Fremy's salt [$(KSO_3)_2NO$] is preferred for oxidation.

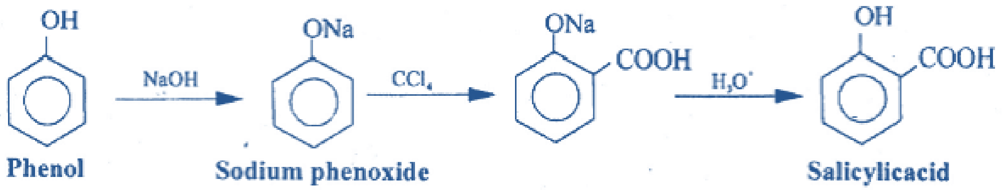


5. Reimer Tiemann Reaction

Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.

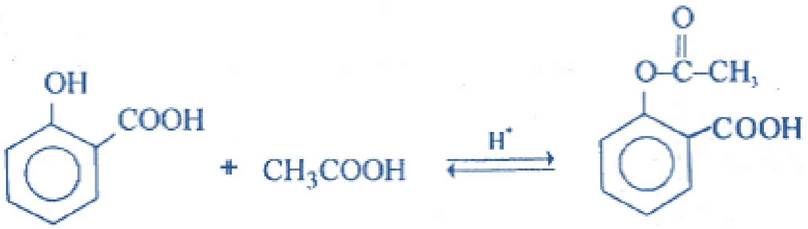


Use of carbon tetrachloride in place of chloroform gives salicylic acid.

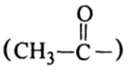


6. Esterification

Similar to alcohols, phenols react with carboxylic acids to give esters.

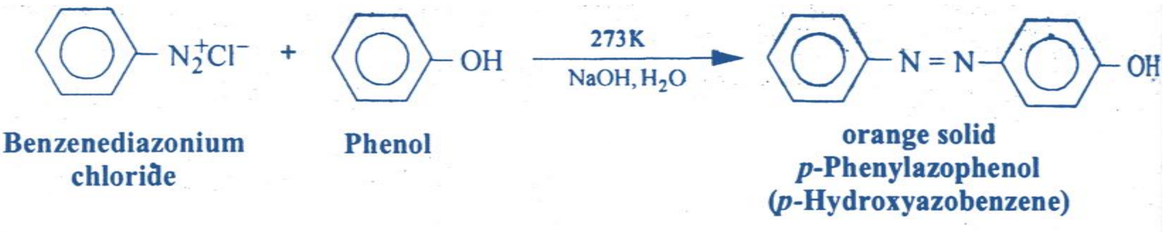


2-Hydroxybenzoic acid   Ethanoic acid   Acetyl salicylic acid

This reaction is an acetylation reaction as the H of - OH the phenol is replaced by the acetyl  $(CH_3-\overset{\overset{O}{\|}}{C}-)$ group.

7. Coupling Reaction

Phenols react with aromatic diazonium salts in slightly alkaline conditions to give *azo* compounds. These *azo* compounds are brightly coloured and are used as *azo* dyes.



Uses

1. Phenol is used as a disinfectant.
2. It is also used in the synthesis of polymers.
3. Phenols are used in the synthesis of many organic compounds.
4. Substituted phenols are used in dyeing and tanning industries.

Intext Questions 28.2

1. How will you convert aniline to phenol?

....

2. What is the starting material in Dow’s process?

....

3. Arrange the following in the increasing order of their acidity:
   Phenol, 2-Methylphenol, 2-Chlorophenol

....

4. How will you prepare salicylic acid from phenol?

....

5. What is an azo dye?

....

28.3 Ethers

Ethers are organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups. Thus, ethers can be represented as R-O-R’ where Rand R’ may be alkyl or aryl groups. When the two substituent groups (R and R’) are identical, then the ether is called a symmetrical ether, otherwise if these two groups are different, then the ether is known as an unsymmetrical ether.

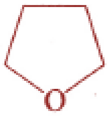
$CH_3CH_2-O-CH_2CH_3$

A symmetricalether

$CH_3-O-CH_2CH_3$

An unsymmetrical ether

The oxygen atom of the ether can also be part of a ring, in which case the ether is known as a cyclic ether. Tetrahydrofuran is one such cyclic ether which is used as a solvent.



Tetrahydrofuran (THF)

Ethers are commonly used as solvents for organic reactions. The symmetrical ether shown here is diethyl ether and is commonly also referred to simply as ether because of its nature as solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years.

28.3.1 Nomenclature of Ethers

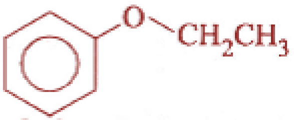
Common names of ethers are arrived by alphabetically naming the two groups attached to the oxygen followed by the word ether. The common names for some ethers are given below:

$CH_3OCH_2CH_3$

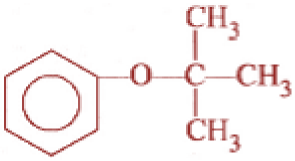
Ethyl methyl ether

$CH_3CH_2OCH_2CH_3$

Diethyl ether



Ethyl phenyl ether



***tert*-Butyl phenyl ether**

$Cl-CH_2-O-CH_3$

Chloromethyl methyl ether

In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the alkane and the smaller alkyl group is treated as an alkoxy substituent on this alkane. For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this ether is treated as the ethane derivative.

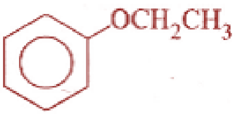
$$CH_3OCH_2CH_3$$

Ethyl methyl ether

The remaining portion, *i.e.*, -OCH_3 part in this case, is called the methoxy substituent. Hence, the above ether is called methoxyethane. Some more examples of IUPAC names of ethers are given below:

$CH_3CH_2OCH_2CH_3$

Ethoxy ethane



Ethoxybenzene

$CH_3O\overset{1}{C}H_2\overset{2}{C}H_2OCH_3$

1,2-Dimethoxyethane

28.3.2 General Methods of Preparation

You have already studied under the reactions of alcohols that ethers can be obtained by the dehydration of alcohols. Ethers can also be prepared by **Williamson synthesis** which is explained below :

Williamson Synthesis: It involves the reaction of a metal alkoxide with a primary alkyl halide. The metal alkoxide is prepared by adding sodium or potassium metal or sodium hydride (NaH) to the alcohol.

$$\mathrm{ROH + Na \longrightarrow \underset{\substack{\text{Metal}\\\text{alkoxide}}}{RO^{-}\,Na^{+}} + \frac{1}{2}H_2}$$

$$\mathrm{ROH + NaH \longrightarrow \underset{\substack{\text{Metal}\\\text{alkoxide}}}{RO^{-}\,Na^{+}} + H_2}$$

$$\mathrm{\underset{\substack{\text{Metal}\\\text{alkoxide}}}{RO^{-}\,Na^{+}} + \underset{\substack{\text{Alkyl}\\\text{halide}}}{R'{-}X} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX}$$

$$\mathrm{\underset{\text{propan-l-ol}}{CH_3CH_2CH_2OH} + NaH \longrightarrow \underset{\text{Sodium propoxide}}{CH_3CH_2CH_2ONa} \xrightarrow{CH_3CH_2I} \underset{\substack{\text{l-Ethoxypropane}\\\text{(Ethyl propyl ether)}}}{CH_3CH_2CH_2OCH_2CH_3} + NaI}$$

Williamson synthesis involves the displacement of the halide ion by the alkoxide ion.

28.3.3 Structure and Properties of Ethers

Ethers have geometry similar to water and alcohols. The oxygen atom is sp3 hybridised. There are two lone pairs of electrons present on the oxygen atom as is shown in Fig. 2.8.6.

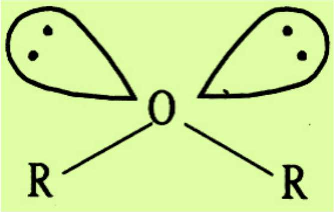


Fig. 28.6 : Geometry of an ether molecule

Note that the ether molecule has a bent structure. Since the carbon-oxygen bond is polar and the molecule has a bent structure, there is a net dipole moment and the ether molecule is polar in nature (Fig. 28.7). Ethers, thus, act as polar solvents.

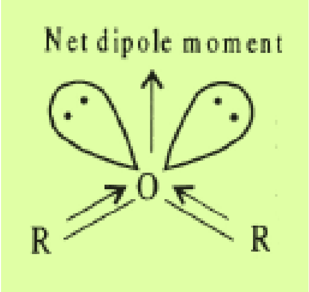
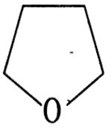
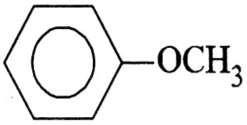


Fig. 28.7: Polar ether molecule

Since ethers do not have a hydrogen atom linked to the oxygen atom, they cannot form hydrogen bonds amongst their own molecules. Due to the absence of hydrogen bonding, they have lower boiling points as compared to alcohols having similar molecular masses. The boiling points of some ethers are listed in Table 28.5.

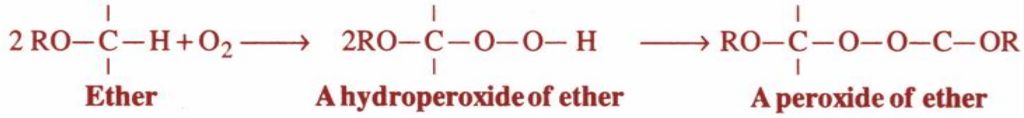
Table 28.5 : Boiling points of some common ethers

Ether	Boiling point (K)
CH_3OCH_3	248.1
$CH_3OCH_2CH_3$	283.8
$CH_3CH_2OCH_2CH_3$	307.6
$CH_3OCH_2CH_2OCH_3$	356
	338.4
	431.3

28.3.4 Reactions of Ethers

Ethers are normally unreactive in nature. Their unreactivity makes them good solvents. However, they show some reactions which are discussed below :

1. Reaction with Oxygen : Ethers slowly react with oxygen to form hydroperoxides and peroxides.



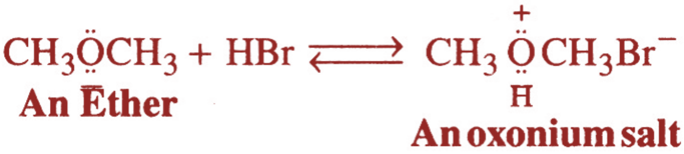
$$2\,RO-\overset{|}{\underset{|}{C}}-H+O_2 \longrightarrow 2RO-\overset{|}{\underset{|}{C}}-O-O-H \longrightarrow RO-\overset{|}{\underset{|}{C}}-O-O-C-OR$$

Ether A hydroperoxide of ether A peroxide of ether

Peroxides have a tendency to explode. Therefore, one should be very careful in handling ethers which may have been stored for sometime because they may contain some peroxide.

2. Reaction with Acids

Since the oxygen atom of ethers contains lone pairs of electrons, they can accept a proton from the acids. Thus, ethers are basic in nature.



$$CH_3\ddot{\underset{\cdot\cdot}{O}}CH_3 + HBr \rightleftharpoons CH_3\,\underset{H}{\overset{+}{\ddot{\underset{\cdot\cdot}{O}}}}CH_3Br^-$$

An Ether An oxonium salt

3. Acidic Cleavage

Heating dialkyl ethers with strong acids such as HI, HBr or H_2SO_4 leads to their cleavage.

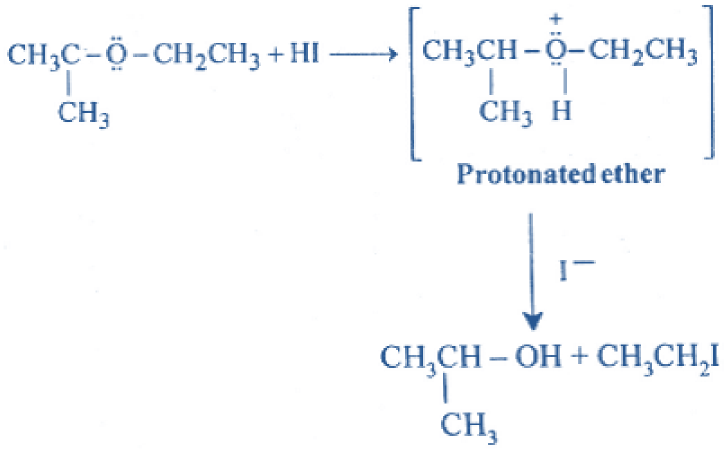
$$CH_3CH_2OCH_2CH_3 + HBr \longrightarrow CH_3CH_2Br + CH_3CH_2OH$$

Ethoxyethane Bromoethane Ethanol

The alcohol formed further reacts with additional HBr to give bromoethane. Hence,

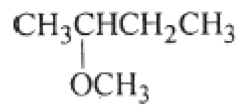
$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

In case of ethers having primary or secondary alkyl groups, the nucleophile (Br or I attacks the less hindered alkyl group. Thus, in case of the following unsymmetrical ether, the products contain alkyl halide formed by the attack of the halide ion on the less hindered primary alkyl group, *i.e.*, ethyl group.



Intext Questions 28.3

I. What are the IUPAC names of the following ethers?

(i) 

$$\underset{\displaystyle OCH_3}{CH_3\overset{|}{C}HCH_2CH_3}$$

(ii) $CH_3 - O - CH_3$

....

2. (i) How will you prepare methyl propyl ether using Williamson synthesis?
   (ii) What is the IUPAC name of methyl propyl ether?

....

3. Why should you be careful in using old stock of ethers.

....

4. Why are ethers good solvents?

....

5. What is tetrahydrofuran ? Give its structure and use.

....

What You Have Learnt

In this lesson, you have learnt that

- Alcohols can be classified as primary, secondary or tertiary.
- Alcohols can be monohydric, dihydric or polyhydric.
- Alcohols can be prepared by the following general methods:
  - Hydrolysis of haloalkanes
  - Hydration of alkenes
  - Reduction of carbonyl compounds

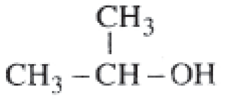
- From aldehydes and ketones using Grignard reagents

- Alcohols behave both as weak acids and weak bases.
- Alcohols can be converted to alkyl halides, alkenes, ethers, aldehydes, ketones, carboxylic acids and esters.
- In the laboratory, phenols can be prepared from arenediazonium salts and sodium benzene sulphonate. Their industrial preparation is done by Dow's process and from cumene hydroperoxide.
- Similar to alcohols, phenols can also behave both as acids and bases.
- Typical reactions of phenols being electrophilic substitution reactions such as halogenation, sulphonation, nitration, etc.
- Phenols undergo oxidation and also exhibit Reimer Tiemann reaction. They react with aromatic diazonium salts to give azo dyes.
- Ethers can be symmetrical or unsymmetrical.
- Ethers can be prepared by Williamson synthesis.
- Dialkyl ethers are cleaved on heating with strong acids.

Terminal Exercise

1. Give the IUPAC names of the following compounds:

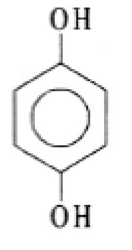
(i)



$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-OH$

(ii) $C_6H_5OCH_2CH_3$

(iii)



2. Compare the boiling points of ethyl alcohol and dimethyl ether. Which one has higher boiling point and why?
3. Which ester would give ethanol and methanol on reduction?
4. Complete the following reactions:

(i) $CH_3CH_2CH_2Cl + NaOH\ (aq.) \longrightarrow$ ....

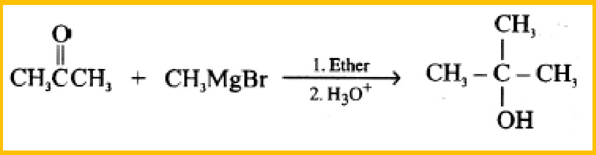
(ii) $CH_3CHO \xrightarrow[2H_3O^+]{1.LiAlH_4,ether}$ ....

(iii) $CH_3OH + Na \longrightarrow$ ....

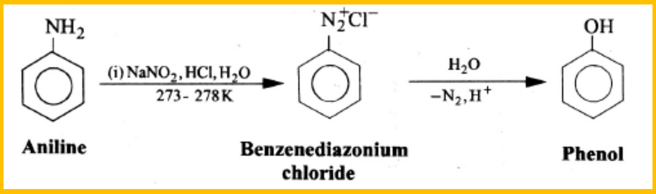
5. How is ethanol prepared using fermentation?
6. What is Lucas test? What is its use?
7. Which reagent is used for oxidising primary alcohols to aldehydes?
8. Why are phenols more acidic than alcohols? Explain.
9. Why are ethers polar in nature?

Answers to Intext Questions

28.1

1. (i) 2-Methylpentan-2-ol (ii) 2-Ethylbut-2-en-1-ol (iii) 1, 4-Pentanediol
2. By reduction with NaBH4 or LiAlH4
3. 
4. (i) Hexanoic Acid (ii) Hexanal

28.2

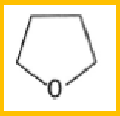
1. 

2. Chlorobenzene
3. 2-Methylphenol < Phenol < 2 - Chlorophenol
4. By Kolbe reaction
5. Azo dyes are azo compounds formed by the reaction of phenols with aromatic diazonium salts. They are brightly coloured.

28.3

1. (i) 2-Methoxybutane (ii) Methoxymethane
2. (i) $CH_3CH_2CH_2O + CH_3Br \longrightarrow CH_3CH_2\text{-}O\text{-}CH_3 + Br$

   (ii) Methoxypropane
3. They may explode due to the presence of peroxides.
4. Because they are unreactive in nature.
5. It is a cyclic ether.



It is used as a solvent.

Chapter 29

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

In the last lesson, you studied about organic compounds containing functional groups having carbon-oxygen single bond. There are other classes of organic compounds in which the functional group contains the carbon- oxygen double bond. The examples of these classes of compounds being carbonyl compounds such as aldehydes and ketones as well as carboxylic acids and their derivatives. These organic compounds are very important both in the industry and in the synthesis of other organic compounds. Therefore, their study forms an important part of the organic chemistry. Let us study the chemistry of these classes of compounds in detail.

Objectives

After reading this lesson, you should be able to

- give IUPAC names of aldehydes and ketones;
- describe the general methods of preparation of aldehydes and ketones;
- discuss the trends in physical properties of the aldehydes and ketones in the light of the polar nature of the carbonyl group;
- explain important reactions exhibited by aldehydes and ketones;
- distinguish between aldehydes and ketones on the basis of certain reactions and tests based on them;
- give IUPAC names of carboxylic acids;
- explain general methods of preparation of carboxylic acids;
- discuss the physical properties and their trends for simple monocarboxylic acids;
- describe important reactions exhibited by carboxylic acids;
- explain the preparation and some interconversion reactions of carboxylic acid derivatives, and
- highlight the importance of aldehydes, ketones and carboxylic acids.

29.1 Aldehydes and Ketones

You have some familiarity with these classes of compounds from previous lessons. These compounds are also referred to as *carbonyl compounds* and have >C=O functionality present in them. These compounds exist widely in nature and are responsible for the flavour and aroma of many foods. They are also important industrially both as reagents in synthesis and as solvents.

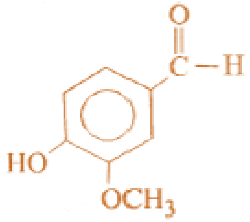
Aldehydes have at least one hydrogen atom bonded to the carbonyl group, the other group may be either a hydrogen or an alkyl (or aryl) group. In *ketones*, the carbonyl group is bonded to two alkyl or aryl groups. The two groups bonded to a ketone may be similar or different resulting in a symmetrical or an unsymmetrical ketone, respectively.

Carbonyl group

an aldehyde

a ketone

You must be familiar with vanilin and camphor. Their structures are given below. You can see that they contain an aldehyde and a keto functional group, respectively.



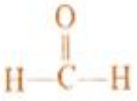
Vanilin
(used for vanila flavour)

Camphor

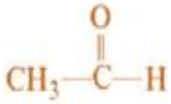
29.1.1 Nomenclature of Aldehydes and Ketones

In the IUPAC system of nomenclature, aliphatic aldehydes are named as alkanals. The final -e in the name of the corresponding alkane is substituted by -al.

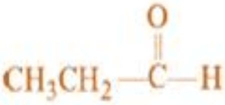
Some common examples of aldehydes and their names are given below:



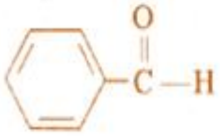
Methanal
(Formaldehyde)



Ethanal
(Acetaldehyde)



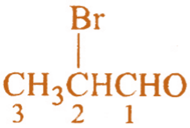
Propanal
(Propionaldehyde)



Benzenecarbaldehyde
(Benzaldehyde)

Note that when the -CHO group is attached to a ring, then the compound is called a *carbaldehyde*.

Remember that the carbonyl carbon of the aldehydes is present at the end of the chain and is assigned 1 position. Therefore, it is not necessary to specify its position in the name of the aldehyde. The examples given below illustrate this point.



$$\underset{3}{CH_3}\underset{2}{\overset{\overset{Br}{|}}{C}H}\underset{1}{CHO}$$

2-Bromopropanal

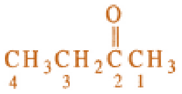
$$Cl\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CHO}$$

4-Chlorobutanal

Ketones are named as alkanones in the IUPAC nomenclature. Their names are obtained by replacing final ***-e*** in the name of alkane by ***-one***. The carbon chain is numbered in such a way that the carbonyl group gets the lowest number. Some examples of ketones are mentioned below:

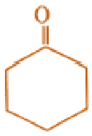
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

Propanone
(Acetone)

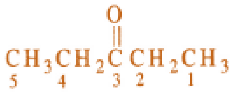


$\underset{4}{C}H_3\underset{3}{C}H_2\underset{2}{\overset{\overset{O}{\|}}{C}}\underset{1}{C}H_3$

Butan-2-one
(Ethyl methyl ketone)



Cyclohexanone

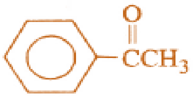


$\underset{5}{C}H_3\underset{4}{C}H_2\underset{3}{\overset{\overset{O}{\|}}{C}}\underset{2}{C}H_2\underset{1}{C}H_3$

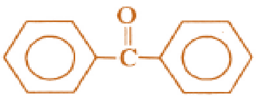
Pentan-3-one
(Diethyl ketone)

$CH_3\overset{\overset{O}{\|}}{C}CH_2CH=CH_2$

Pent-4-en-2-one



1-Phenylethanone
(Acetophenone)



(Benzophenone)

29.1.2 Preparation of Aldehydes and Ketones

You have already studied most of the methods used in the synthesis of aldehydes and ketones in the previous lesson. Let us now refresh them.

1. Oxidation of Primary and Secondary Alcohols

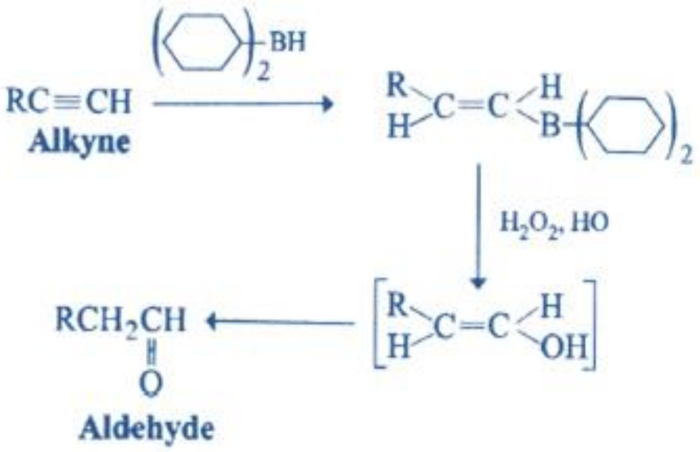
From the last lesson, you know that primary alcohols can be oxidised to aldehydes and secondary alcohols can be oxidised to ketones.

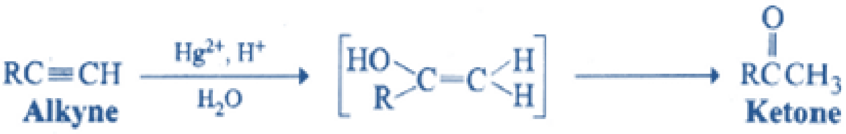
2. Ozonolysis of Alkenes

This reaction has been discussed in lesson 26. The products obtained are aldehydes or ketones depending upon the structure of the starting alkene.

3. Hydration of Alkynes

Hydration of alkynes can give an aldehyde or a ketone. Markovnikov's hydration yields ketones whereas anti-Markovnikov's hydration gives aldehydes.

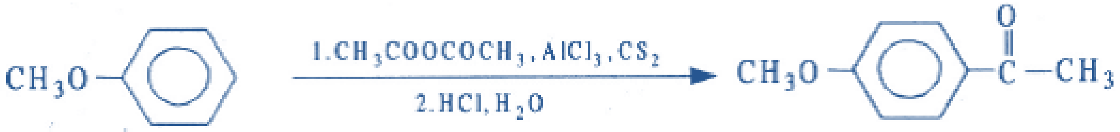




You can go through the details of these reactions as discussed in lesson 26.

4. Friedal-Crafts Acylation

Aromatic ketones can be prepared by Friedel-Crafts acylation (alkanoylation) reaction. One example of this reaction is given below:



Similar acylation reaction using ethanoyl chloride was also discussed in lesson 26 under the electrophilic substitution reactions of aromatic hydrocarbons.

29.1.3 Structure and Physical Properties

In both aldehydes and ketones, the carbonyl carbon is sp^2 hybridised and Oxygen atom is sp hybridised. Therefore, the groups attached to the carbon atom and oxygen are present in a plane. This is shown in Fig. 29.1.

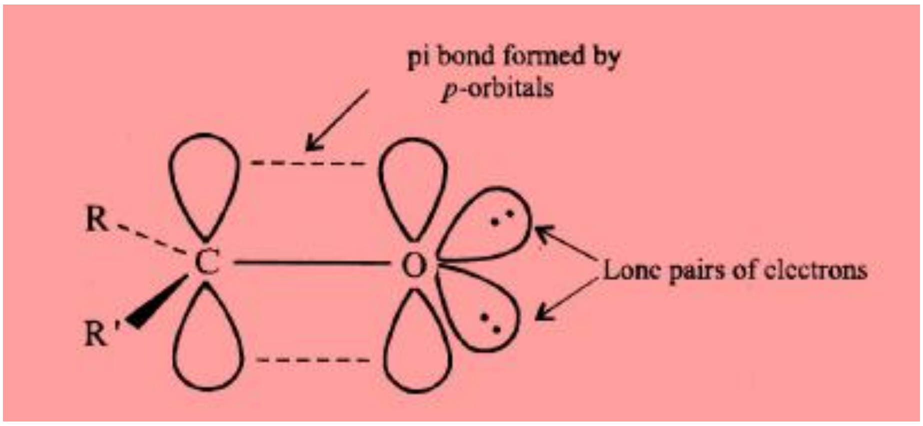
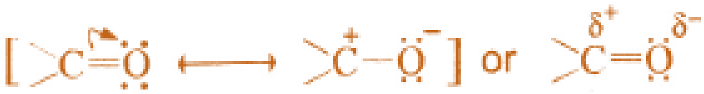


Fig. 29.1 : The structure of the carbonyl functional group

You can see in the figure that σ-bond is formed by the overlap of p-orbitals of carbon and oxygen atoms. The p-orbitals are present in a plane perpendicular to the plane of the molecule. Note the presence of two lone pairs of electrons on oxygen atom.

You also know that oxygen is more electronegative than carbon. Hence, it attracts the electrons of the carbon-oxygen double bond (>C=O bond) resulting in its appreciable polarisation.

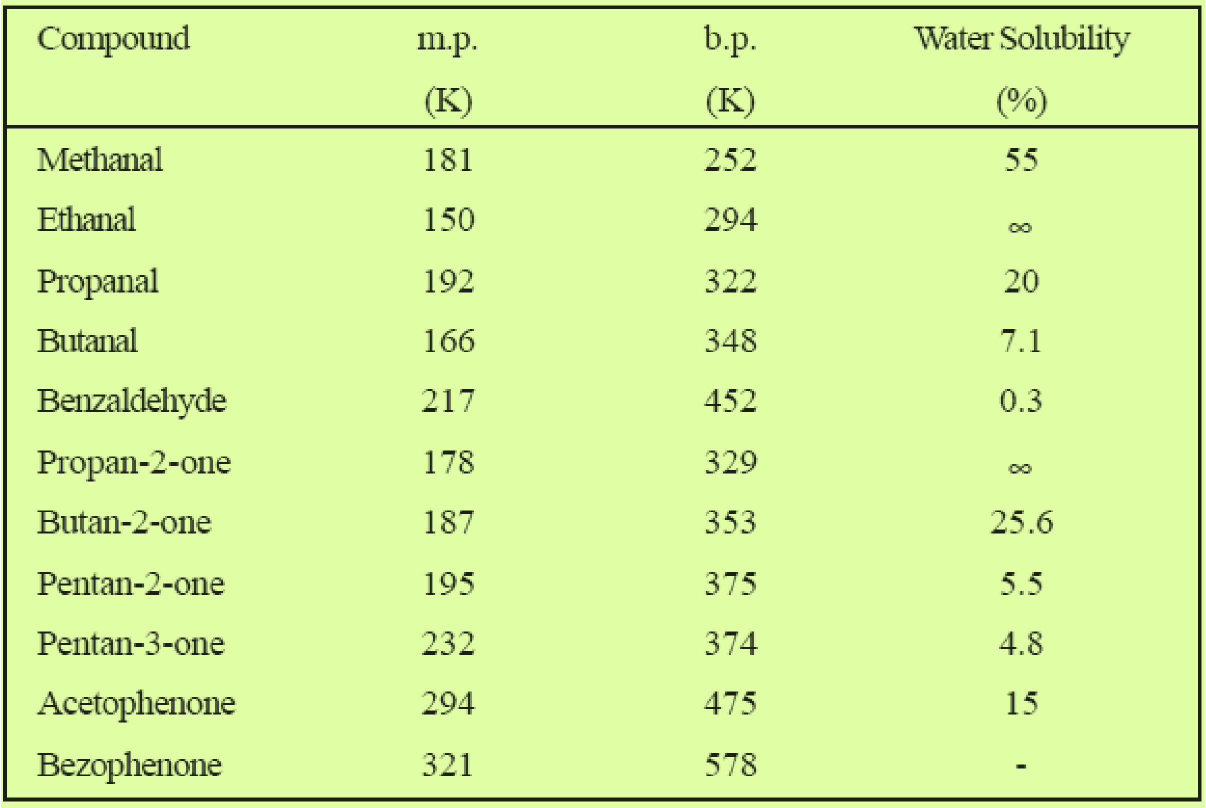


$$\left[>C=\ddot{O}: \longleftrightarrow >\overset{+}{C}-\ddot{\underset{..}{O}}^{-} \right] \text{ or } >\overset{\delta^{+}}{C}=\ddot{O}^{\delta^{-}}$$

`The oxygen atom, thus, acquires a partial negative charge (δ-) whereas the carbon atom gets a partial positive charge (δ+). This polar nature of the carbonyl group makes the oxygen atom nucleophilic and basic while the carbon atom becomes electrophilic. The physical properties and chemical reactions of aldehydes and ketones are a direct consequence of this polarisation.

The dipole-dipole attraction between the molecules of aldehydes and ketones results in their higher boiling points as compared to the hydrocarbons of similar molecular weight. The physical properties of some aldehydes and ketones are given in Table 29.1.

Table 29.1 Physical properties of some representative aldehydes and ketones



Compound	m.p. (K)	b.p. (K)	Water Solubility (%)
Methanal	181	252	55
Ethanal	150	294	∞
Propanal	192	322	20
Butanal	166	348	7.1
Benzaldehyde	217	452	0.3
Propan-2-one	178	329	∞
Butan-2-one	187	353	25.6
Pentan-2-one	195	375	5.5
Pentan-3-one	232	374	4.8
Acetophenone	294	475	15
Bezophenone	321	578	-

You can see from Table 29.1 that these compounds have appreciable water solubility. This is because of the hydrogen bonding possible between the oxygen atom of the aldehyde (or the ketone) with hydrogen atom of water molecule, as shown in Fig 29.2.

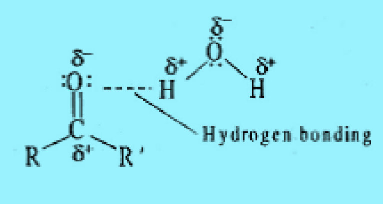
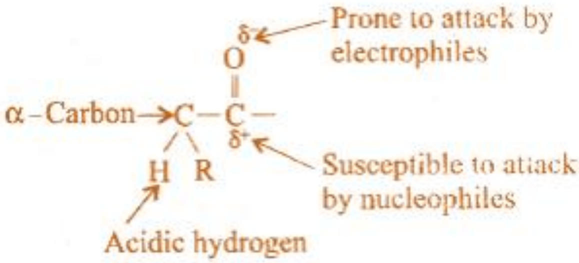


Fig. 29.2 : Hydrogen bonding between carbonyl compound and water molecule

29.1.4 Reactions of Aldehydes and Ketones

If you examine the structure of a molecule of the carbonyl compound, you will find that there are three centres of reactivity in it as shown below:



Since the oxygen atom is *nucleophilic* in nature, it is attacked by the *electrophiles*, whereas the carbonyl carbon is *electrophilic* in nature and hence is attacked by *nucleophiles*. The third site of reactivity is hydrogen atom present at the α-carbon atom. It is *acidic* in nature and gives typical reactions of carbanion which you will study in this section.

It is also important to know here that aldehydes are more reactive than ketones. This is because of the following two reasons:

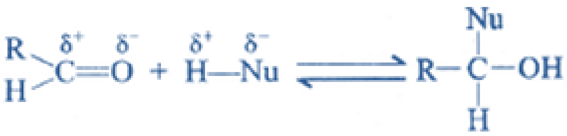
(i) Aldehydes have only one alkyl group whereas ketones have two. Since the alkyl groups are electron donating in nature, the carbonyl carbon in ketones which is bonded to two alkyl groups is less positive (electrophilic) as compared to the aldehydic carbonyl carbon. Hence, it is less susceptible to attack by nucleophiles.

(ii) The two alkyl groups in ketones also make the carbonyl carbon more crowded as compared to carbonyl carbon in aldehydes. This factor also makes the aldehydic carbonyl carbon more accessible for attack by the nucleophiles as compared to carbonyl carbon of the ketone.

With this background in mind, let us now study the reactions of aldehydes and ketones.

A. Nucleophilic Addition Reactions

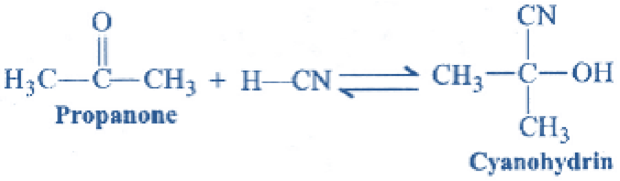
The general reaction of addition of nucleophiles on the carbonyl group can be represented as follows:



Some specific reactions of this category are discussed below :

1. Formation of Cyanohydrins

Carbonyl compounds react with hydrogen cyanide to yield *cyanohydrins*.



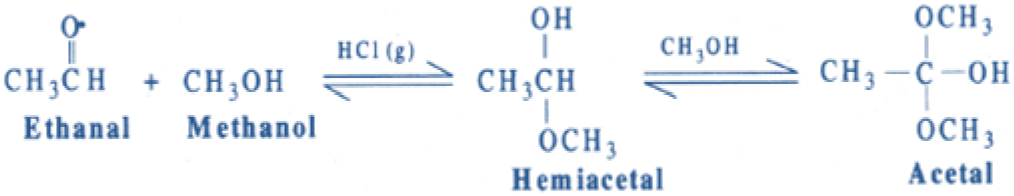
Note that one more carbon atom is present in the cyanohydrin as compared to the starting carbonyl compound.

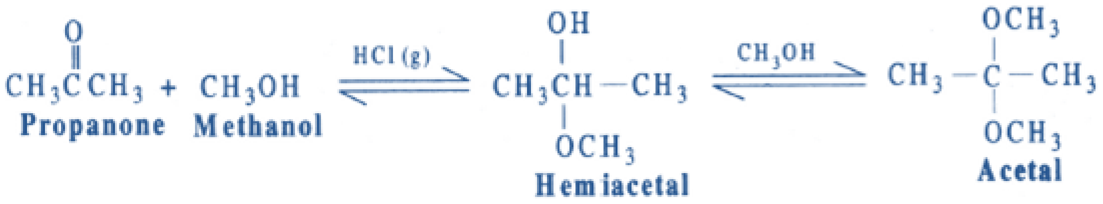
Cyanohydrins are useful in the synthesis of carboxylic acids about it you will study in the next section.

2. Formation of Hemiacetals

Aldehydes and ketones react with alcohols to give *hemiacetals*. *Hemi* in Greek means *half*. Hemiacetals have an -OH and an -OR group attached to the same carbon atom in their molecules.

When an excess of the alcohol is used, a second molecule of the alcohol reacts to give an acetal.





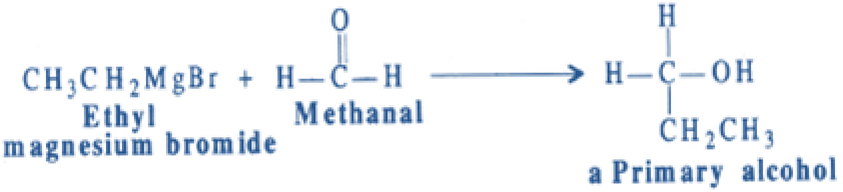
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + CH_3OH \overset{HCl(g)}{\rightleftharpoons} CH_3\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}H}-CH_3 \overset{CH_3OH}{\rightleftharpoons} CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_3$$

Note that an acetal has two -OR groups attached to the same carbon atom.

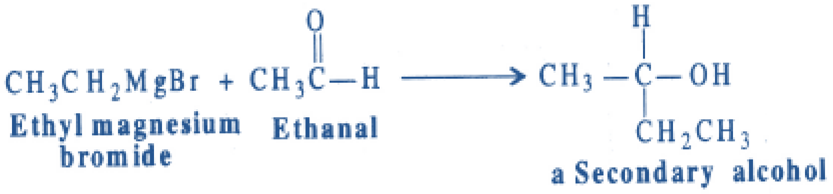
Acetals are stable in basic solutions and are ‘therefore’ used as protecting groups for aldehydes and ketones. Acetals can be converted back to the carbonyl compounds by treating them with dilute acids because of the reversible nature of the above reaction.

3. Formation of Alcohols

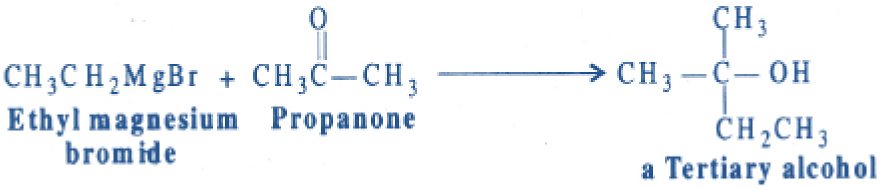
Grignard reagents (RMgX) react with aldehydes and ketones to give alcohols as shown below:



$$CH_3CH_2MgBr + H-\overset{\overset{O}{\|}}{C}-H \longrightarrow H-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OH$$



$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-H \longrightarrow CH_3-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OH$$



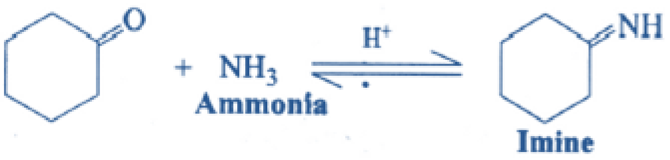
$$CH_3CH_2MgBr + CH_3\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

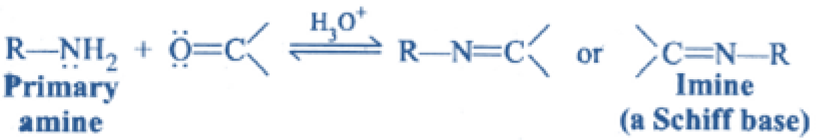
You have already studied these reactions under the preparation of alcohols in lesson 28.

B. Addition-Elimination or Condensation Reactions

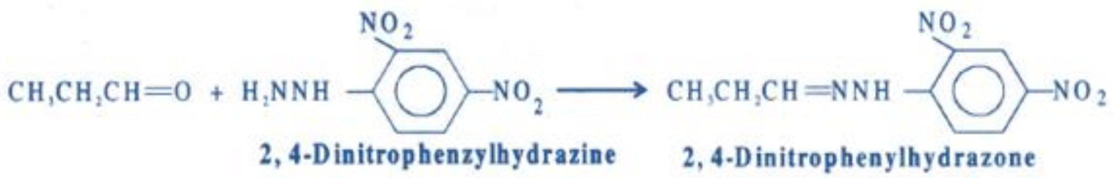
1. Reaction with Ammonia and its Derivatives

Aldehydes and ketones react with ammonia and primary amines to give imines which are compounds having carbon-nitrogen double bond.





It appears that during the above reaction a molecule of water is lost from the primary amine and the carbonyl compound. The reactions with other derivatives of ammonia are given below:



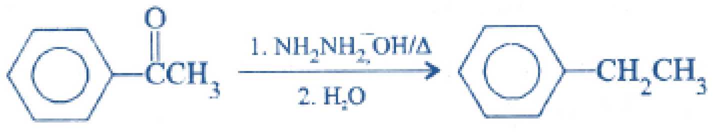
The compounds formed above are relatively insoluble solids and have characteristic melting points. These compounds can be prepared for the unknown aldehyde or ketone and their melting points can be determined. These melting points are matched with the derivatives of already known aldehydes and ketones listed in standard tables and the carbonyl compound is thus identified.

C. De-oxygenation Reactions

De-oxygenation reactions are reactions involving removal of oxygen. Aldehydes and ketones can be reduced to the corresponding alkanes by the following two reactions:

1. Wolff - Kishner Reduction

When an aldehyde or a ketone is heated in a basic solution of hydrazine in a high-boiling alcohol, then the carbonyl group gets converted to a methylene (>CH_2) group.



Ethylbenzene

2. Clemmensen Reduction

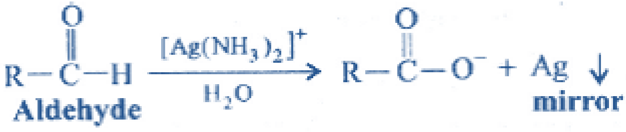
It is carried out in acidic medium using amalgamated zinc and hydrochloric acid.

$$CH_3(CH_2)_5CHO \xrightarrow[HCl,\ H_2O]{Zn(Hg)} CH_3(CH_2)_5-CH_3$$

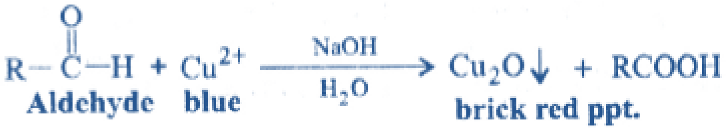
Heptanal **Heptane**

D. Oxidation of Aldehydes

Unlike ketones, aldehydes can be easily oxidised to carboxylic acids using a variety of oxidising agents. These reagents can be chromic acid, chromium trioxide, permanaganate or silver oxide. You have already read about oxidation with some of these reagents. *Silver ions selectively oxidise -CHO group*. This forms the basis of *Tollen's test*. It involves the addition of a mixture of aqueous silver nitrate and aqueous ammonia which is known as *Tollen's reagent* to the carbonyl compound. Tollen's reagent contains $[Ag(NH_3)_2]^+$ complex ion. If an aldehyde is present, it gets oxidised to the carboxylic acid whereas the Ag^+ ions are reduced to form silver metal which gets deposited on the walls of the test tube and this gives a mirror like shining appearance.

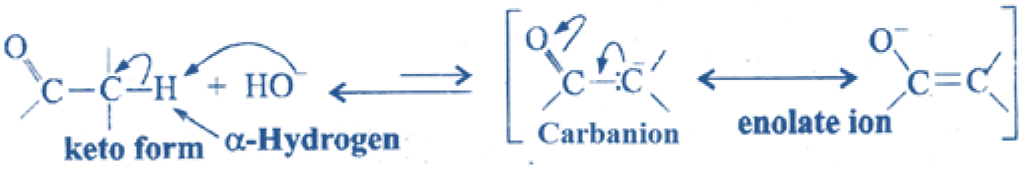


Aldehydes are also oxidised by Fehling solution, which contain Cu^{2+} (cupric) ions complexed with tartarate ions as the oxidant. These Cu^{2+} ions are reduced by the aldehydes in alkaline medium to give a brick red precipitate of cuprous oxide.

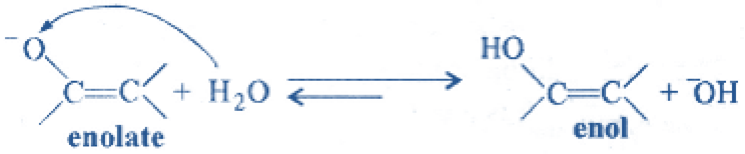


E. Reactions at α - carbon

The α- hydrogen in aldehydes and ketones is quite acidic and can be easily abstracted by a strong base.



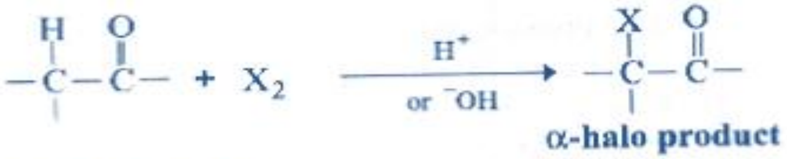
The resulting anion can stabilise by resonance as shown above. It is called an *enolate ion*. On protonation, it gives an *enol*.



Thus, keto form and enol form are in equilibrium. This is also known as *keto-enol tautomerism*. Other reactions feasible due to the presence of a. hydrogen are as follows:

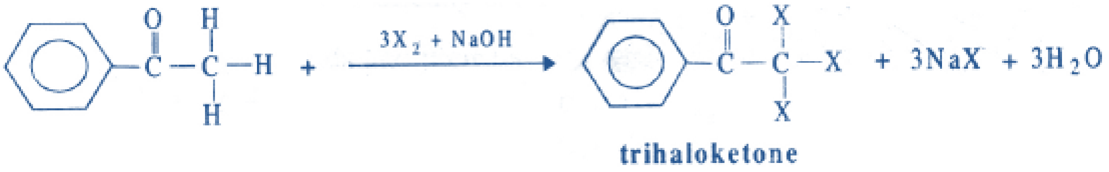
1. Halogenation

Ketones having α-hydrogen-atom react readily with halogens and α-haloketones are obtained as the product. The reaction is promoted both by acids and bases.

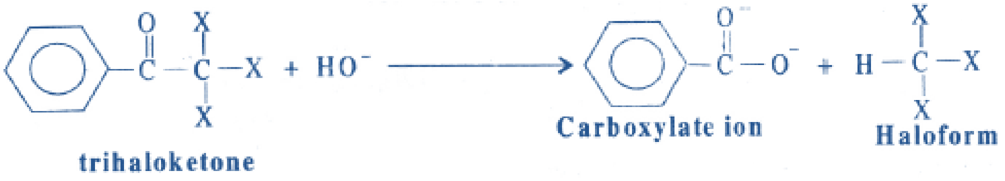


$(X_2 = Cl_2, Br_2 \text{ or } I_2)$

In presence of the base, multiple halogenation occurs to give the trihalo product.



The trihalo group is a good leaving group and the trihalo ketone reacts with OH- which finally gives a carboxylate ion and a haloform.

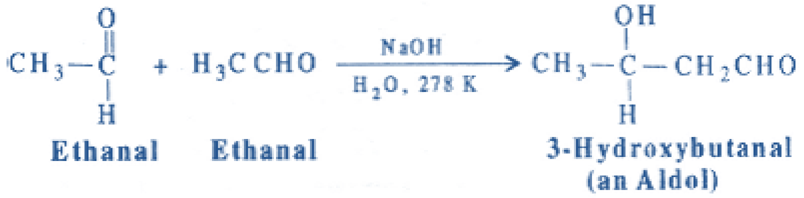


This reaction is called the *halform reaction* after the name of the product.

If iodine is used as the halogen, then we get *iodoform* (CHI_3) as the product. The iodoform is a bright yellow solid having a characters tic melting point. This reaction, thus, forms the basis of the *iodoform test*. Thus, methyl ketones give a positive iodoform test. You had studied the iodoform formation in lesson 27 also.

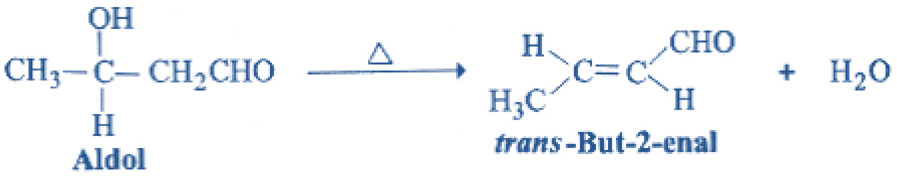
2. Aldol Condensation

Aldehydes having - hydrogen atom on reaction with dil. NaOH give aldols. The reaction is illustrated below by using ethanal as the example.



$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_3CCHO \xrightarrow[H_2O,\ 278\ K]{NaOH} CH_3-\overset{OH}{\underset{H}{C}}-CH_2CHO$$

Note that the product contains both the *aldehyde* and the *alcohol* functional groups and therefore, it is called an *aldol*, The aldol addition product on heating undergoes dehydration to give an , α,β-unsaturated aldehyde which is a condensation product.



This complete sequence of reactions is called *aldol condensation*.

Aldol condensation is also possible with ketones, Can you now think of a little more complex situation? What will be the products of aldol condensation when two different aldehydes having α-hydrogen atoms are used as reactants? In this case, the reaction is called a *crossed-aldol condensation*. This is left as an exercise for you. There is a hint of course. Suppose the two aldehyde molecules are represented by A and B; then condensation can occur between two molecules of the same aldehyde or different aldehydes. Thus, the products obtained would be the following types:

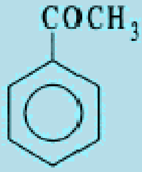
A-A, B-B, A-B and B-A.

With this background in mind, you can now proceed to write the aldol addition products of ethanal and propanal.

Intext Questions 29.1

1. Classify the following as aldehydes or ketones and give their IUPAC names:

(i) CH_3CHO (ii) $CH_3COCH_2CH_3$

(iii)  (iv) $OHCCH_2CH_3$

....

2. How will you prepare propanone from propyne ?

....

3. Why are aldehydes more reactive than ketones towards nucleophilic addition reactions?

....

4. Write the general structure for the following:

(i) cyanohydrin (ii) acetal (iii) hemiacetal

....

5. How can you convert the carbonyl (>C=O) group to (>CH_2) group?

....

6. What is an aldol?

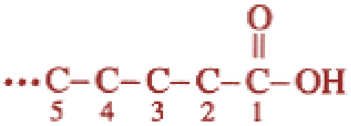
....

29.2 Carboxylic Acids

You already know that carboxylic acids contain a carboxyl (-COOH) functional group. They are most widely distributed in nature and are also industrially important chemicals. *Acetic acid* in the form of vinegar is produced in large quantities. It is also a very important building block in complex biological molecules. You must have also heard about *fatty acids* which are long chain aliphatic acids derived from the hydrolysis of fats and oils. Stearic acid is a fatty acid containing a long chain of eighteen carbon atoms.

29.2.1 Nomenclature

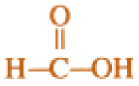
Several carboxylic acids have been known since long and their common names are based on their sources. However, in the IUPAC nomenclature, carboxylic acids are named by choosing the longest carbon chain containing the -COOH group. The final **-e** in the name of the alkane is replaced by -*oic acid*. While numbering the carbon chain, the -COOH carbon is always given number 1 as shown below:



$$\cdots\underset{5}{C}-\underset{4}{C}-\underset{3}{C}-\underset{2}{C}-\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

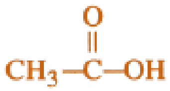
The other groups and substituents are numbered and named according to the usual rules of nomenclature which you have already studied.

Some common carboxylic acids and their names are given below:



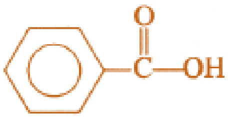
$$H-\overset{O}{\overset{\|}{C}}-OH$$

Methanoic acid
(Formic acid)



$$CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Ethanoic acid
(Acetic acid)



Phenylmethanoic acid
(Benzoic acid)

Carboxylic acids containing two carboxyl groups are called **dicarboxylic acids**. They are named by adding **dioic acid** as a suffix to the name of the corresponding hydrocarbon. Both the carboxyl carbon atoms are numbered as a part of the main chain. Note that in this case, final- *e* of the alkane is not dropped.

$$HO\underset{1}{\overset{O}{\overset{\|}{C}}}\underset{2}{\overset{O}{\overset{\|}{C}}}OH$$

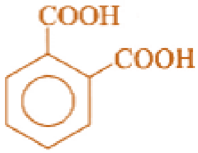
Ethanedioic acid
(Oxalic acid)

$$HO\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OH$$

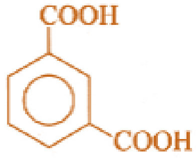
Propanedioic acid
(Malonic acid)

$$HOO\overset{4}{C}\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$$

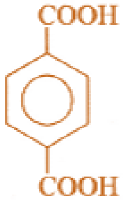
Butane-1,4-dioic acid
(Succinic acid)



***o*-Phthalic acid**
(Phthalic acid)



***m*-Phthalic acid**
(Isophthalic acid)



***p*-Phthalic acid**
(Terephthalic acid)

29.2.2 Preparation of Carboxylic Acids

The following methods are generally used for the synthesis of carboxylic acids. You have already studied some of these methods in the earlier lessons.

1. Oxidation of Alkenes

Alkenes on oxidation with hot alkaline $KMnO_4$ yield carboxylic acids.

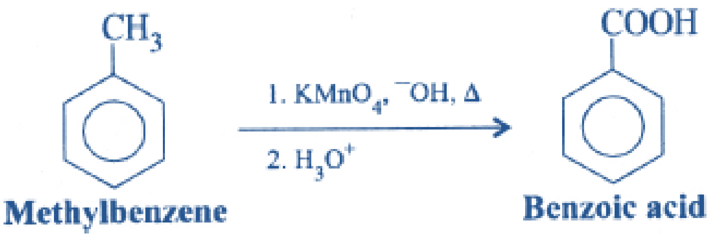
$$RCH{=}CHR' \xrightarrow[2.\,H_3O^+]{1.\,KMnO_4,\ ^-OH} RCOOH + R'COOH$$

2. Oxidation of Alcohols and Aldehydes

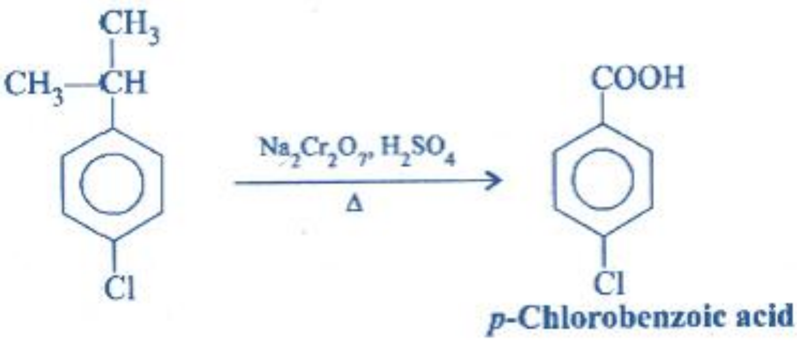
You have read in the last lesson and the previous section of this lesson that alcohols and aldehydes can be oxidized to carboxylic acids using a variety of oxidising agent. You can refer back to the details of these reactions.

3. Oxidation of Alkylbenzenes

Primary and secondary alkyl groups attached to the benzene ring can be oxidised, using alkaline $KMnO_4$ to the carboxyl group.

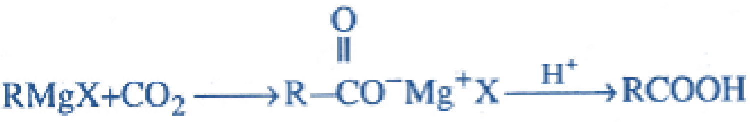


Acidified sodium dichromate can also be used for this oxidation.



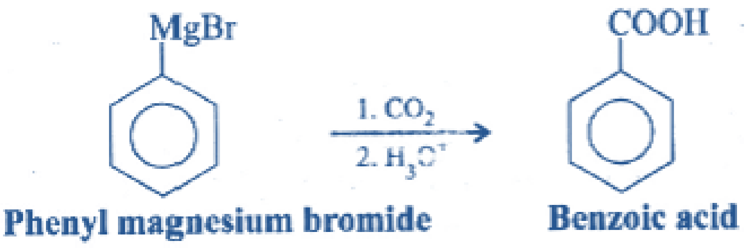
4. Carbonation of Grignard Reagents

Grignard reagents (RMgX) react with carbon dioxide to give magnesium carboxylates which on acidification yield carboxylic acids.



$$\mathrm{RMgX + CO_2 \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}O^{-}Mg^{+}X \xrightarrow{H^+} RCOOH}$$

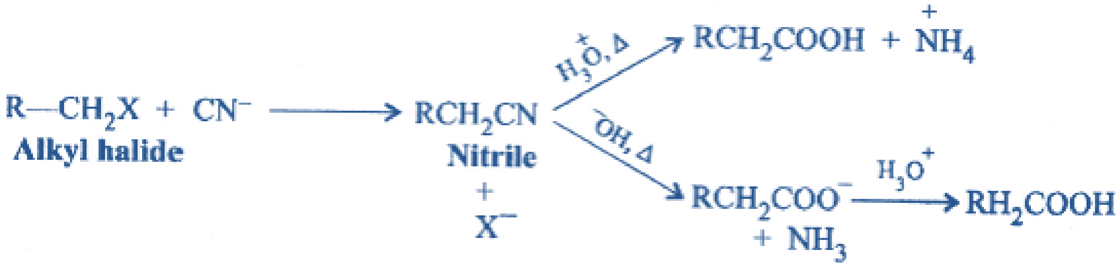
$$\underset{\substack{\textbf{Chloroethane}\\\textbf{(an alkyl halide)}}}{CH_3CH_2Cl} \xrightarrow[Et_2O]{Mg} \underset{\textbf{Grignard reagent}}{CH_3CH_2MgCl} \xrightarrow[2\text{-}H_3O^+]{1\text{-}CO_2} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$



Note that there is an increase of one carbon atom in the carboxylic acid as compared to the starting alkyl halide.

5. Hydrolysis of Nitriles and Cyanohydrins

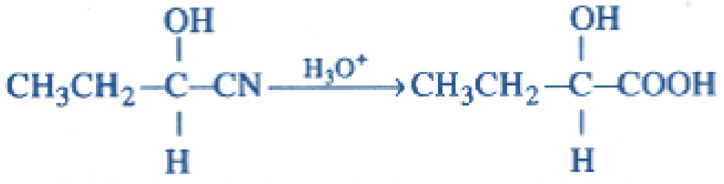
Alkyl halides can be converted to *nitriles* which on hydrolysis yield carboxylic acids having *one more carbon atom than the starting alkyl halide*.



$$Br\text{-}CH_2CH_2\text{-}Br \xrightarrow{NaCN} NC\text{-}CH_2CH_2\text{-}CN \xrightarrow{H_3O^+} HOOCCH_2CH_2COOH$$

1,2-Dibromoethane Butanedinitrile Butanedioicacld

Cyanohydrins obtained from aldehydes also yield 2-hydroxycarboxylic acids on hydrolysis.



$$CH_3CH_2\text{—}\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}\text{—}CN \xrightarrow{H_3O^+} CH_3CH_2\text{—}\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}\text{—}COOH$$

2-Hydroxybutanenitrile **2-Hydroxybutanoicacid**

29.2.3 Structure and Physical Properties

Similar to the aldehydes and ketones, the carboxyl carbon atom is sp^2 hybridised. Thus, the three atoms attached to this carbon which lie in the same plane with an approximate bond angle of 120° between them, see Fig. 29.3.

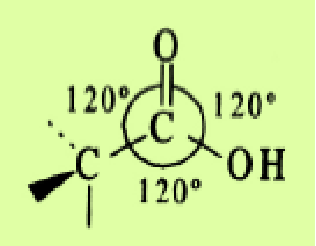
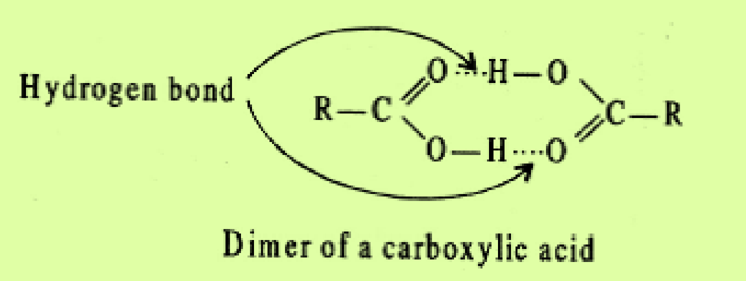


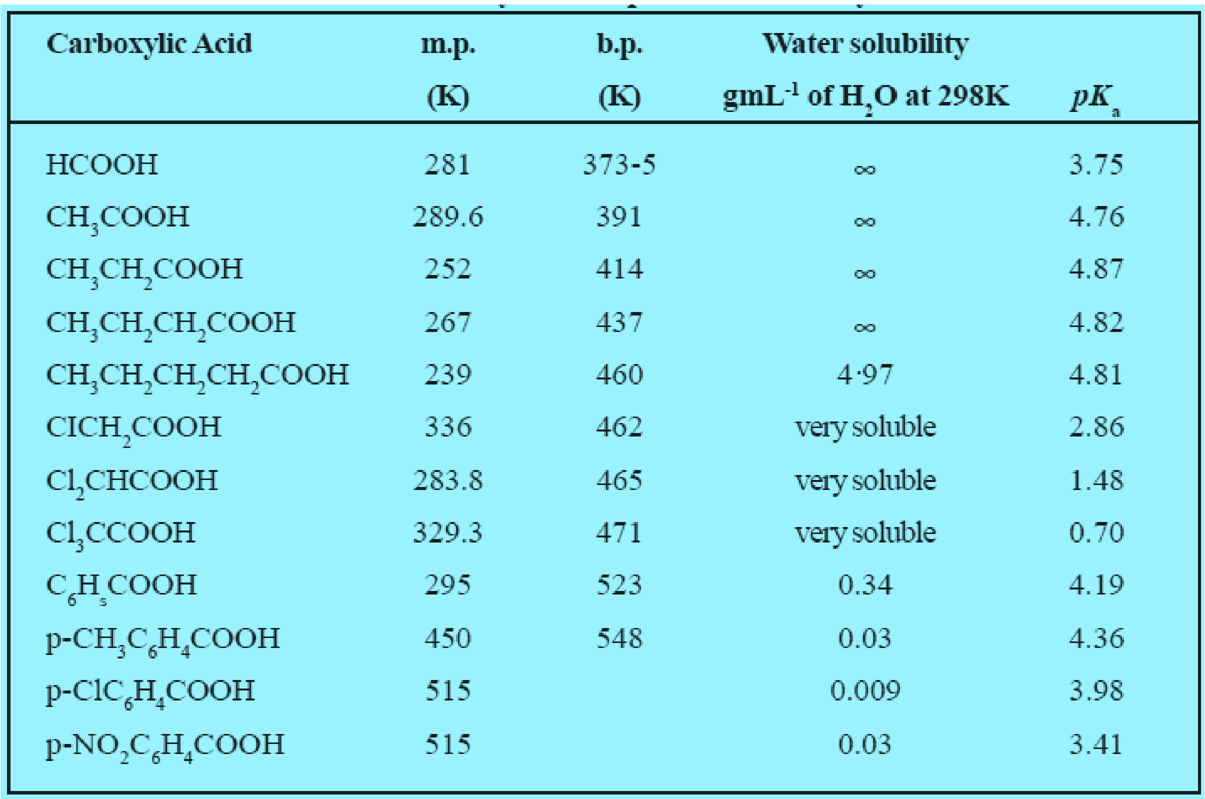
Fig. 29.3 : Structure of the carboxyl group

Carboxylic acids form hydrogen bonds because of the presence of polar carbonyl and hydroxyl groups. Most carboxylic acids exist in dimeric form in which two carboxylic acid molecules are held together by two hydrogen bonds. This is shown below :



Intermolecular hydrogen bonding is in fact responsible for high melting and boiling points of carboxylic acids. The melting and boiling points of some carboxylic acids are listed in Table 29.2. You can also see in the table that the lower members have appreciable solubility in water. This is due to the presence of hydrogen bonding between the carboxylic acid molecule and solvent water molecules.

Table 29.2 : Some Physical Properties of Carboxylic Acids

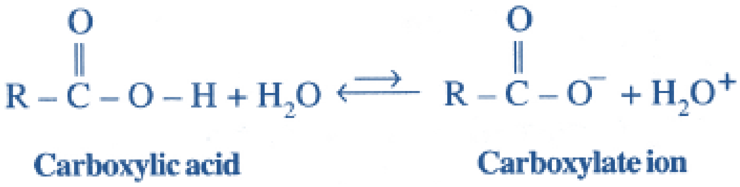


Carboxylic Acid	m.p. (K)	b.p. (K)	Water solubility gmL^{-1} of H_2O at 298K	pK_a
HCOOH	281	373-5	∞	3.75
CH_3COOH	289.6	391	∞	4.76
CH_3CH_2COOH	252	414	∞	4.87
$CH_3CH_2CH_2COOH$	267	437	∞	4.82
$CH_3CH_2CH_2CH_2COOH$	239	460	4·97	4.81
$ClCH_2COOH$	336	462	very soluble	2.86
$Cl_2CHCOOH$	283.8	465	very soluble	1.48
Cl_3CCOOH	329.3	471	very soluble	0.70
C_6H_5COOH	295	523	0.34	4.19
p-$CH_3C_6H_4COOH$	450	548	0.03	4.36
p-ClC_6H_4COOH	515		0.009	3.98
p-$NO_2C_6H_4COOH$	515		0.03	3.41

Do not worry about the pK_a values listed in the last column of the table. We will refer to them when we discuss the acidic nature of carboxylic acids in the following section.

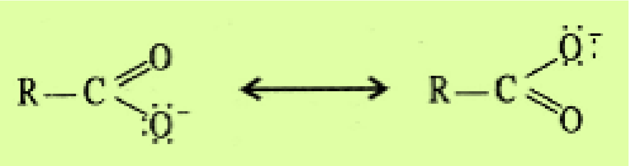
29.2.4 Acidity of Carboxylic Acids

Carboxylic acids are acidic in nature. They dissociate in water according to following equilibrium to give a proton and the carboxylate ion.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

The pKa values of some carboxylic acids are given in the last column of Table 29.2. Remember that the ***lower pKa indicates greater acidity*.** If you compare these pKa value with those of alcohols, you will note that the carboxylic acids are much more acidic than alcohols. This can be explained on the basis of the anion formed as a result of ionisation. The carboxylate ion obtained by the dissociation of carboxylic acids can be represented as a resonance hybrid of the following two structures :



Resonance structures of Carboxylate Ion

These structures show that the negative charge is delocalised over two oxygen atoms. Thus, the carboxylate ion gets stabilised. The greater stability of carboxylate ion facilitates the release of proton from the -COOH group.

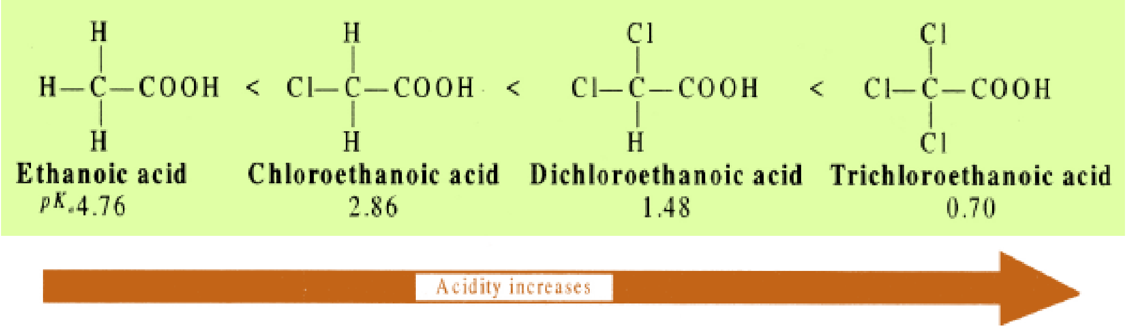
If you compare this situation with the alkoxide ion (RO-) obtained by the dissociation of an alcohol molecule, you will see that no such resonance stabilisation is possible in the alkoxide Ion.

Let us now analyse the acid strength of different acids and correlate them with their structure. If we examine the first five acids listed in table 29.2, we find that their *pKa* values keep on increasing which means that as we go down, their acid strength decreases.

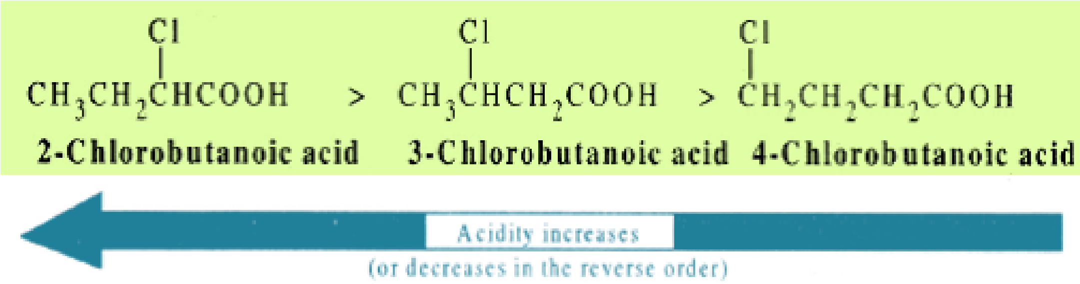
Since the alkyl groups are electron releasing in nature, they make the release of H^+ difficult and hence decrease the acidity. Thus, ethanoic acid is less acidic than methanoic acid. Therefore, we can say that **the electron-donating substitutents decrease the acidity of carboxylic acids**.

Let us next see what will be the effect of electron withdrawing substituents such as halogens and nitro-group on the acidity. The comparison of pK_a values of ethanoic acid (4.76) and chloroethanoic acid (2.86) suggests that chloroethanoic acid is a stronger acid than ethanoic acid. The chloro substituent has -I effect and pulls the electrons towards itself which facilitates the release of H+ ions.

You can also see below that as the number of halogen groups increases in the carboxylic acid, its acidity increases. This is because they make the release of H+ ion more and more easy.



Since the inductive effect decreases with increase in the distance of the group in the carbon chain, 2-chlorobutanoic acid (pK_a 2.86) is more acidic than 3-chlorobutanoic acid (pK_a 4.05) which is in turn more acidic than 4-chlorobutanoic acid (pK_a 4.50).

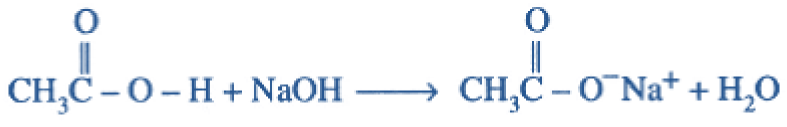


29.2.5 Reactions of Carboxylic Acids

Let us now study the reactions given by carboxylic acids.

1. Formation of Salts

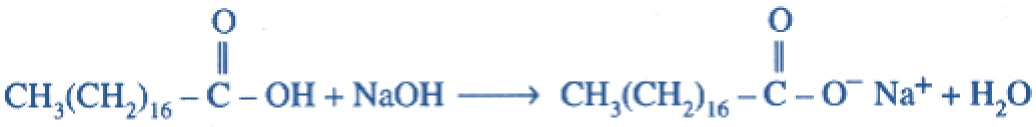
Carboxylic acids are completely deprotonated by strong bases such as metal hydroxides to give salts.



$$CH_3\overset{O}{\overset{\|}{C}}-O-H+NaOH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-O^-Na^++H_2O$$

Ethanoic acid **Sodium ethanoate**

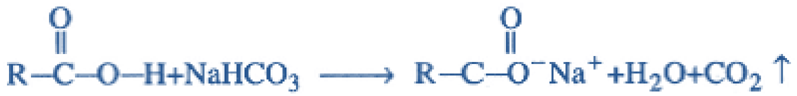
It will be interesting to know that soaps are sodium salts of long chain carboxylic acids which are called fatty acids.



$$CH_3(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-OH+NaOH \longrightarrow CH_3(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-O^-\ Na^++H_2O$$

Stearic acid **Sodium stearate (soap)**

Caboxylic acids are also deprotonated by the weak bases such as sodium bicarbonate. In this reaction, they form sodium salt of the acid, carbon dioxide and water.



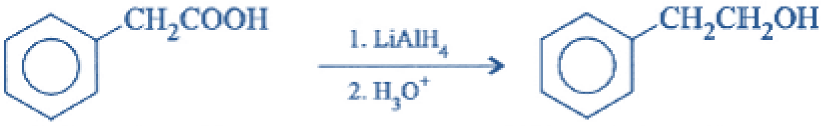
$$R-\overset{O}{\overset{\|}{C}}-O-H+NaHCO_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Na^++H_2O+CO_2\uparrow$$

This reaction is also used as a test for carboxylic acids in the laboratory. The liberation of CO in the form of bubbles on treatment with $NaHCO_3$ indicates a carboxyl functional group in the compound.

This test is not given by phenols since they are weaker acids than the carboxylic acids. Hence, the two categories of compounds can be distinguished on the basis of the above test.

2. Reduction of Carboxylic Acids

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride ($LiAlH_4$) .



Phenylethanoic acid **2-Phenylethanol**

3. Hell- Volhard-Zelinski Reaction

Similar to aldehydes and ketones, carboxylic acids undergo halogenation at α-carbon atom using Br_2(or Cl_2) in the presence of phosphorus or phosphorus trihalide.

$$CH_3CH_2CH_2COOH \xrightarrow[2\cdot H_2O]{1\cdot Br_2,P} CH_3CH_2\overset{Br}{\overset{|}{C}}HCOOH$$

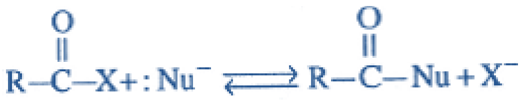
Butanoic acid **2 - Bromobutanoic acid**

α-Haloacids so obtained are useful intermediates in the synthesis of other organic compounds.

4. Synthesis of Acid Derivatives

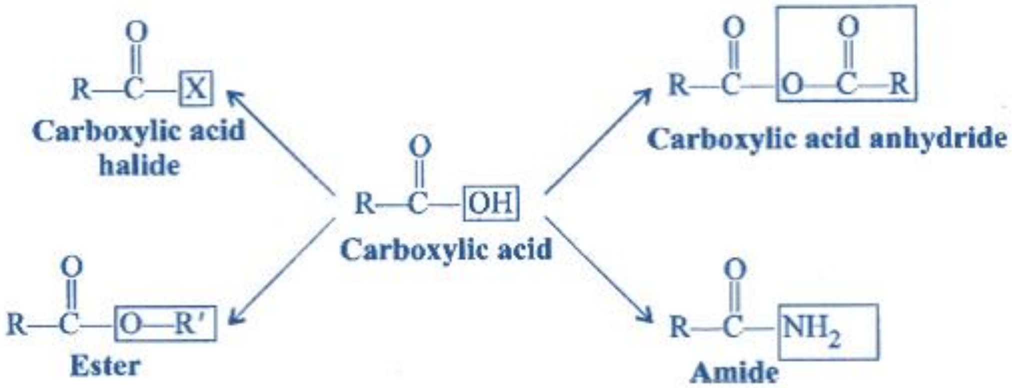
This is one of the very important reactions of carboxylic acids. The nucleophilic addition to the carboxyl carbon of the carboxylic acids is followed by elimination of the leaving group leading to a substitution product. If you remember the reactions of aldehydes and ketones, the addition of nucleophile is followed by addition of the proton to give an addition product.

In case of carboxylic acids, since the substitution takes place at the acyl carbon atom as shown below. It is also known as **nucleophilic acyl substitution.**



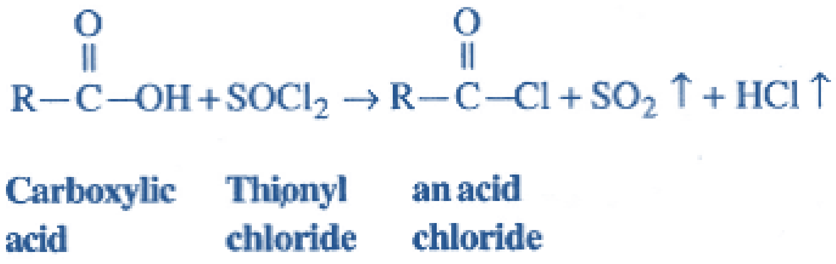
$$R-\overset{O}{\overset{\|}{C}}-X + :Nu^- \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-Nu + X^-$$

Here, X = OH in case of the carboxylic acids and Nu- can be a halide ion, $^-O-\overset{O}{\overset{\|}{C}}-R$, $^-O-R'$ or $^-NH_2$ group leading, respectively to **carboxyl acid halides**, **anhydrides, esters or amides** as the substitution products which are known as **derivatives of carboxylic acids** because they are derived from carboxylic acids.

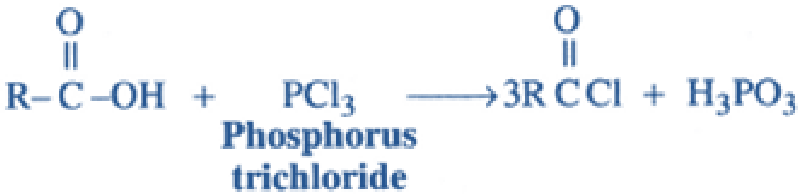


(i) Formation of Acid Chlorides

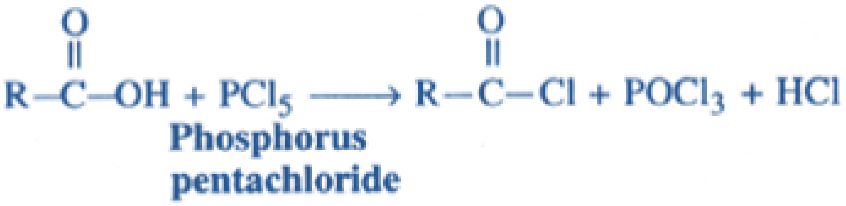
Carboxylic acids react with $SOCl_2$, PCl_3 or PCl_5 to give carboxylic acid chlorides also known as acyl chlorides, as shown below :



$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$$

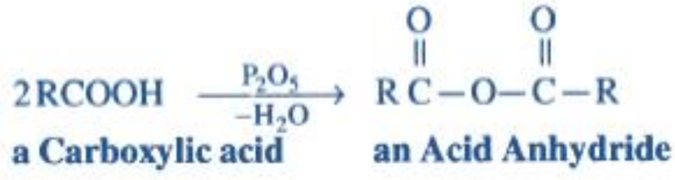


$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \longrightarrow 3R\overset{O}{\overset{\|}{C}}Cl + H_3PO_3$$

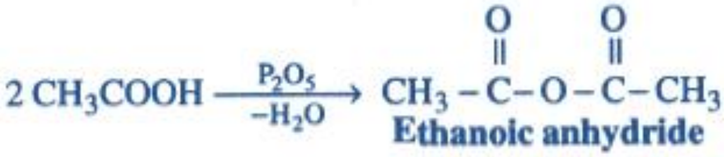


$$R-\overset{\overset{\large O}{\|}}{C}-OH + PCl_5 \longrightarrow R-\overset{\overset{\large O}{\|}}{C}-Cl + POCl_3 + HCl$$

(ii) Formation of Acid Anhydrides



$$2RCOOH \xrightarrow[-H_2O]{P_2O_5} R\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-R$$



$$2\,CH_3COOH \xrightarrow[-H_2O]{P_2O_5} CH_3-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_3$$

Since the carboxylic acid anhydrides are formally derived from carboxylic acids by loss of water, their names are derived from the corresponding acids by using the word *anhydride* in place of the acid. As the anhydride formed in the above reaction is derived from ethanoic acid, it is called ethanoic anhydride.

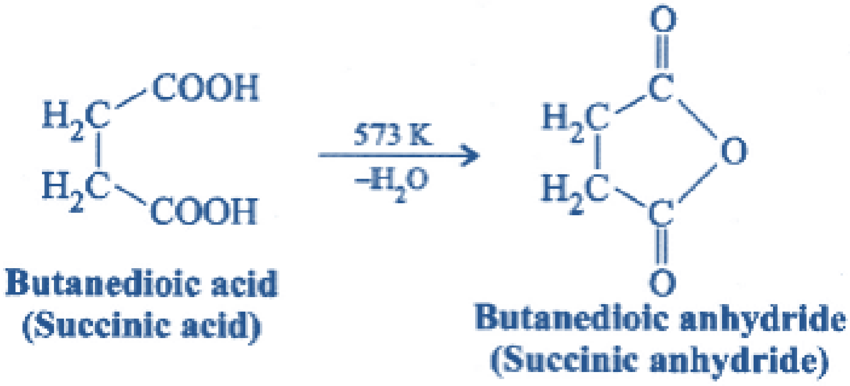
This method is used for the *preparation of symmetrical anhydrides*.

Carboxylic acid also react with acyl chlorides in the presence of pyridine to give carboxylic acid anhydrides.

$$CH_3CH_2CH_2\overset{\overset{\large O}{\|}}{C}OH + Cl\overset{\overset{\large O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow[\text{Pyridine}]{\Delta} CH_3CH_2CH_2\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_2CH_2CH_3$$

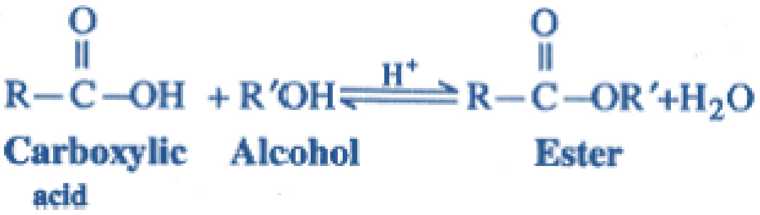
We can prepare unsymmetrical anhydrides by this method.

Cylic anhydrides are obtained by the dehydration of dicarboxylic acids at higher temperature.



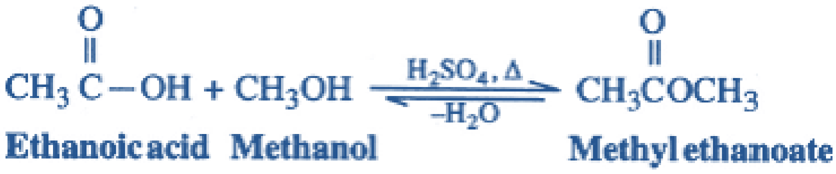
(iii) Formation of Esters

Carboxylic acids react with alcohols to form esters.



$$R-\overset{\overset{O}{\|}}{C}-OH + R'OH \xrightleftharpoons{H^+} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

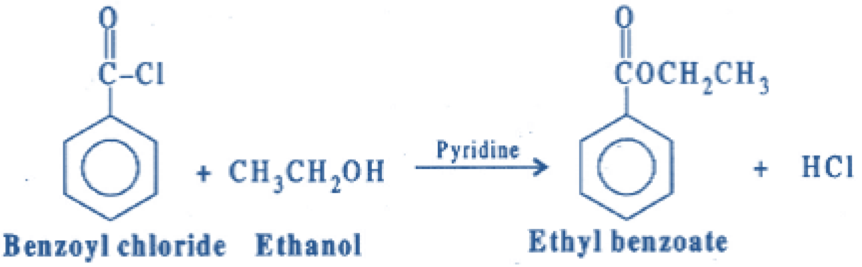
Note that the acid catalysed esterification is an equilibrium reaction. The equilibrium can be shifted to the right side towards products if we are able to remove water or the ester from the reaction mixture. Also if we use excess of one reagent, then the equilibrium shifts towards the right side to give the ester. Normally, we take excess of alcohol and use it as a solvent to carry out esterification.

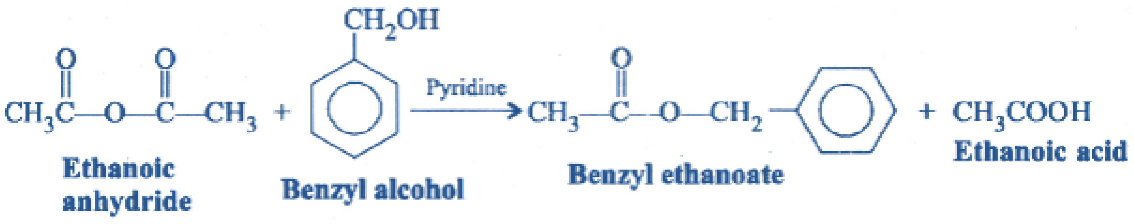


$$CH_3\overset{\overset{O}{\|}}{C}-OH + CH_3OH \xrightleftharpoons[-H_2O]{H_2SO_4,\ \Delta} CH_3\overset{\overset{O}{\|}}{C}OCH_3$$

Esters are named as **alkyl alkanoates**. The alkyl part comes from the alcohol while the alkanoate portion is derived from the carboxylic acid. Therefore, the above ester is called **methyl ethanoate** because it is obtained from *methyl alcohol and ethanoic acid*.

Esters can also be prepared by the reaction of acid chlorides or acids anhydrides with alcohols. Thus we can see that these acid derivatives can be converted to one-another.



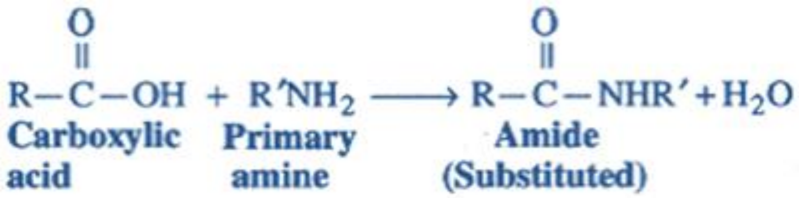


(iv) Formation of Amides

Carboxylic acids react with ammonia or amines to give amides. The reaction involves the formation of an ammonium carboxylate salt as an intermediate which on heating gives amide.

$$R-\overset{O}{\overset{\|}{C}}-OH + :NH_3 \rightleftharpoons R\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

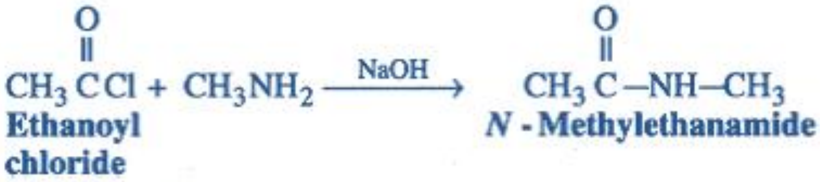
Carboxylic acid **Ammonium carboxylate** **Amide**



$$R-\overset{O}{\overset{\|}{C}}-OH + R'NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR' + H_2O$$

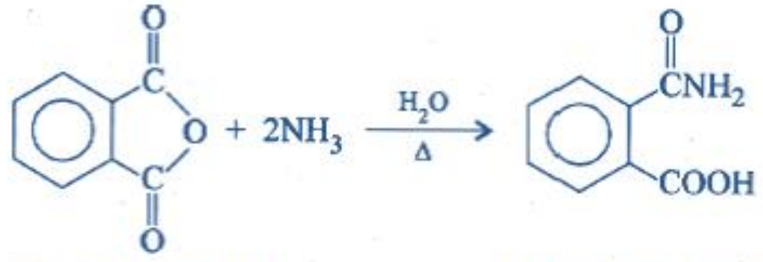
Carboxylic acid **Primary amine** **Amide (Substituted)**

Amides can also be obtained by the reaction of ammonia or amines with carboxylic acid halides, anhydrides and esters.



$$CH_3\overset{O}{\overset{\|}{C}}Cl + CH_3NH_2 \xrightarrow{NaOH} CH_3\overset{O}{\overset{\|}{C}}-NH-CH_3$$

Ethanoyl chloride ***N*-Methylethanamide**



Phthalic anhydride **Pnhthalamic acid**

$$ClCH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NH_3 \xrightarrow{273\text{-}278\,K} ClCH_2-\overset{O}{\overset{\|}{C}}-NH_2 + C_2H_5OH$$

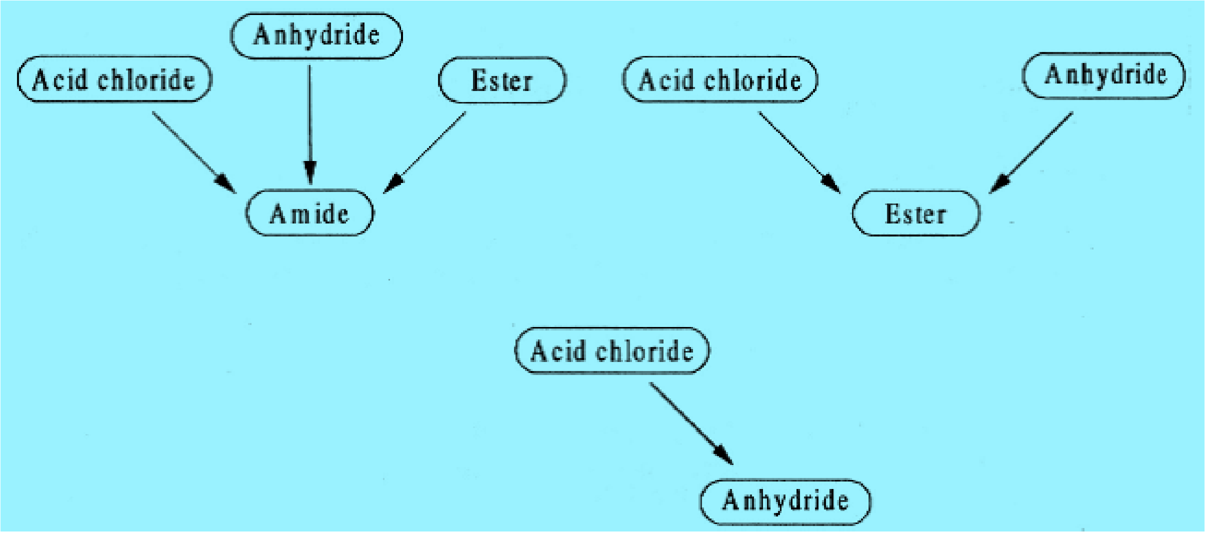
Ethyl chloroethanoate **Chloroethanamide** **Ethanol**

Thus, we can make one carboxylic acid derivative from another. Generally, the less reactive acid (acyl) derivatives can be prepared from the more reactive ones.
The order of reactivity of various carboxylic acid derivatives is as follows:

Acid chloride > Acid anhydride > Ester > Amide

Thus, acid chlorides are the most reactive ones whereas the amides are the least reactive.

Since the ***least reactive derivative can be prepared from the more reactive ones***, we can summarise which derivative can be prepared from which other one in the following way:



Of, course, *these derivatives can be synthesised from the carboxylic acids as well.*

Intext Questions 29.2

1. Match the following compounds given in column I and their classes given in column 11:

	Column I	**Column II**
(i)	CH_3COOH	(a) Carboxylic acid halide
(ii)	CH_3CONH_2	(b) Carboxylic acid
(ill)	CH_3COOCH_3	(c) Carboxylic acid anhydride
(iv)	CH_3COCl	(d) Carboxylic acid amide
(v)	$CH_3COOCOCH_2Cl$	(e) Ester

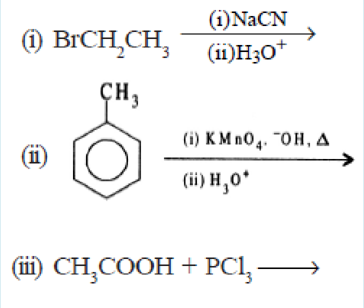
2. Arrange the following acids in the increasing order of their solubility in water:
   CH_3COOH, $CH_3(CH_2)_3COOH$, p-ClC_6H_4COOH

....

3. Which one of the following will be most acidic and why?
   Butanoic acid, 2-Chlorobutanoic acid, 3-Chlorobutanoic acid, 4-Chlorobutanoic acid

....

4. Give the products of the following reactions:



(i) $BrCH_2CH_3 \xrightarrow[\text{(ii)}H_3O^+]{\text{(i)}NaCN}$

(ii) $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4,\ ^-OH,\ \Delta}$

(iii) $CH_3COOH + PCl_3 \longrightarrow$

....

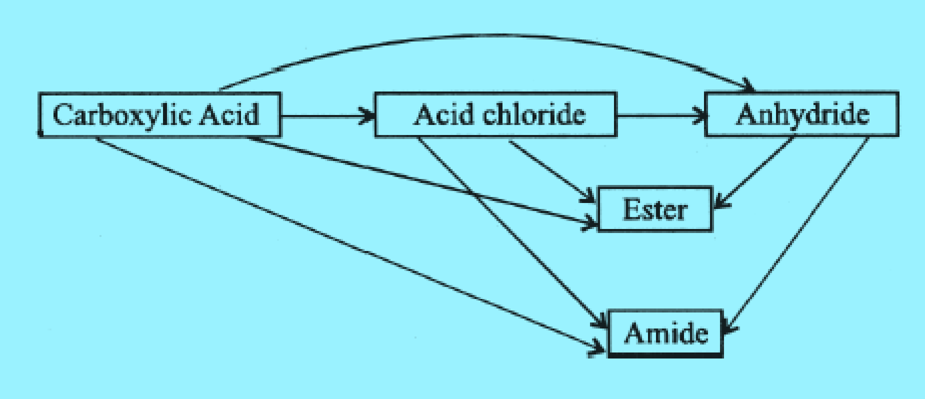
5. Why are carboxylic acids more acidic than alcohols?

....

What You Have Learnt

In this lesson, you have learnt that

- Aldehydes and ketones constitute the carbonyl compounds. Aldehydes are known as **alkanals**
- whereas ketones are called **alkanones**.
- Aldehydes and ketones can be prepared by oxidation of alcohols, ozonolysis of alkenes, hydration of alkynes and Friedel-Craft's acylation.
- Carbonyl group is polar in nature and carbonyl-carbon is susceptible to nucleophilic attack. Thus, aldehydes and ketones undergo nucleophilic addition reactions with many reagents. They also exhibit condensation reactions.
- Since the α-hydrogen is acidic in nature, aldehydes and ketones show specefic reactions at *a*- carbon atom such as halogenation and aldol condensation.
- Carboxylic acids are an important class of compounds.
- The methods of preparation of carboxylic acids being oxidation of alkenes, aldehydes and ketones and alkylbenzene, hydrolysis of nitriles and carbonation of Grignard reagents.
- The molecules of carboxylic acids show hydrogen bonding and can exist as dimers.
- Carboxylic acids are acidic in nature. Their acidity is affected by various factors including the nature of substituents attached to the carbon chain bearing the carboxylic group.
- Carboxylic acids form salts with strong bases such as metal hydroxides. They undergo halogenation at *a*-carbon atom and can be reduced to primary alcohols using $LiAlH_4$.
- Carboxylic acids gives rise to a number of carboxylic acid derivatives such as carboxylic acid halides, anhydrides, esters and amides by nucleophilic acyl substitution reactions. They can be prepared from one another as shown below :



Terminal Exercise

1) Write the structural formulae and IUPAC names of the compounds containing a carbonyl functional group and having the molecular formula C_3H_6O.
2) How can you prepare primary, secondary or tertiary alcohols using aldehydes or ketones?
3) What is Tollen's Test?
4) Explain keto-enol tautomerism.
5) What is haloform reaction?
6) How will you test a carboxylic acid in the laboratory ?
7) Which reagent can reduce a carboxylic acid to a primary alcohol ?

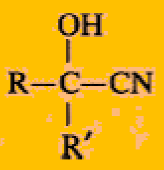
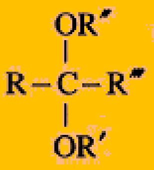
8) What are carboxylic acid anhydrides? Give their method of preparation from carboxylic acids.

9) Which carboxylic acid derivative is most reactive?

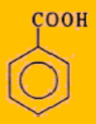
(a) Acid amide (b) Ester (c) Acid halide (d) Acid anhydride

Answers to Intext Questions

29.1

1. (i) aldehyde, Ethanal (ii) ketone, Butane-2-one
   (iii) ketone, I-Phenylethanone (iv) aldehyde, Propanal
2. Using hydration with Hg^{2+}, H^+.
3. Because they have one alkyl group whereas a ketone has two alkyl groups. Hence, the carbonyl carbon in aldehydes is more positive.
4. Also, the two alkyl groups lead to more crowding in ketones.
5. (i) 
$R-\overset{OH}{\underset{R'}{C}}-CN$
(ii) 
$R-\overset{OR''}{\underset{OR'}{C}}-R''$
(iii) 
$R-\overset{R'}{\underset{OH}{C}}-R''$
6. By Wolff- Kishner reduction or Clemmensen reduction.
7. The product formed by the condensation of two aldehyde molecules having α-hydrogen atom. Aldol contains both an aldehyde and an alcohol functional group.

29.2

1. (i). (b) (ii). (d) (ill). (e) (iv). (a) (v) e
2. p-$ClC_6H_4COOH < CH_3(CH_2)_3COOH < CH_3COOH$
3. 2-Chlorobutanoic acid, because of maximum **-I** effect of -el at 2 - position.
4. (i) $HOOCCH_2CH_3$, (ii) 

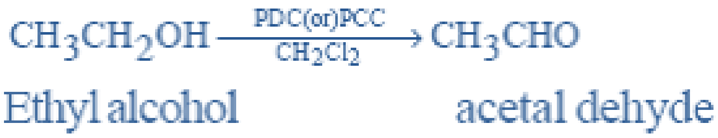
(iii) $3CH_3COCl + H_3PO_3$
5. Because of resonance stabilization of carboxylate anion. The alkoxide ion cannot stabilize by resonance.

29.1.2.a Methods of preparation of Carbonyl compounds:

Acetaldehyde and acetone preparations:

1) From alcohols:

Ethyl alcohol (1^0 alcohol) upon oxidation with pyridium dichromate (PDC) or pyridium chloro chromate (PCC) in anhydrous media like dichloro methane gives acetal dehyde. Isopropyl alcohol (2^0 alcohol) on oxidation with suitable oxidizing agent gives acetone.



$$CH_3CH_2OH \xrightarrow[CH_2Cl_2]{PDC(or)PCC} CH_3CHO$$

$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 \xrightarrow{PDC(or)PCC} CH_3-CO-CH_3$$

Iso propyl alcohol acetone

2) From alkenes (Wacker process):

When ethylene is passed through an acidified aqueous solution of $PdCl_2$, acetaldehyde is formed. Acetone is formed from propene by the same method.

$$CH_2=CH_2+PdCl_2+H_2O \xrightarrow[H^+]{CuCl_2} CH_3-CO-H+Pd+2\,HCl$$

Ethylene acetal dehyde

$$CH_3-CH=CH_2+PdCl_2+H_2O \xrightarrow[H^+]{CuCl_2} CH_3-CO-CH_3+Pd+2\,HCl$$

Propene acetone

3) From calcium salts of carboxylic acids:

Carbonyl compounds are formed when calcium salts of carboxylic acids are heated. Acebaldehyde is formed when the mixture of calcium formate and calcium acetate is heated. Acetone is formed when calcium acetate is heated.

$$Ca(HCOO)_2+Ca(CH_3COO)_2 \xrightarrow{\Delta} 2\,CH_3CHO+2\,CaCO_3$$

calcium formate calcium acetate Acebaldehyde

$$Ca(CH_3COO)_2 \xrightarrow{\Delta} 2\,CH_3COCH_3+CaCO_3$$

calcium acetate Acetone

4) Rosenmund reaction:

Ketones cannot be prepared with this method. Acetaldehyde is prepared by the reduction of acetyl chloride with hydrogen in the presence of palladium Catalyst supported on barium sulphate.

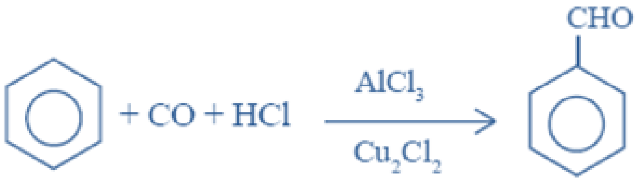
$$CH_3COCl+H_2 \xrightarrow{Pd-BaSO_4} CH_3CHO+HCl$$

Acetyl chloride acetal dehyde

Aromatic aldehyde (Benzaldehyde) preparation:

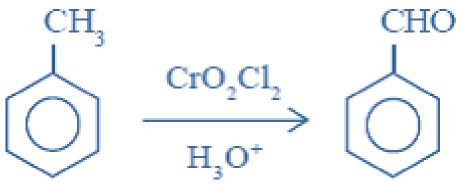
1. Gatterman – Koch reaction:

When benzene is treated with CO and HCl in the presence of anhydrous $AlCl_3$ and Cu_2Cl_3 benzaldehyde is formed.



2. Etard reaction:

When toluene is treated with chromyl chloride followed by hydrolysis benzaldehyde is formed.



29.1.2.a *Intext Questions:*

1. How will you prepare Acetone from propene?

……

2. What is Rosen mund reaction?

……

3. What is the product when methyl benzene with chromyl chloride?

……

29.1.2.a *Answers to Intext Questions:*

1. Acetone is formed when propene is treated with acidified $PdCl_2$ solution and $CuCl_2$.
2. Reduction of Acetyl Chloride in the presence of Pd–$BaSO_4$ gives acetaldehyde is Rosenmund reaction.
3. Benzaldehyde is formed when methyl benzene treated with chromyl chloride.

Chapter 30

COMPOUNDS OF CARBON CONTAINING NITROGEN

In the previous lesson, you have studied the chemistry of organic compounds containing oxygen atom as a part of the functional group. Now, you will learn about organic compounds containing nitrogen atom as a part of the functional group. An historical importance can be associated with these compounds as the first ever organic compound synthesised in the laboratory was urea which contains nitrogen. Nitrogen containing compounds have wide applications in our daily life. They form a part of dyes, drugs, fertilizers, alkaloids, proteins, etc. Only two classes of nitrogen containing compounds, viz. amines and nitro compounds are discussed in this lesson. First, the IUPAC nomenclature of amines has been explained followed by their preparation and chemical properties. The difference in the basicities of aliphatic and aromatic amines has also been described. Finally, the chemistry of nitro compounds is briefly discussed.

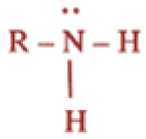
Objectives

After reading this lesson, you will be able to:

- classify amines as primary, secondary, or tertiary amines;
- write the IUPAC names of amines and nitro compounds;
- describe the general methods of preparation, properties and uses of primary amines and nitro compounds and
- explain the relative basicities of primary, secondary and tertiary aliphatic amines and compare them with the basicities of ammonia and aromatic amines.

30.1 Amines

Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified into three different types as primary (1^0), secondary (2^0) and tertiary (3^0) depending on the number of hydrogen atoms replaced by alkyl or aryl groups. In primary amines, only one alkyl or aryl group is attached to the nitrogen atom. In secondary amines, two alkyl or aryl groups are attached to the nitrogen while tertiary amines contain three alkyl or aryl groups attached to the nitrogen atom.
This is illustrated below.

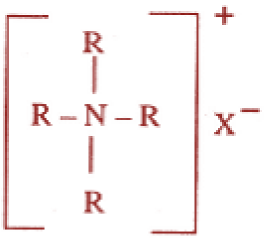


A primary amine

A secondary amine

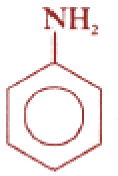
A tertiary amine

If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.



A quaternary ammonium salt

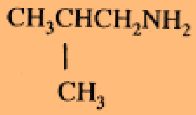
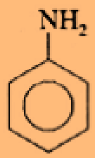
The amino group in aromatic amines is directly bonded to the benzene ring. Aromatic amines are aryl derivatives of ammonia. The parent aromatic amine is known as aniline.



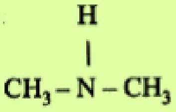
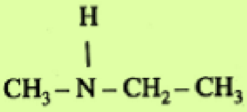
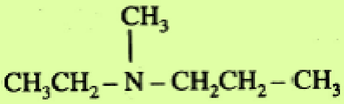
Aniline

30.1.1 IUPAC Nomenclature of Amines

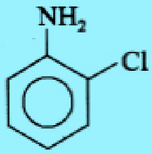
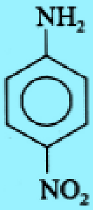
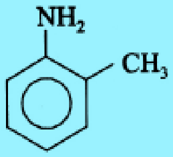
Similar to other classes of compounds which you have studied, amines can also be named according to the IUPAC system. In case of primary aliphatic amines, the longest continuous chain of carbon atoms determines the root name of the compound. The ending *-e* in the name of the corresponding alkane is changed to *-amine*. The other substituents along the carbon chain are given numbers. This is illustrated by the following examples.

Compounds	IUPAC name	Common name
CH_3NH_2	Methanamine	Methyl amine
$CH_3CH_2N_2$	Ethanamine	Ethyl amine
$CH_3CH_2CH_2NH_2$	Propan-l-amine	Propyl amine
 $CH_3\underset{\large CH_3}{\underset{\vert}{C}H}CH_2NH_2$	2-Methyl propan-I-amine	–
	Benzenamine	Aniline

Secondary and tertiary amines are named by using the prefix N for each substituent on the nitrogen atom.

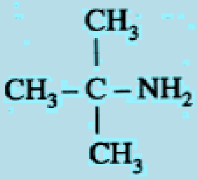
Compound	IUPAC name	Common name
 $CH_3-\overset{\overset{H}{\mid}}{N}-CH_3$	N-Methylmethanamine	Dimethylamine
 $CH_3-\overset{\overset{H}{\mid}}{N}-CH_2-CH_3$	N-Methylethanamine	Ethylmethylamine
 $CH_3CH_2-\overset{\overset{CH_3}{\mid}}{N}-CH_2CH_2-CH_3$	N-Ethyl-N-methylpropan-I-amine	-

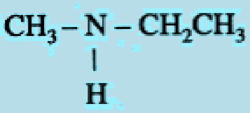
The IUPAC names of other aromatic amines are given as derivatives of aniline shown below:

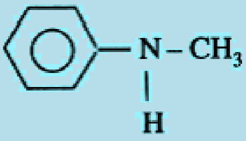
Compound	IUPAC name	Common name
	2-Chloroaniline	o-Chloroaniline
	4-Nitroaniline	*p*-Nitroaniline
	Methylaniline	*o*-Toluidine

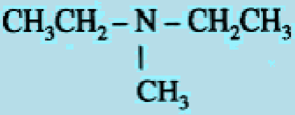
Intext Questions 30.1

1. Classify the following as primary, secondary, tertiary amines and quaternary ammonium salts :

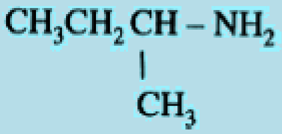
(i)  $CH_3-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-NH_2$

(ii)  $CH_3-\underset{\underset{H}{\mid}}{N}-CH_2CH_3$

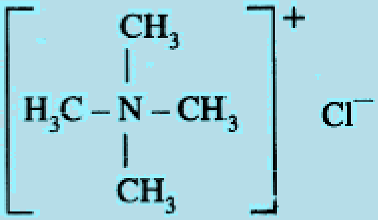
(iii) 

(iv)  $CH_3CH_2-\underset{\underset{CH_3}{\mid}}{N}-CH_2CH_3$

....

(v) 

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-NH_2$

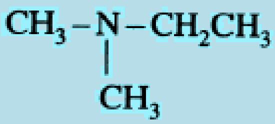
(vi) 

$\left[H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N}}}}-CH_3\right]^+ Cl^-$

....

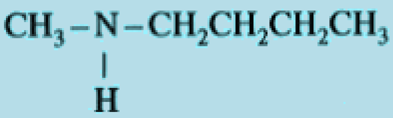
2. Write IUPAC names for the following amines :

(i) **CH_3 - $CH_2CH_2CH_2CH_3$**

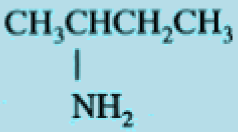
(ii) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2CH_3$

....

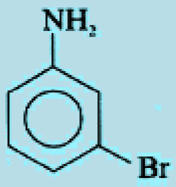
(iii) 

$CH_3-\underset{\displaystyle H}{\underset{|}{N}}-CH_2CH_2CH_2CH_3$

(iv) 

$CH_3\underset{\displaystyle NH_2}{\underset{|}{CH}}CH_2CH_3$

....

(v) 

(vi) 

....

30.1.2 Preparation of Amines

Several methods are available for the preparation of primary aliphatic and aromatic amines. In this section, you will learn some of the methods which are generally used for their preparation.

(i) From alkyl halides

Alkyl halides react with ammonia to form primary amines.

$$R-X+2NH_3 \longrightarrow R\,NH_2+NH_4X$$

The primary amine so formed may further react to give a secondary amine, tertiary amine or a quaternary ammonium salt. So in order to get good yield of the primary amine, the reaction is carried out using excess of ammonia. For example, bromoethane on reaction with excess of ammonia gives ethanamine.

$$\underset{\text{Bromoethane}}{C_2H_5Br+2\,NH_3} \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2}+NH_4Br$$

(ii) By reduction of nitriles (cyanides), am ides and nitro compounds

Compounds containing cyano, amido or nitro groups can be reduced into the corresponding primary amines.

Nitriles can be reduced by hydrogen in the presence of platinum catalyst or by sodium in presence of ethanol to corresponding primary amines, For example, propanenitrile (cyano ethane) on reduction gives propan-1-amine.

$$CH_3CH_2C \equiv N \xrightarrow[\text{or } Na/C_2H_5OH]{H_2/Pt} CH_3\,CH_2CH_2 - NH_2$$

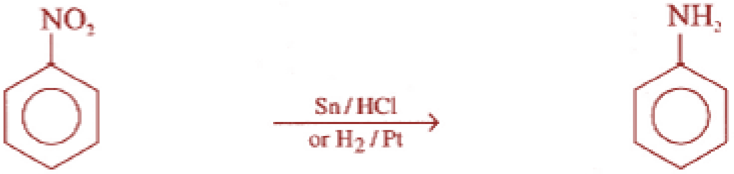
Propanenitrile Propan-1-amine

Similarly, amides are reduced by LiAlH4 to primary amines having same number of carbon atoms as in the starting amide. For example, ethanamide gives ethanamine on reduction.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2-NH_2$$

Ethanamide **Ethanamine**

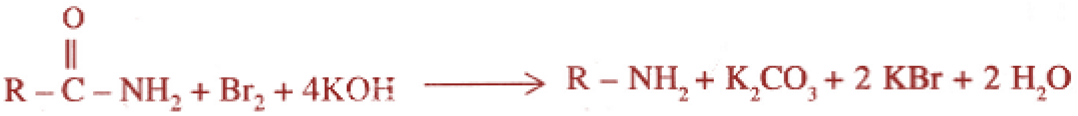
Reduction of nitro compounds can be carried out by using hydrochloric acid and a metal, such as Sn or Fe. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. Such a reduction of nitrobenzene by any of these methods provides aniline.



Nitrobenzene **Aniline**

(iii) *By Hofmann bromamide reaction*

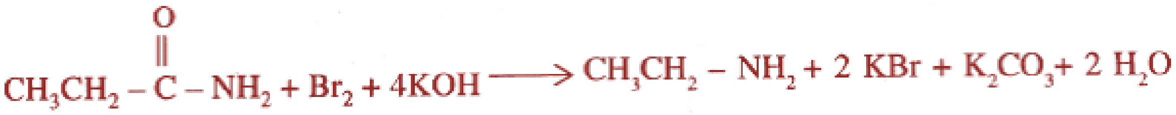
Aliphatic amides on treatment with bromine and a strong base like potassium hydroxide are converted into primary amines having one carbon less than those present in the starting amide.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow R-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

Amide **Amine**

Thus, ethanamine is obtained by treating propanamide with bromine and KOH.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3CH_2-NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O$$

Propanamide **Ethanamine**

30.1.3 Physical Properties of Amines

Aliphatic amines containing up to three carbon atoms are gases whereas higher amines are liquids. Some higher aromatic amines are even solids. Methyl and ethyl amines have smell like ammonia. Amines have higher boiling points than the corresponding hydrocarbons because they form hydrogen bonds amongst themselves. Lower amines are soluble in water and the solubility decreases with the increase in size of the alkyl group. This solubility is because of the presence of hydrogen bonding between the amino group and water molecules. All amines are soluble in organic solvents like benzene, alcohol, ether etc.

30.1.4 Chemical Properties of Amines

(i) Basic Character

Amines are basic in nature due to the presence of a lone pair of electrons on nitrogen. You know that the strength of a base depends upon the availability of electrons. Basicities of amines can be compared with respect to ammonia, by comparing the availability of pair of electrons on nitrogen. Ammonia and amines, both when dissolved in water, attract a proton from water to form an ammonium or alkylammonium ion, respectively, and a hydroxide ion.

$$\ddot{N}H_3 + H-O-H \longrightarrow \underset{\text{Ammonium ion}}{NH_4^+} + OH^-$$

$$R-\ddot{N}H_2 + H-O-H \longrightarrow \underset{\text{Alkylammonium ion}}{R-NH_3^+} + OH^-$$

You know that aliphatic amines contain one or more alkyl groups in place of hydrogen atoms of ammonia. Since alkyl groups are electron releasing groups, they increase the electron density on nitrogen. This makes the lone pair of electrons on nitrogen atom to be easily available for sharing and hence, this increases the basicity of the amine. So, we expect that the basicities of the amines would increase as we move from primary to secondary to tertiary amines.

But the order of the basicities has been found to be (**$2^0 > 1^0 > 3^0$**)

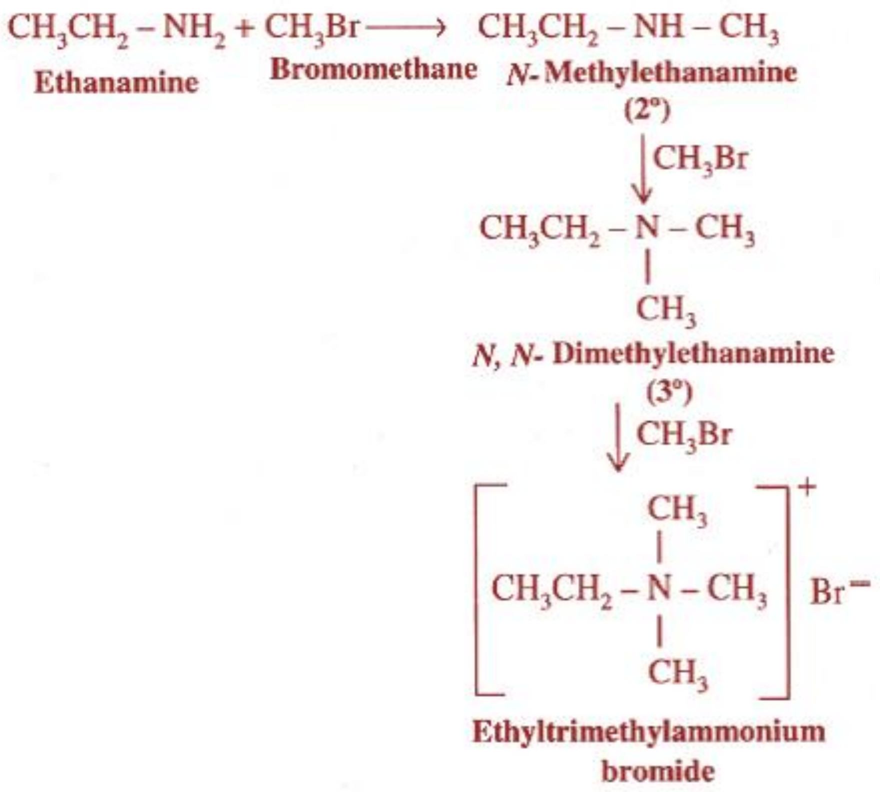
$$\begin{array}{ccccc} R-NH_2 & < & R_2NH & > & R_3N \\ \text{Primary } (1^0) & & \text{Secondary } (2^0) & & \text{Tertiary } (3^0) \end{array}$$

The tertiary amines are less basic than secondary amines. The reason is that a tertiary amine, though has three alkyl groups which can donate electrons to the nitrogen atom but they also cause crowding (also called *steric hinderance*) around nitrogen. This hinders the protonation at nitrogen atom and hence, reduces the basicity.

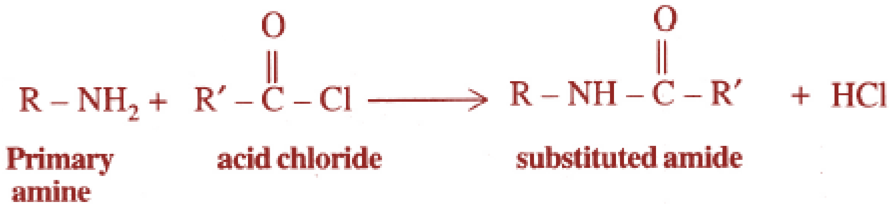
The aromatic amines are weaker bases than ammonia because the aromatic ring is electron withdrawing, It reduces the electron density at nitrogen and makes the aromatic amines less basic. So we can express the basic character of aliphatic and aromatic amines as shown below.

Aromatic amines < Ammonia < Aliphatic amines

(ii) Alkylation : Primary amines react with alkyl halides to give secondary amines. The reaction may continue further to form a tertiary amine and a quaternary ammonium salt. For example, the reaction of ethanamine with bromomethane proceeds as shown below.

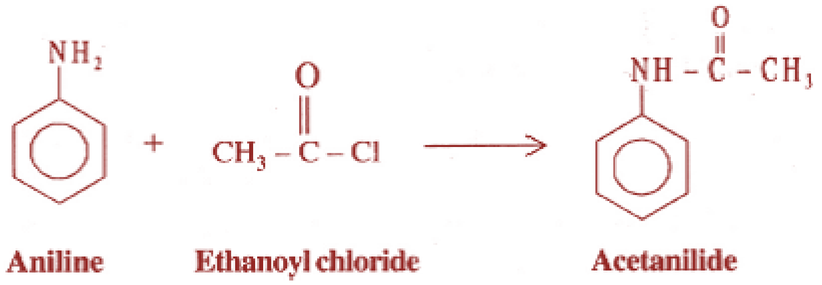


(iii) Acylation : Primary amines on reaction with acid chlorides or acid anhydrides give N- substituted amides.



$$\underset{\text{Primary amine}}{R-NH_2} + \underset{\text{acid chloride}}{R'-\overset{\overset{O}{\|}}{C}-Cl} \longrightarrow \underset{\text{substituted amide}}{R-NH-\overset{\overset{O}{\|}}{C}-R'} + HCl$$

For example, aniline on reaction with ethanoyl chloride (acetyl chloride) gives acetanilide.



(iv) Carbylamine reaction: When a primary amine is heated with chloroform in the presence of alcoholic potassium hydroxide, then the corresponding isocyanide is formed. Isocyanides are also known as **carbylamines**, hence this reaction is called as **carbylamine reaction**. For example, aminoethane on undergoing this reaction, gives ethyl carbylamine.

$$\underset{\text{Ethylamine}}{CH_3CH_2-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Ethyl carbylamine}}{CH_3CH_2N \equiv C} + 3KCl + 3H_2O$$

Isocyanides give a very offensive odour, so this reaction is also used as a test for primary amines.

(v) Reaction with nitrous acid: Primary aromatic amines react with nitrous acid to give diazonium salts and this reaction is known as **diazotisation.** Nitrous acid is an unstable compound and cannot be stored, so it is prepared during the reaction by mixing sodium nitrite and hydrochloric acid. The reaction is specifically carried out at low temperature between 273 - 278 K. For example, aniline reacts with nitrous acid to give benzene diazonium chloride.

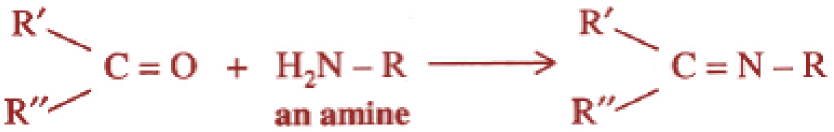
Aniline

Benzene diazonium chloride
(a diazonium salt)

Primary aliphatic amines also react in a similar way but the diazonium salts formed are unstable and decompose to give alcohols and nitrogen gas. Thus, ethanamine gives ethanol when subjected to this reaction.

$$\underset{\text{Ethanamine}}{CH_3CH_2-NH_2} \xrightarrow{NaNO_2/HCl} \underset{\substack{\text{Ethyldiazonium chloride}\\ \text{Unstable diazonium salt}}}{[CH_3CH_2N_2^+\,Cl^-]} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2-OH} + N_2 + HCl$$

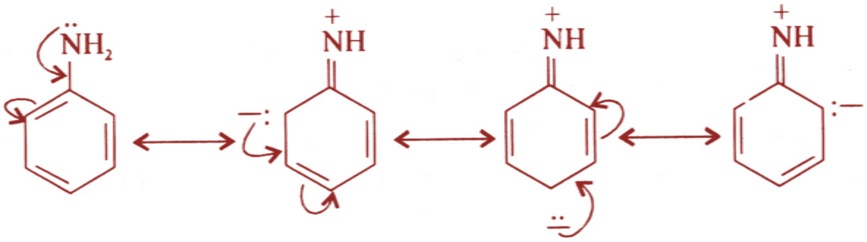
(vi) Primary amines undergo condesnsation with aldehydes or ketones to form **imines**. These products are also called **Schiffs bases**. The reaction can be shown as follows:



$$\begin{matrix} R' \\ R'' \end{matrix}\!\!>C=O + \underset{\text{an amine}}{H_2N-R} \longrightarrow \begin{matrix} R' \\ R'' \end{matrix}\!\!>C=N-R$$

a Schiff's base

(vii) Ring substitution in aromatic amines: You know that -NH_2 group is a strong activating and *ortho-*, *para-* directing group for electrophilic aromatic substitution reactions. This directive influence can be explained by the following resonating structures of aniline.

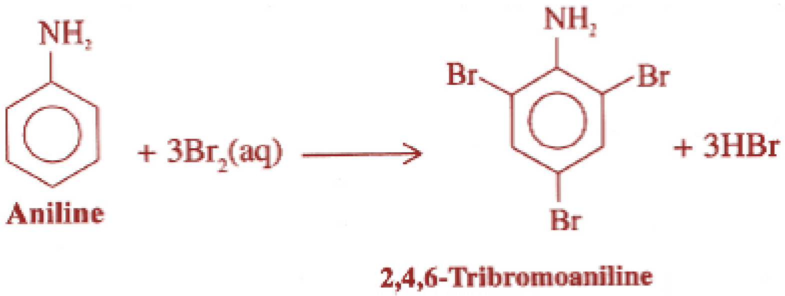


Resonance structures of aniline

As a result of this resonance, the electron density is more at ortho- and para-positions; hence, the electrophilic substitution occurs at these positions.

Some important ring substitution reactions of aromatic amines are halogenation, nitration and sulphonation.

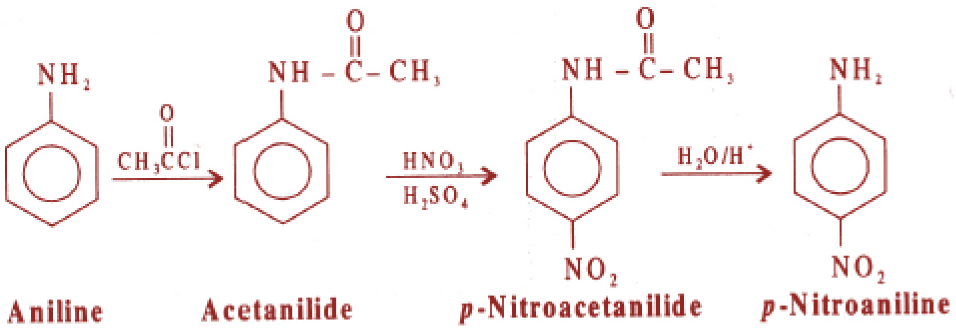
(a) Halogenation: Aniline on treatment with an aqueous solution of bromine gives 2,4,6 - tribromoaniline.



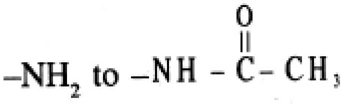
Aniline is very reactive and all the three hydrogen atoms at ortho- and para- positions are substituted with bromine atoms.

(b) Nitration: Nitration of aniline is carried out on the acetylated amine (acetanilide) rather than on the free amine itself. There are two reasons for this.

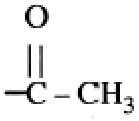
1. The free amine is very susceptible to oxidation and thus much of it is lost in the form of a black-sticky material which is formed as result of its oxidation.
2. The free amine is very reactive but acetyl the group protects it and reduces its reactivity. The nitration of aniline with the protection of the amino group is shown below:



The first step consists of acetylation of the amino group in aniline. The conversion of

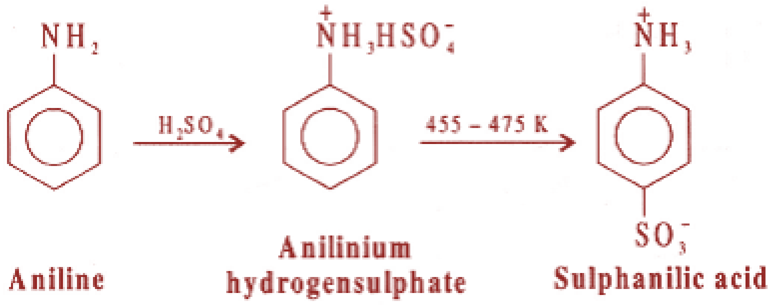


$-NH_2$ to $-NH-\overset{\overset{\Large O}{\|}}{C}-CH_3$ lowers the activity of -NH2 group because of electron withdrawal by



$-\overset{\overset{\Large O}{\|}}{C}-CH_3$ This step is followed by nitration (conc. HNO/ H_2SO_4) which gives mainly the *p*-nitroacetanilide. This, ‘on acid hydrolysis’ yields the desired product p-nitroaniline.

(c) Sulphonation : Sulphonation is carried out in the presence of sulphuric acid. The amino group in aniline is a basic group. Therefore, an acid-base reaction takes place to form anilinium hydrogensulphate salt. This salt undergoes rearrangement at a high temperature to give sulphanilic acid.



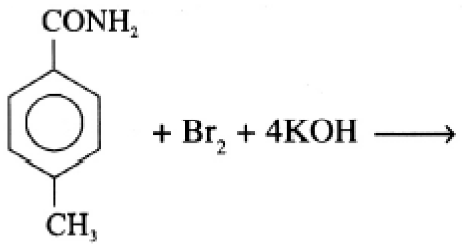
30.1.5 Uses of Amines

Amines are very useful compounds. They are used for a variety of purposes in the laboratory as well as in the industry. Some aliphatic amines are used as solvents and intermediates in drug synthesis. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents. Aromatic amines e.g. aniline and its derivatives, are used for the production of dyes, drugs and photographic developers. 1,4-Diaminobenzene is the main ingredient of all hair dyes. Many dithiocarbamates which are the compounds derived from primary amines, are used as herbicides. Diazonium salts obtained from primary aromatic amines form the basis of synthesis of many other organic compounds.

Intext Questions 30.2

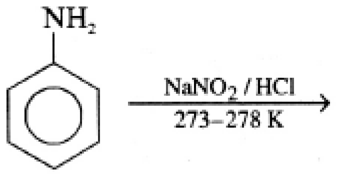
1. Predict the major product of the following reactions:

(a)

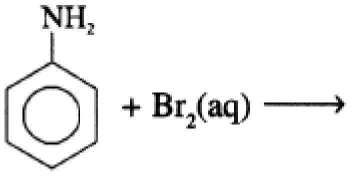


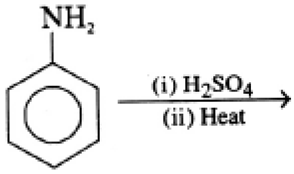
(b) $CH_3CH_2NH_2 \xrightarrow{NaNO_2/HCl}$

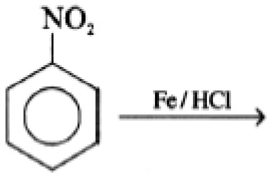
(c)



(d)



(e) 

(f) 

....

2. Why is aniline very reactive towards bromination?

....

3. Name the test which uses potassium hydroxide and chloroform for identifying a primary amine.

....

4. Can aniline be nitrated directly?

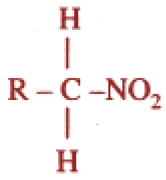
....

5. How will you obtain sulphanilic acid from benzene?

....

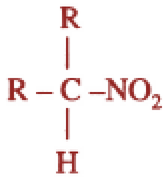
30.2 Nitro Compounds

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom is replaced by a nitro (NO2) group. They may be aliphatic or aromatic. Nitroalkanes are divided into primary (1^0), secondary (2^0) or tertiary (3^0) nitro alkanes depending upon the attachment of nitro group to primary, secondary or tertiary carbon atom, respectively.



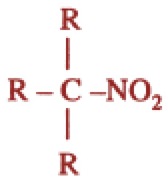
$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-NO_2$$

***p*-nitroalkane**



$$R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-NO_2$$

sec-nitroalkane

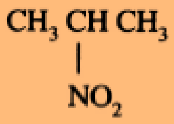
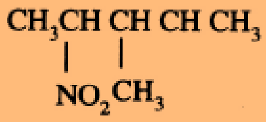
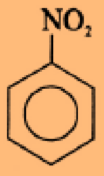
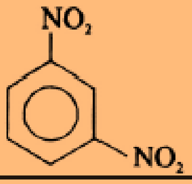


$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-NO_2$$

tert-nitroalkane

30.2.1 IUPAC Nomenclature of Nitro Compounds

According to IUPAC system, nitro compounds are named by prefixing the word nitro before the name of the parent hydrocarbon. The number of nitro groups and their positions are suitably indicated as shown in some examples given below.

Compound	IUPACName
CH_3-NO_2	Nitromethane
$CH_3CH_2-NO_2$	Nitroethane
 $CH_3\underset{\underset{NO_2}{\vert}}{CH}CH_3$	2-Nitropropane
 $CH_3\underset{\underset{NO_2}{\vert}}{CH}\underset{\underset{CH_3}{\vert}}{CH}CHCH_3$	2-Nitro - 3- methylbutane
	Nitrobenzene
	1,3 - Dinitrobenzene (m - Dinitrobenzene)

30.2.2 Preparation of Nitro Compounds

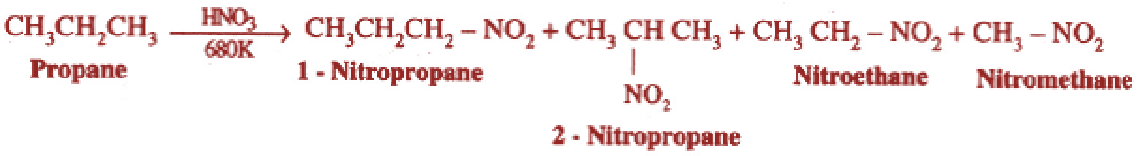
i. **From alkylhalides:** Nitroalkanes are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite. In this reaction, a small amount of isomeric alkyl nitrites (R-O-N = O) is also obtained.

$$R-X+AgNO_2 \longrightarrow R-NO_2+AgX$$

For example. bromoethane on reaction with silver nitrite gives nitroethane.

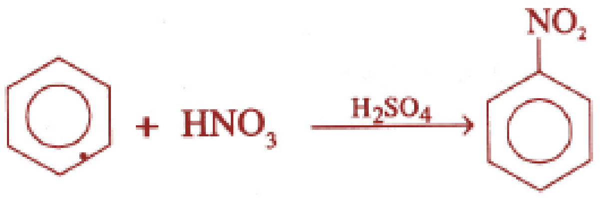
$$\underset{\text{Bromoethane}}{CH_3CH_2Br}+AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{CH_3CH_2NO_2}+AgBr$$

ii. **By nitration of alkanes:** Nitroalkanes can also be prepared by the nitration of alkanes in vapour phase. For this reaction, a mixture of the alkane and nitric acid is passed through a metal tube at about 680K. This reaction always yields a mixture of compounds due to the cleavage of the starting alkane. For example, propane on nitration gives a mixture of following compounds:



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[680K]{HNO_3} \underset{\text{1 - Nitropropane}}{CH_3CH_2CH_2-NO_2} + \underset{\text{2 - Nitropropane}}{CH_3\underset{\underset{NO_2}{\vert}}{CH}CH_3} + \underset{\text{Nitroethane}}{CH_3CH_2-NO_2} + \underset{\text{Nitromethane}}{CH_3-NO_2}$$

iii. **By nitration of aromatic compounds:** Aromatic nitro compounds are almost always prepared by direct nitration. For example, nitration of benzene gives nitrobenzene. The reaction is generally carried out with a mixture of concentrated nitric acid and concentrated sulphuric acid.



Benzene **Nitrobenzene**

30.2.3 Physical Properties of Nitro Compounds

Nitroalkanes are colourless oily liquids in the pure state. They have pleasant smell. They possess higher boiling points than the corresponding alkanes because of their polar nature. Amongst the aromatic nitro compounds, nitrobenzene is a yellow liquid with the smell of bitter almonds. Most other aromatic nitro compounds are yellow crystalline solids. All the nitro compounds are heavier than water and insoluble in it. They are, however, soluble in organic solvents like alcohol, ether, benzene, chloroform etc.

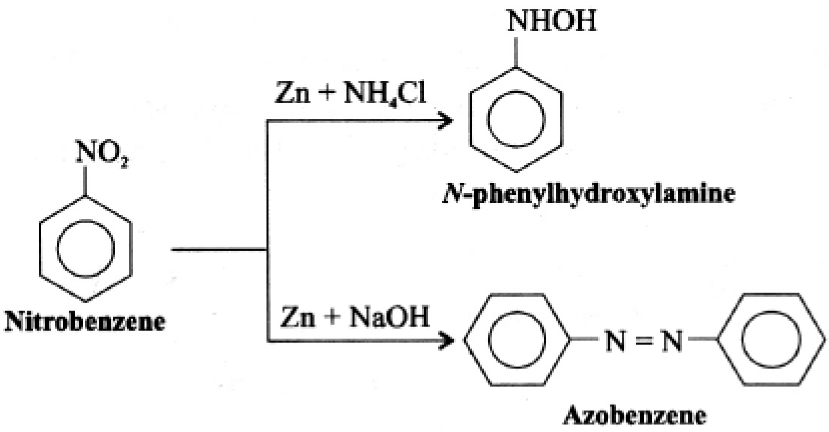
30.2.4 Chemical Properties of Nitro Compounds

(i) Reduction: One of the important reactions of nitro compounds is reduction. Nitro compounds can be readily reduced to primary amines by a variety of reducing agents. For example, (a) hydrogen in presence of catalyst like nickel or platinum (b) a metal like tin or iron in presence of hydrochloric acid and (c) lithium aluminium hydride. Reduction of nitroethane and nitrobenzene provides ethanamine and aniline, respectively.

$$\underset{\text{Nitroethane}}{CH_3CH_2-NO_2} + 3H_2 \xrightarrow{Ni} \underset{\text{Ethanamine}}{CH_3CH_2-NH_2} + 2H_2O$$

Nitrobenzene **Aniline**

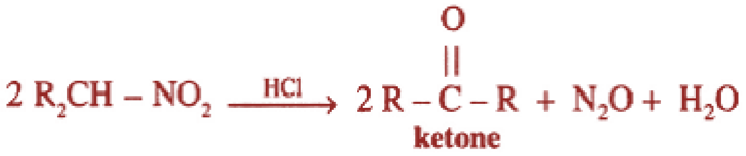
Nitrobenzene on reduction in neutral medium, using zinc dust and ammonium chloride yields N-phenylhydroxylarnine whereas its reduction in alkaline medium using zinc and sodium hydroxide yields azobenzene.



(ii) **Hydrolysis:** Primary nitroalkanes on reaction with dilute hydrochloric acid or sulphuric acid undergo hydrolysis to produce carboxylic acids and hydroxylamine.

$$RCH_2-NO_2+H_2O\xrightarrow{HCl}\underset{\text{A carboxylic acid}}{R-COOH}+\underset{\text{Hydroxylamine}}{NH_2OH}$$

Secondary nitroalkanes on hydrolysis form ketones.

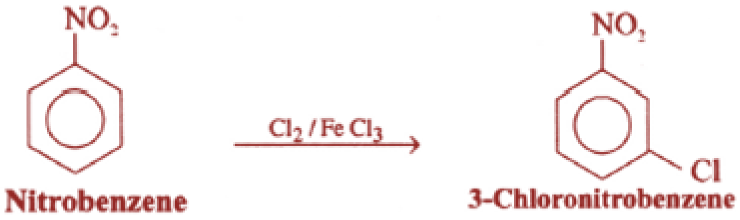


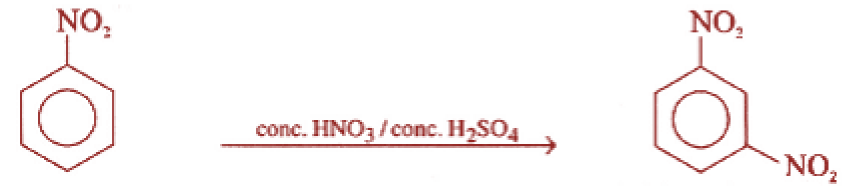
$$2\,R_2CH-NO_2\xrightarrow{HCl}2\,\underset{\text{ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R}+N_2O+H_2O$$

(iii) **Thermal decomposition:** Nitroalkanes decompose with explosion on heating. Advantage is taken of this reaction in the commercial use of nitroalkanes as explosives. It is due to the formation of large volume of gaseous products on heating which produce high pressure.

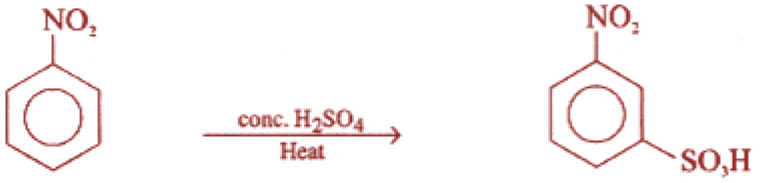
$$2\,CH_3NO_2\xrightarrow{\Delta}N_2+2\,CO_2+3\,H_2$$

(iv) Ring substitution in aromatic nitro compounds: You know that NO_2 group is a deactivating and *meta* - directing group for electrophilic substitution reactions. It is due to the electron withdrawing tendency of NO_2 group. Thus, nitrobenzene on halogenation, nitration or sulphonation gives the meta-substituted products as shown below.





Nitrobenzene **1, 3-Dinitrobenzene**



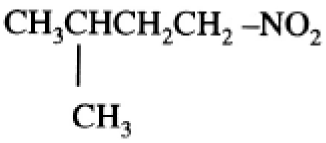
Nitrobenzene **3-Nitrobenzenesulphonic acid**

30.2.5 Uses of Nitro Compounds

1. Nitroalkanes are used as solvents for rubber, cellulose acetate etc.
2. They are used as intermediates in the industrial production of explosives, detergents, medicines, amines etc.
3. Nitro compounds are also used as fuel in small engines and rockets.

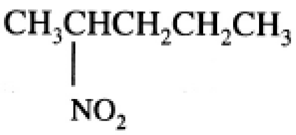
Intext Questions 30.3

1. Write IUPAC names of the following:

(a) 

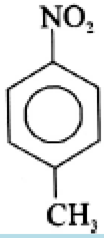
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2-NO_2$

……………………………………………………………………………………………

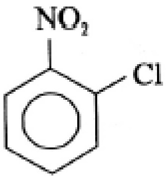
(b) 

$CH_3\underset{\underset{NO_2}{|}}{C}HCH_2CH_2CH_3$

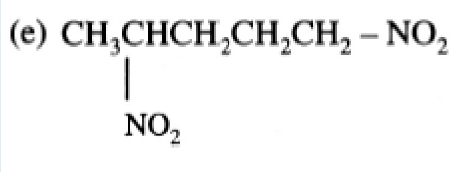
……………………………………………………………………………………………

(c) 

……………………………………………………………………………………………

(d) 

……………………………………………………………………………………………

(e) 

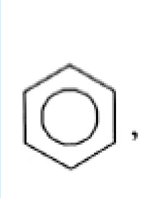
$CH_3\underset{\displaystyle NO_2}{\underset{|}{C}}HCH_2CH_2CH_2-NO_2$

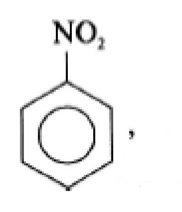
....

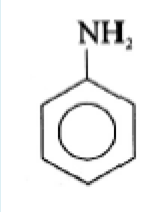
2. Write the product formed when 1,3 - dinitrobenzene is treated with tin and hydrochloric acid.

....

3. Arrange the following compounds in increasing order of their reactivity towards halogenation.







....

4. Which reaction of nitroalkanes makes them suitable to be used as rocket fuel?

....

What You Have Learnt

- Amines are considered as derivatives of ammonia. They are classified as primary, secondary or tertiary based on how many alkyl groups have replaced the hydrogen atoms of ammonia.
- Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines along with quaternary ammonium salts.
- Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms.
- In Hofmann bromamide reaction, the amine formed has one carbon less than the starting amide.
- Both aliphatic and aromatic amines are basic in nature. But aromatic amines are less basic and aliphatic amines are more basic than ammonia. An aliphatic secondary amine is more basic than primary and tertiary amines .
- Primary amines can be differentiated from secondary and tertiary amines by carbylamine reaction.
- Aliphatic primary amines undergo diazotisation to form alcohols whereas aromatic primary amines form diazonium salts.
- The amino group (-NH) is an activating and *ortho*-, *para*-directing group towards the electrophilic aromatic substitution reactions.
- Nitroalkanes are obtained by the reaction of alkyl halides with alcoholic silver nitrite.
- Nitrobenzene is obtained by the direct nitration of benzene with cone. HNO_3 in the presence of cone. H_2SO_4,

- Primary nitroalkanes are hydrolysed in acidic medium to give carboxylic acids whereas secondary nitroalkanes give ketones.
- All nitro compounds are reduced into amino compounds by (i) hydrogen in presence of catalyst or (ii) tin or iron in presence of hydrochloric acid.
- Nitro group is deactivating and *meta*-directing group towards electrophilic aromatic substitution reactions.

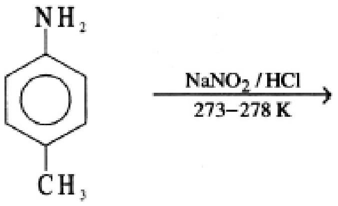
Terminal Exercise

1. Write the structural formula of the following compounds:

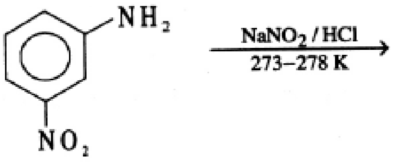
(i) 2-Methylpropan - 2-amine
(ii) Butan - 2-amine
(iii) N - Ethyl- N - methylbutan - 1- amine
(iv) 2 - Methyl- 2-nitropropane
(v) 4 - Nitrotoluene

2. What do you understand by diazotisation? Write the product of following reactions.

(i)



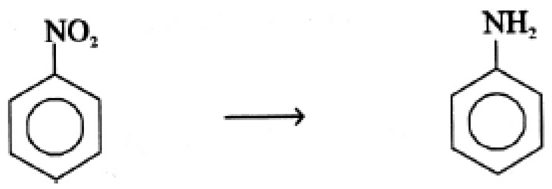
(ii)



(iii) $CH_3 - CH_2 - CH_2 - NH_2 \xrightarrow[273-278K]{NaNO_2/HCl}$

3. How will you prepare butan-1-amine starting from a suitable amide? Name the reaction involved.

4. What different reagents can be used for the following conversion?



5. Arrange the following amines in increasing order of their basicities:

Ethanamine, N-Methylethanamine, Aniline.

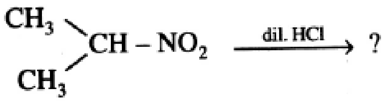
6. How will you prepare sulphanilic acid from nitrobenzene?

7. What happens when ethanamine is treated with excess of chloroethane?

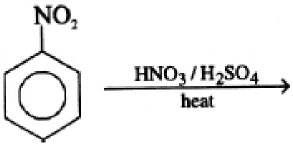
8. Write the reaction sequence to convert nitromethane into ethanamine.

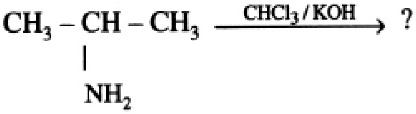
9. How will you prepare *para-bromoaniline* from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.

10. Complete the following reactions:

(i) 

(ii) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2/KOH} ? \xrightarrow[273-278K]{NaNO_2/HCl}$

(iii) 

(iv) 

$CH_3-CH(NH_2)-CH_3 \xrightarrow{CHCl_3/KOH} ?$

(v) $CH_3CH_2CH_2-Br + AgNO_2 \xrightarrow{alcohol} ?$

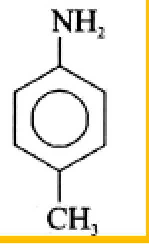
Answers to Intext Questions

30.1

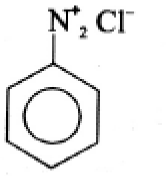
1. (i) Primary amine (ii) Secondary amine (iii) Secondary amine
   (iv) Tertiary amine (v) Primary amine (vi) Quaternary ammonium salt
2. (i) Butan-l-amine (ii) N, N-Dimethylethanamine (iii) N-Methylbutan-l- amine
   (iv) Butan-2-amine (v) 3-Bromoaniline (vi) 2-Ethylaniline

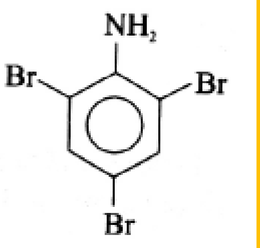
30.2

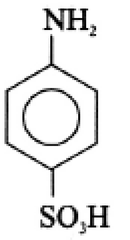
I.

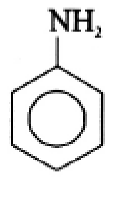
(i) 

(ii) CH_3CH_2OH

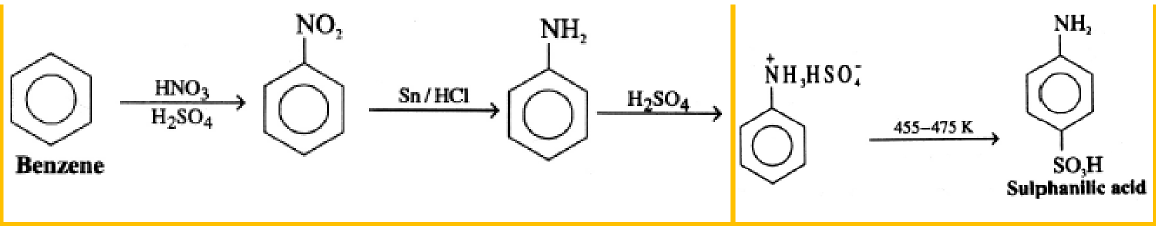
(iii) 

(iv) 

(v) 

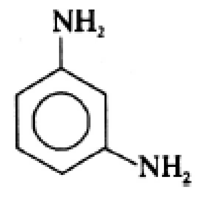
(vi) 

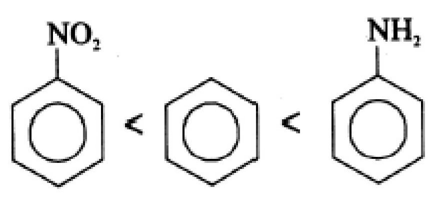
2. Aniline is very reactive towards bromination because the -NH2 group is a highly activating group.
3. Carbylamine test.
4. No

5. 

30.3

1. (i) 3-Methyl-l-nitrobutane (ii) 2-Nitropentane
(iii) 4- Nitrotoluene (iv) 2-Chloronitrobenzene
(v) 1,4 -Dinitropentane

2. 

3. 

4. Nitroalkanes decompose on heating and produce large volume of gases. The formation of gaseous products at high pressure produces the thrust which is necessary for the movement of rocket

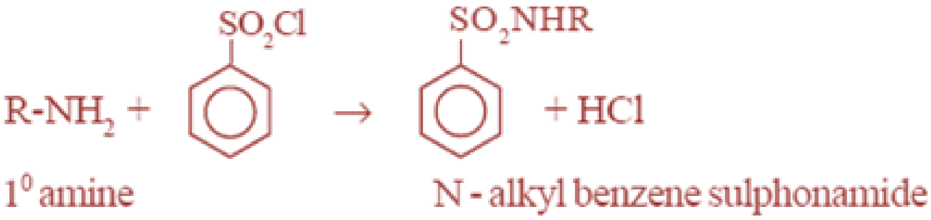
.

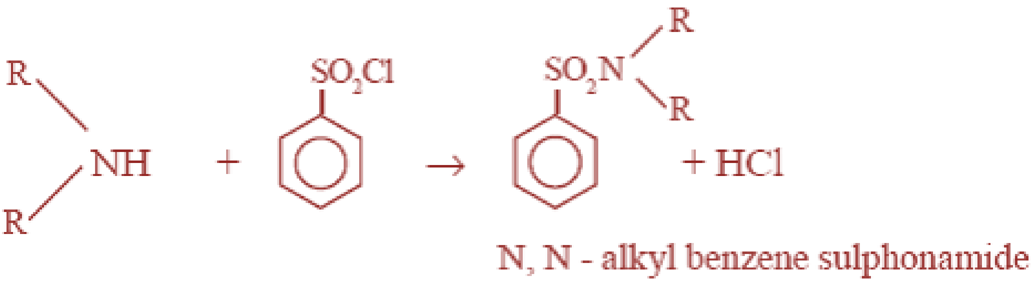
30.1.3.a Identification of Primary, Secondary and tertiary amines

1. Hinsberg's test:

Amine reacts with benzene sulphonyl chloride primary amine gives N-alkyl benzene sulphonamide and it dissolves in alkali.

Secondary amine gives N, N- dialkyl benzene sulphonamide and it is insoluble in alkali. Tertiary amine does not reacts with benzene sulphonyl chloride.





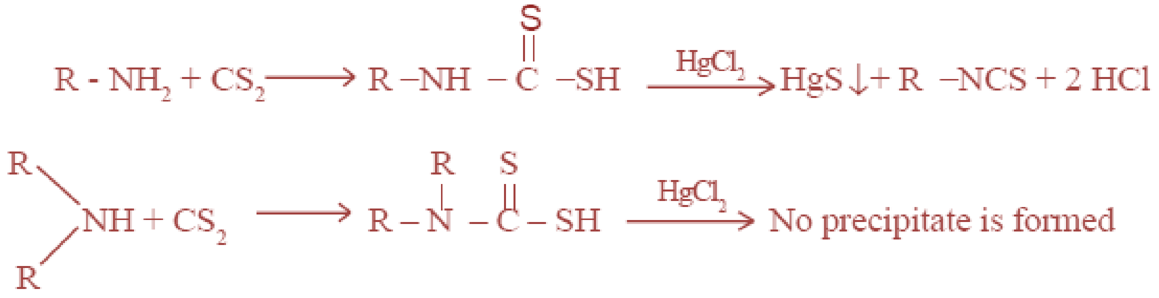
2. Hofmann mustard oil reaction:

Here amine is reacted with CS_2 followed by $HgCl_2$.

Primary amine reacts with CS_2 and the products reacts with $HgCl_2$ and black precipitate is formed.

Secondary amine reacts with CS_2, the products formed also reacts with $HgCl_2$ and no precipitate is formed.

Tertiary amine does not undergo any reaction with CS_2.



$$R-NH_2 + CS_2 \longrightarrow R-NH-\overset{\overset{S}{||}}{C}-SH \xrightarrow{HgCl_2} HgS\downarrow + R-NCS + 2\,HCl$$

$$R_2NH + CS_2 \longrightarrow R-\overset{\overset{R}{|}}{N}-\overset{\overset{S}{||}}{C}-SH \xrightarrow{HgCl_2} \text{No precipitate is formed}$$

30.1.3.a Intext Question:

1. How does a Secondary amine reacts with benzene sulphonyl chloride?

....

30.1.3.a Answer to Intext Question:

1. Secondary amine gives N.N. – di alkyl benzene sulphonamide with benzene sulphonyl chloride. It is not soluble in alkali.

Chapter 31

BIOMOLECULES

You are aware that our body, plants and other animals are made up of many chemical substances. There are certain complex organic molecules which form the basis of life. These are building materials of living organisms which are required for their growth and maintenance. Such molecules are called biomolecules. The main classes of biomolecules are carbohydrates, proteins, lipids, nucleic acids, enzymes, hormones etc. In this lesson, you will study about the structures and functions of some important biomolecules.

Objectives

After reading this lesson you will be able to:

- identify and define different types of biomolecules;
- describe the important structural features of biomolecules;
- classify carbohydrates, proteins and lipids on the basis of their structure & functions;
- give the composition of proteins and nucleic acids;
- explain the difference between DNA and RNA;
- differentiate between oils and fats;
- explain the action of enzymes and their characteristic features and
- list the functions of biomolecules in biological systems.

31.1 Carbohydrates

Carbohydrates form a very large group of naturally occurring organic compounds which play a vital role in daily life. They are produced in plants by the process of **photosynthesis**. The most common carbohydrates are glucose, fructose, sucrose, starch, cellulose etc. Chemically, the carbohydrates may be defined as **polyhydroxy aldehydes** or **ketones** or substances which give such molecules on hydrolysis. Many carbohydrates are sweet in taste and all sweet carbohydrates are called as sugars. The chemical name of the most commonly used sugar in our homes is sucrose.

31.1.1 Classification of Carbohydrates

Carbohydrates are classified into three groups depending upon their behaviour on hydrolysis.

(i) Monosaccharides: A polyhydroxy aldehyde or ketone which cannot be hydrolysed" further to a smaller molecule containing these functional groups, is known as a *monosaccharide*. About 20 monosaccharides occur in nature and glucose is the most common amongst them.

Monosaccharides are further classified on the basis of the number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an aldose and if it contains a keto group, it is known as a ketose. The number of carbon atoms present is also included while classfying the compound as is evident from the examples given in Table 31.1. Name of some naturally occuring monosaccharides are given in brackets.

Table 31.1 Classification of monosaccharides

No. of carbon atoms present	Type of monosaccharide	
	Aldose	Ketose
3	Aldotriose (Glyceraldehyde)	Ketotriose
4	Aldotetrose (Xylose)	Ketotetrose
5	Aldopentose (Erythrose)	Ketopentose
6	Aldohexose (Glucose)	Ketohexose
7	Aldoheptose	Ketoheptose

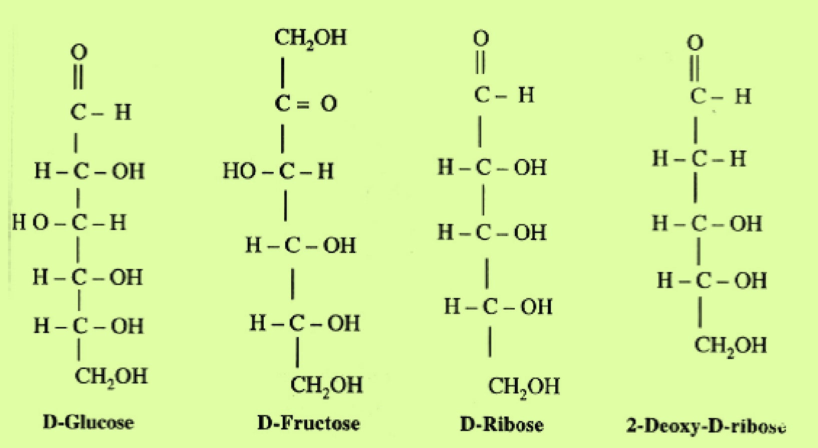
(ii) Disacccharides: Carbohydrates which give two monosaccharide molecules on hydrolysis are called disaccharides e.g. sucrose, maltose, lactose etc.

(iii) Polysaccharides: Carbohydrates which yield a large number of monosaccharide units on hydrolysis e.g. starch, glycogen, cellulose etc.

31.1.2 Structure of Monosaccharides

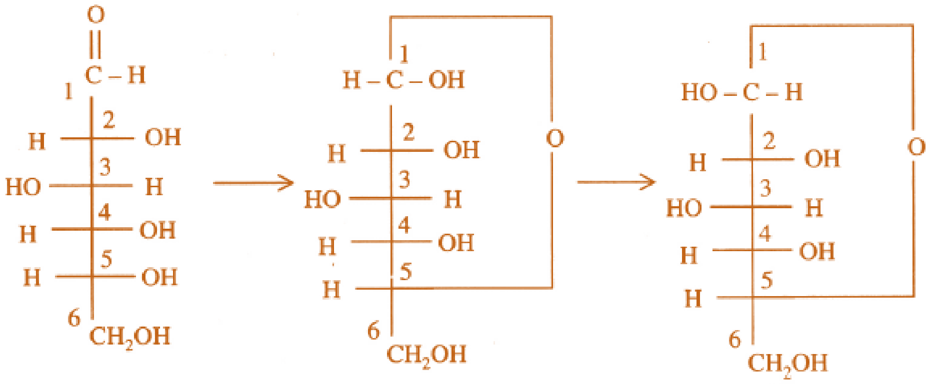
Although a large number of monosaccharides are found in nature, we will confine our discussion here to four of them only viz. D-glucose, D-fructose,D-ribose and 2-deoxy-D-ribose.

D-Glucose (an aldohexose) is the monomer for many other carbohydrates. Alone or in combination, glucose is probably the most abundant organic compound on the earth. D-Fructose (a ketohexose) is a sugar that is found with glucose in honey and fruit juices. D-Ribose (an aldopentose) is found in ribonucleic acids (RNA) while. 2-Deoxy-D-ribose is an important constituent of the eoxyribonucleic acids(DNA). Here, the prefix 2-Deoxy indicates that it lacks oxygen at carbon no. 2.



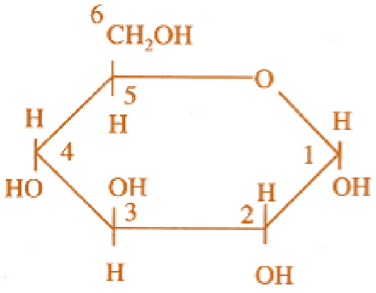
These monosaccharides generally exist as cyclic compounds in nature. A ring is formed by a reaction between the carbonyl group and one of the hydroxyl groups present in the molecule. Glucose preferentially forms the six membered ring which can be in two different isomeric forms called α, β-forms (shown below as I & II). The two forms differ only in the arrangement of the hydroxyl group at carbon No.1. Such isomers are called anomers.

Formation of these cyclic structures (I and II) from the open chain structure can be shown as follows.

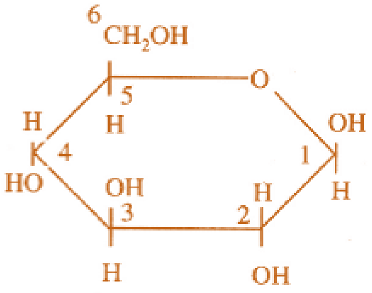


(I) α – D – glucose (II) β – D –glucose

The cyclic structures I and II are more appropriately represented as Ia and IIa.

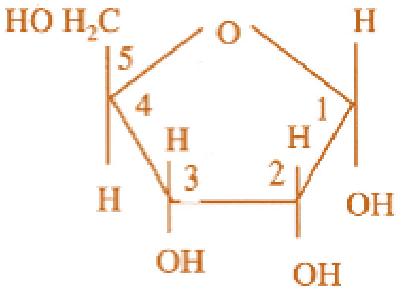


(Ia)

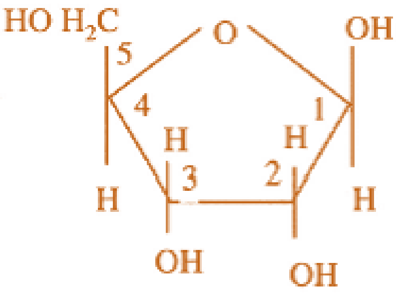


(IIa)

The α, β-forms of other sugars also exist in the cyclic form. D-Ribose forms a five membered ring structure as shown below

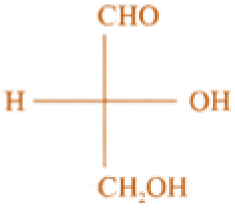


α – D – ribose

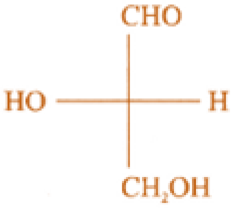


β – D – ribose

D-before the name of above example indicates the configuration of particular stereoisomer. Stereoisomers are assigned relative configurations as D or L. This system of assigning the relative configuration refers to their relation with glyceraldehyde. Glyceroldehyde contains one asymmetric carbon atom so exists in two enantiomeric forms as shown below.

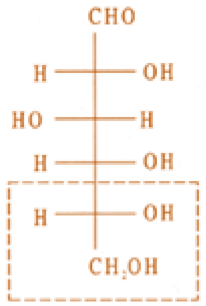


D (+) –glycaraldehyde

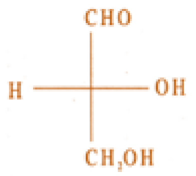


L (–) –glyceraldehyde

All those compounds which can be correlated to (+) -glyceraldehyde are said to have D-configuration and those can be correlated to () -glyceraldehyde are said to have L-configuration. In monosaccharides it is the lowest asymmetric carbon atom (shown in the box) by which the correlation is made. As in (+) glucose the lowest asymmetric carbon atom has OH group on the right side which matches with (+) glyceraldehyde hence it is assigned D-configuration.



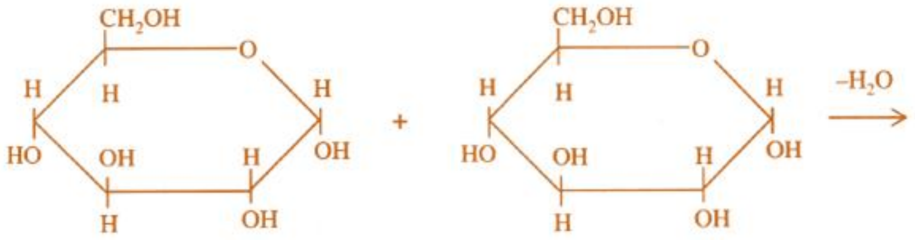
D (+) – glucose or
D-glucose



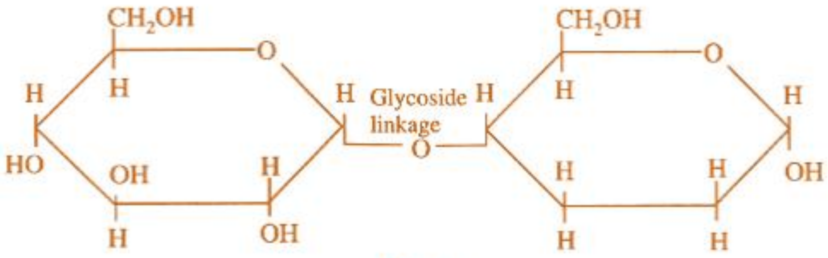
D (+) – glyceraldehyde or
D-glyceraldehyde

31.1.3 Structure of Di-Saccharides and Polysaccharides

Disaccharides are formed by the condensation of two monosaccharide molecules. These monosaccharides join together by the loss of a water molecule between one hydroxyl group on each monosaccharide. Such a linkage, which joins the monosaccharide units together is called glycoside linkage. If two α-glucose molecules are joined together, the disaccharide maltose is formed.



2 molecules of α – glucose



Maltose

Similarly, sucrose (the common sugar) consists of one molecule of glucose and one molecule of fructose joined together. Lactose(or milk sugar) is found in milk and contains one molecule of glucose and one molecule of galactose.

If a large number of monosaccharide units are joined together, we get polysaccharides. These are the most common carbohydrates found in nature. They have mainly one of the following two functions- either as food materials or as structural materials.

Starch is the main food storage polysaccharide of plants. It is a polymer of α-glucose and consists of two types of chains- known as amylose and amylopectin.

Amylose is a water soluble fraction of starch and is a linear polymer of α-D-glucose. On the other hand amylopectin is a water insoluble fraction and consists of branched chain of α-D-glucose.

The carbohydrates are stored in animal body as glycogen which is also a polymer of α-glucose and its structure is similar to amylopectin.

Cellulose is another natural polysaccharide which is the main component of wood and other plant materials. It consists of long chain of -D-glucose molecules.

31.1.4 Biological Importance of Carbohydrates

(i) Carbohydrates act as storage molecules. For example they are stored as starch in plants and as glycogen in animals.

(ii) D-Ribose and 2-deoxy-D-ribose are the constituents of RNA and DNA, respectively.

(iii) Cell walls of bacteria and plants are made up of cellulose. It may be of interest to note that human digestive system does not have the enzymes required for the digestion of cellulose but some animals do have such enzymes.

(iv) Some carbohydrates are also linked to many proteins and lipids. These molecules are known as glycoproteins and glycolipids, respectively. These molecules perform very specific functions in organisms.

Intext Questions 31.1

1. Name three constituents of your diet which provide carbohydrates.

....

2. How are carbohydrates produced in nature?

....

3. What are the hydrolysis products of starch and sucrose?

....

4. Write the linear and ring forms of D-glucose.

....

31.2 Proteins

Proteins are the most abundant macromolecules in living cells. The name protein is derived from the Greek word ‘**proteios**’ meaning 'of prime importance'. These are high molecular mass complex amino acids. You will study about amino acids in the next section. Proteins are most essential class of biomolecules because they play the most important role in all biological processes. A living system contains thousands of different proteins for its various functions. In our every day food pulses, eggs, meat and milk are rich sources of proteins and are must for a balanced diet.

31.2.1 Classification of Proteins

Proteins are classified on the basis of their chemical composition, shape and solubility into two major categories as discussed below.

(i) Simple proteins: Simple proteins are those which, on hydrolysis, give only amino acids. According to their solubility, the simple proteins are further divided into two major groups fibrous and globular proteins.

(a) Fibrous Proteins: These are water insoluble animal proteins ego collagen (major protein of connective tissues), elastins (protein of arteries and elastic tissues), keratins (proteins of hair, wool, and nails) are good examples of fibrous proteins. Molecules of fibrous proteins are generally long and thread like.

(b) Globular Proteins: These proteins are generally soluble in water, acids, bases or alcohol. Some examples of globular proteins are albumin of eggs, globulin (present in serum), and haemoglobin. Molecules of globular proteins are folded into compact units which are spherical in shape.

(ii) Conjugated proteins: Conjugated proteins are complex proteins which on hydrolysis yield not only amino acids but also other organic or inorganic components. The non-amino acid portion of a conjugated protein is called prosthetic group.

Unlike simple proteins, conjugated proteins are classified on the basis of the chemical nature of their prosthetic groups. These are

a. Nucleoproteins (protein + nucleic acid)
b. Mucoproteins and glycoproteins (protein+ carbohydrates)
c. Chromoproteins (proteins + a coloured pigment)
d. Lipoproteins (proteins + lipid)
e. Metalloproteins (metal binding proteins combined with iron, copper or zinc)
f. Phosphoproteins (proteins attached with a phosphoric acid group).

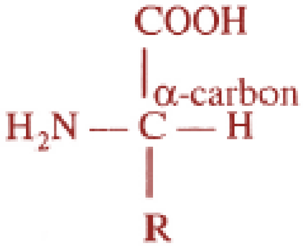
Proteins can also be classified on the basis of functions they perform, as summarized in table 31.2.

Table 31.2: Classification of proteins according to their biological functions

Class	Functions	Examples
1. Transport Proteins	Transport of oxygen, glucose and other nutrients	Haemoglobin Lipoproteins
2. Nutrient and storage Proteins	Store proteins required for the growth of embryo	Gliadin(wheat) Ovalbumin(egg) Casein (milk)
3. Structural Protiens	Give biological structures, strength or protection	Keratin(Hair, nails,etc.) collagen(cartilage)
4. Defence Proteins	Defend organisms against invasion by other species	Antibodies Snake venoms
5. Enzymes	Act as catalysts in biochemical reactions	Trypsin,Pepsin
6. Regulatory Proteins	Regulate cellular or Regulate cellular or	Insulin

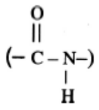
31.2.2 Structure of Proteins

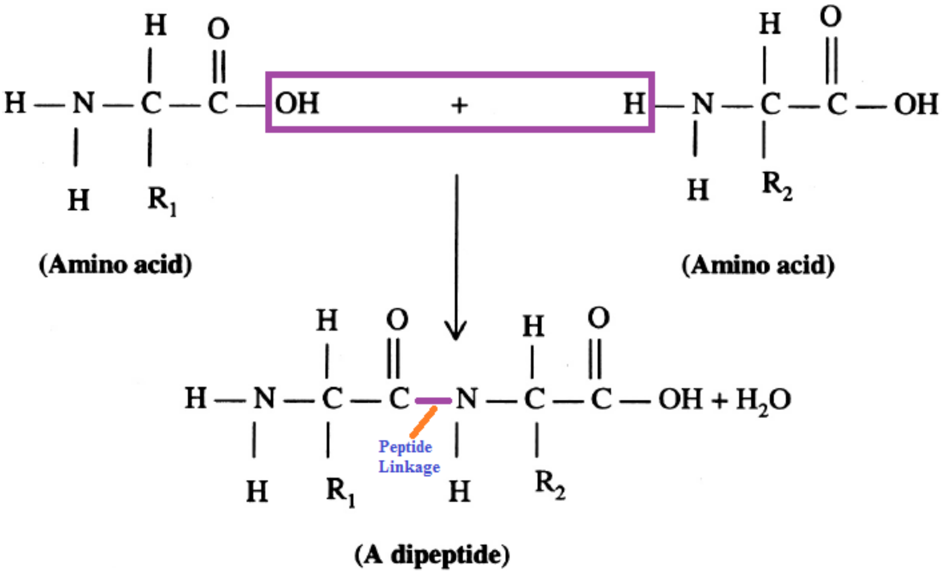
Protein molecules are polymers of different sizes and shapes with different physical and chemical properties. The monomer units for proteins are amino acids. All the amino acids that are found in proteins have an amino group(-NH_2) on the carbon atom adjacent to carbonyl group, hence are called α-amino acids. The general formula of α-amino acids is shown below.



$$H_2N-\overset{\overset{\displaystyle COOH}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-H$$

All proteins found in nature are the polymers of about twenty (20) different -amino acids and all of these have L-configuration. Out of these ten (10) amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called essential amino acids.

All proteins have one common structural feature that their amino acids are connected to one another by peptide linkages. By a peptide linkage we mean an amide  $(-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-)$ bond formed when the carboxyl group of one amino acid molecule reacts with the (α-amino group of another. In the process, a molecule of water is given off. The product of the reaction is called a peptide or more precisely a dipeptide because it is made by combining two amino acids, as shown below:



If a third amino acid is joined to a **dipeptide** in the same manner, the product is a **tripeptide**. Thus, a tripeptide contains three amino acids linked by two peptide linkages. Similar combinations of four, five, six amino acids give a **tetrapeptide**, a **pentapeptide**, a **hexapeptide**, respectively. Peptides formed by the combination of more than ten amino acid units are called **polypeptides**. Proteins are polypeptides formed by the combination of **large number of amino acid units**. There is no clear line of demarcation between polypeptides and proteins. For example insulin, although it contains only 51 amino acids, is generally considered a small protein.

The amino acid unit with the free amino group is known as the N-terminal residue and the one with the free carboxyl group is called the C-terminal residue. By convention, the structure of peptide or proteins written with the N-terminal residue on the left and the C-terminal on the right.

The actual structure of a protein can be discussed at four different levels.

(i) Primary structure: Information regarding the sequence of amino acids in a protein chain is called its primary structure. The primary structure of a protein determines its functions and is critical to its biological activity.

(ii) Secondary structure: The secondary structure arises due to the regular folding of the polypeptide chain due to hydrogen bonding between >C=O and >N - H group.

Two types of secondary structures have been reported. These are α-helix (Fig. 31.1) when the chain coils up and β-pleated sheet (Fig. 31.2) when hydrogen bonds are formed between the chains.

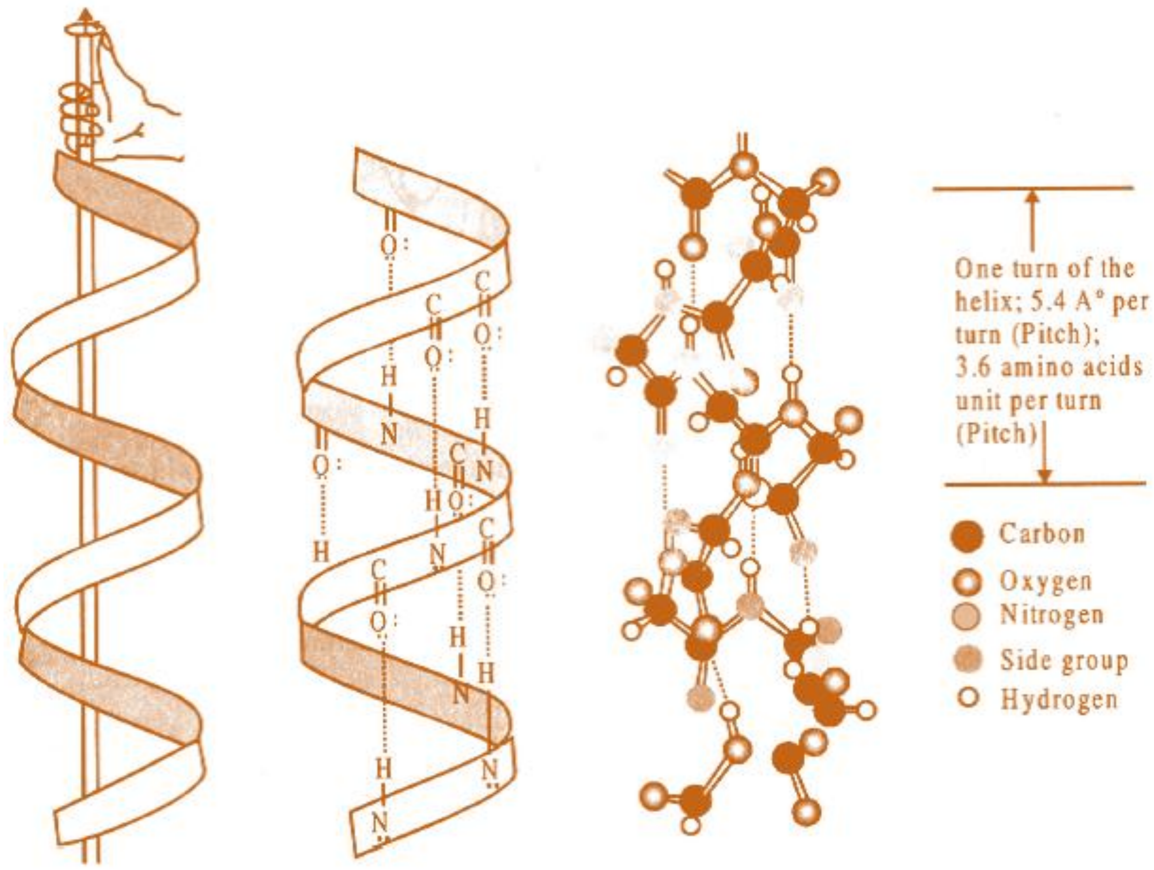
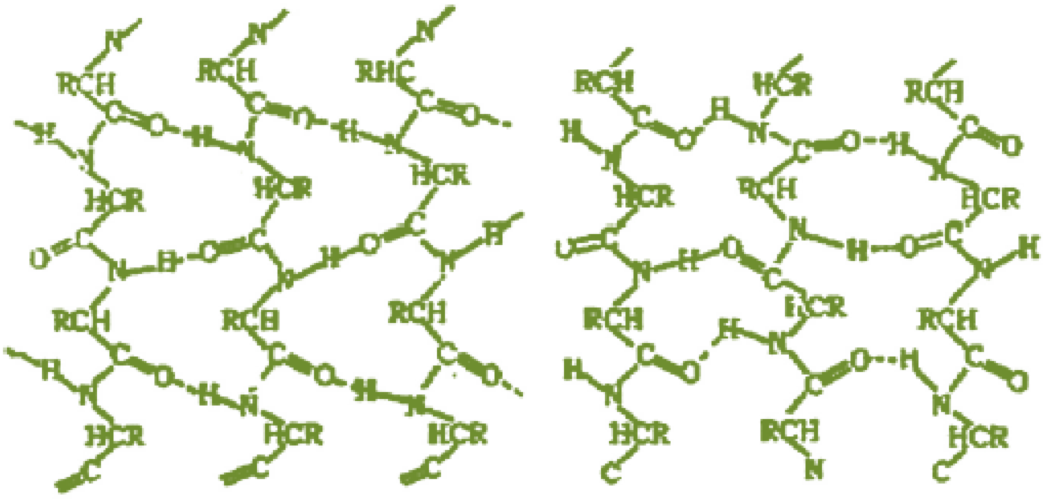


Fig. 31.1 : *The α -helix structure of protein*



Parallel β-Conformation

Antiparallel β-Conformation

Fig. 31.2 : The β-pleated-sheet structure of protein

(iii) Tertiary structure: It is the three-dimensional structure of proteins. It arises due to folding and superimposition of various α-helical chains or β-plated sheets. For example Fig. 31.3 represents the tertiary structure for the protein myoglobin.

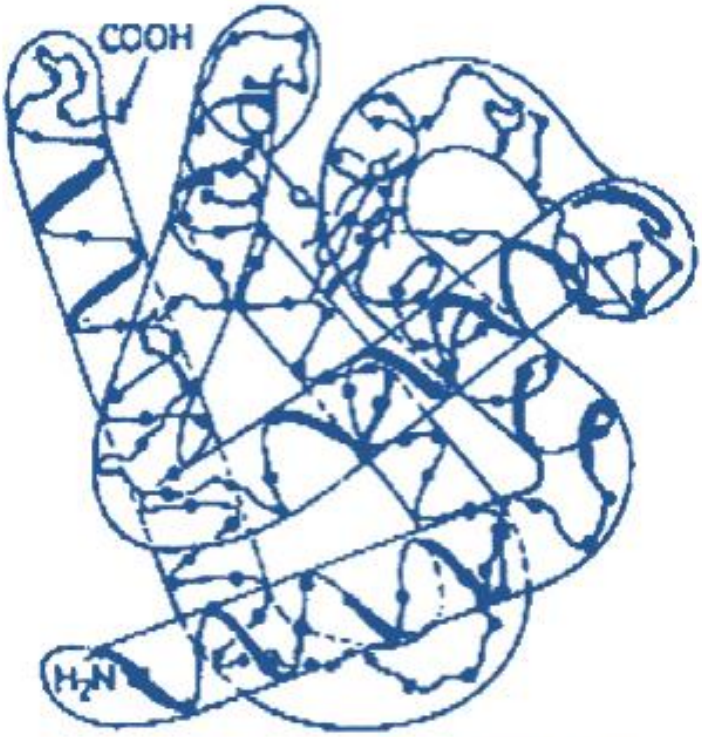


Fig. 31.3 : *Structure of myoglobin*

(iv) Quaternary structure: The quaternary structure refers to the way in which simple protein chains associate with each other resulting in the formation of a complex protein.

By different modes of bonding in secondary and tertiary structural levels a protein molecule appears to have a unique three-dimensional structure.

31.2.3 Denaturation

One of the great difficulties in the study of the structure of proteins is that if the normal environment of a living protein molecule is changed even slightly, such as by a change in *pH* or in temperature, the hydrogen bonds are disturbed and broken. When attractions between and within protein molecules are destroyed, the chains separate from each other, globules unfold and helices uncoil. We say that the protein has been denatured.

Denaturation is seen in our daily life in many forms. The curdling of milk is caused by bacteria in the milk which produces lactic acid. The change in *pH* caused by the lactic acid causes denaturation, coagulation and precipitation of the milk proteins. Similarly, the boiling of an egg causes precipitation of the albumin proteins in the egg white. Some proteins (such as those in skin, fingernails, and the stomach lining) are extremely resistant to denaturation.

31.2.4 Biological Importance of Proteins

(i) Proteins are structural components of cells.
(ii) The biochemical catalysts known as enzymes are proteins.
(iii) The proteins known as immunoglobins serve in defense against infections.
(iv) Many hormones, such as insulin and glucagon are proteins.
(v) Proteins participate in growth and repair mechanism of body tissues.
(vi) A protein called fibrinogen helps to stop bleeding.
(vii) Oxygen is transported to different tissues from blood by haemoglobin which is a protein attached to haeme part.

Intext Questions 31.2

1. What do you understand by primary structure of protein ?

....

2. What do you mean by a peptide bond?

....

3. Write the general structural formula of an -amino acid?

....

4. What are conjugated proteins ?

....

31.3 Lipids

The lipids include a large number of biomolecules of different types. The term lipid originated from a Greek word '*Lipos*' meaning fat. In general, those constituents of the cell which are insoluble in water and soluble in organic solvents of low polarity (such as chloroform, ether, benzene etc.) are termed as *lipids*. Lipids perform a variety of biological functions.

3-1.3.1 Classification of Lipids

Lipids are classified into three broad categories on the basis of their molecular structure and the hydrolysis products.

(i) Simple Lipids: Those lipids which are esters and yield fatty acids and alcohols upon hydrolysis are called simple lipids. They include oils, fats and waxes.

(ii) Compound Lipids: Compound lipids are esters of fatty acids and alcohol with additional compounds like phosphoric acid, sugars, proteins etc.

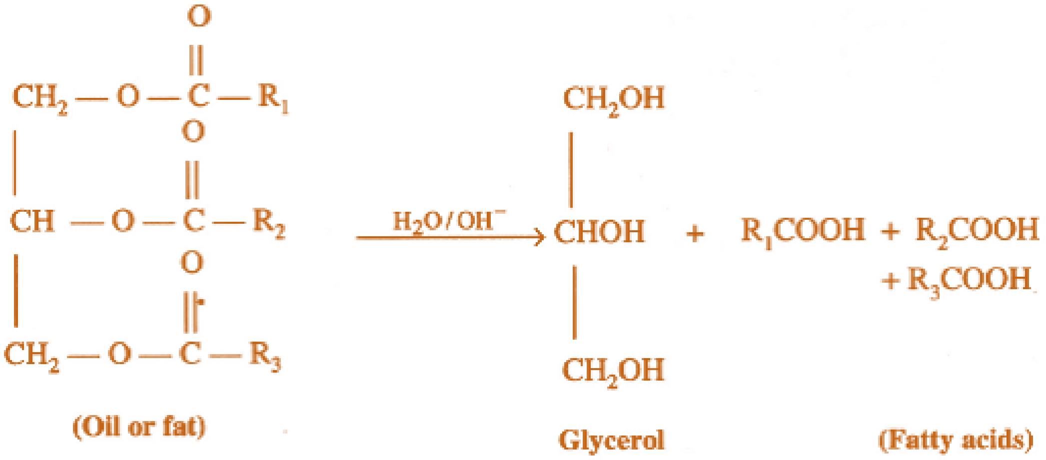
(iii) Derived Lipids: Compounds which are formed from oils, fats etc. during metabolism. They include steroids and some fat soluble vitamins.

31.3.2 Structure of lipids

The structure of all three types of lipids are briefly discussed below.

(i) Simple Lipids

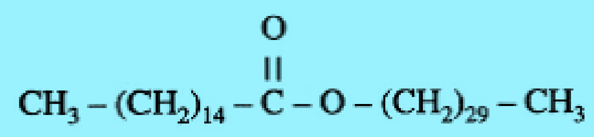
The simple lipids are esters. They are subdivided into two groups, depending on the nature of the alcohol component. Fats and oils are triglycerides, i.e. they are the esters of glycerol with three molecules of long chain fatty acids. Variations in the properties of fats and oils is due to the presence of different acids. These long chain acids may vary in the number of carbon atoms (between C_{12} to C_{26}) and may or may not contain double bonds. On hydrolysis of a triglyceride molecule, one molecule of glycerol and three molecules of higher fatty acids are obtained as shown below:



By definition, a fat is a triglyceride which is solid or semisolid at room temperature and an oil is one, that is liquid at room temperature, Saturated fatty acids form higher melting triglycerides than unsaturated fatty acids. The saturated triglycerides tend to be solid fats, while the unsaturated triglycerides tend to be oils. The double bonds in an unsaturated triglyceride are easily hydrogenated to give a saturated product, and in this way an oil may be converted into a fat. Hydrogenation is used in the manufacture of *vanaspati ghee* from oils.

Fats and oils are found in both plants and animals. Our body can produce fats from carbohydrates. This is one method that the body stores the energy from unused, carbohydrates. The vegetable oils are found primarily in the seeds of plants.

The second type of simple lipids is waxes. They are the esters of fatty acids with long chain monohydroxy alcohols 26 to 34 carbons atoms. Waxes are wide-spread in nature and occur usually as mixtures. They form a protective coating on the surfaces of animals and plants. Some insects also secrete waxes. The main constitutent of bees wax obtained from the honey comb of bees is myricyl palmitate:



$$CH_3-(CH_2)_{14}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{29}-CH_3$$

myricyl palmitate

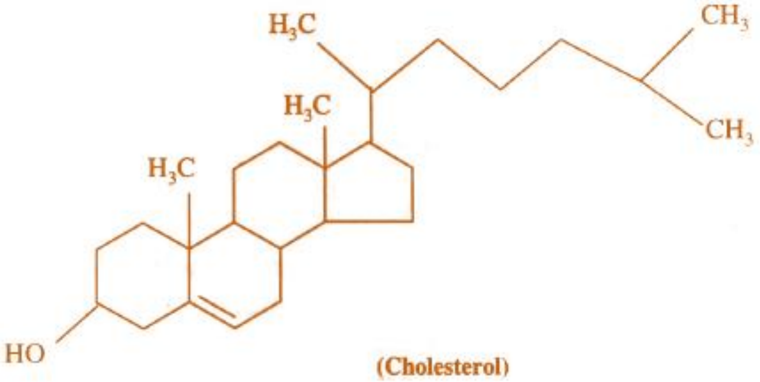
The waxes discussed above should not be confused with household paraffin wax which is a mixture of straight chain hydrocarbons.

(ii) Compound Lipids

Compound lipids on hydrolysis yield some other substances in addition to an alcohol and fatty acids. The first type of such lipids are called phospholipids, because they are the triglycerides in which two molecules of fatty acids and one molecule of phosphoric acid are present. Glycolipids contain a sugar molecule in addition to fatty acid attached to an alcohol.

(iii) Derived Lipids

Steroids are another class of lipids which are formed in our body during metabolism. These are the compounds with a distinctive ring system that provides the structural backbone for many of our hormones. Steroids do not contain ester groups and hence cannot be hydrolysed. Cholesterol is one of the most widely distributed steroids in animal and human tissues.



(Cholesterol)

Another important group of derived lipids is that of fat-soluble vitamins. This includes vitamins A, D, E and K, whose deficiency causes different diseases.

31.3.3 Biological Importance of Lipids

i. Fats are main food storage compounds and serve as reservoir of energy.
ii. Presence of oils or fats is essential for the efficient absorption of fat soluble vitamins A, D, E and K.
iii. Subcutaneous fats serve as biological insulator against excessive heat loss.
iv. Phospholipids are the essential component of cell membrane.
v. Steroids control many biological activities in living organisms.
vi. Some enzymes require lipid molecules for maximum action.

Intext Questions 31.3

1. What are lipids?

....

2. What are the products of hydrolysis of an oil?

....

3. Name two important types of compound lipids.

....

4. What is the basic difference between fats and oils?

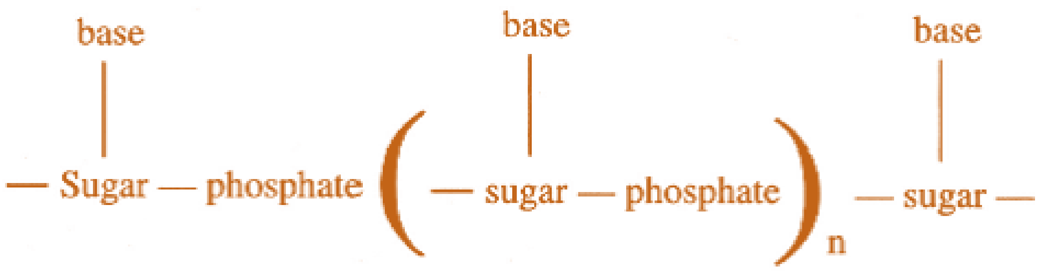
....

31.4 Nucleic Acids

Why is a dog, a dog and not a cat? Why do some people have blue or brown eyes and not black? From a chemical standpoint, how does the body know what particular type of protein is to be synthesized? How is this information transmitted from one generation to the next? The study of the chemistry of heredity is one of the most fascinating fields of research today. It was recognized in the 19th century that the nucleus of a living cell contains particles responsible for heredity, which were called chromosomes. In more recent years, it has been discovered that chromosomes are composed of nucleic acids. These are named so because they come from the nucleus of the cell and are acidic in nature. Two types of nucleic acids exist which are called DNA (deoxyribonucleic acid) and RNA(Ribonucleic acid). They differ in their chemical composition as well as in functions.

31.4.1 Structure of Nucleic Acids

Like all natural molecules, nucleic acids are linear polymeric molecules. They are chain like polymers of thousands of nucleotide units, hence they are also called polynucleotides. A nucleotide consists of three subunits: a nitrogen containing heterocyclic aromatic compound (called base), a pentose sugar and a molecule of phosphoric acid. So a nucleic acid chain is represented as shown below.



In DNA molecules, the sugar moity is 2-deoxyribose, whereas in RNA molecules it is ribose. In DNA, four bases have been found. They are adenine (A), guanine (G), cytosine (C) and thymine (T). The first three of these bases are found in RNA also but the fourth is uracil (U).

The sequence of different nucleotides in DNA is termed as its primary structure. Like proteins, they also have secondary structure. DNA is a double stranded helix. Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. The hydrogen bonds are specific between pairs of bases that is guanine and cytosine form hydrogen bonds with each other, whereas adenine forms hydrogen bonds with thymine. The two stands are complementary to each Fig. 31.4: Watson and Crick's double helix structure of DNA other. The overall secondary structure resembles a flexible ladder (Fig. 31.4). This structure for DNA was proposed by James Watson and Francis Crick in 1953. They were honoured with a Nobel Prize in 1962 for this work.

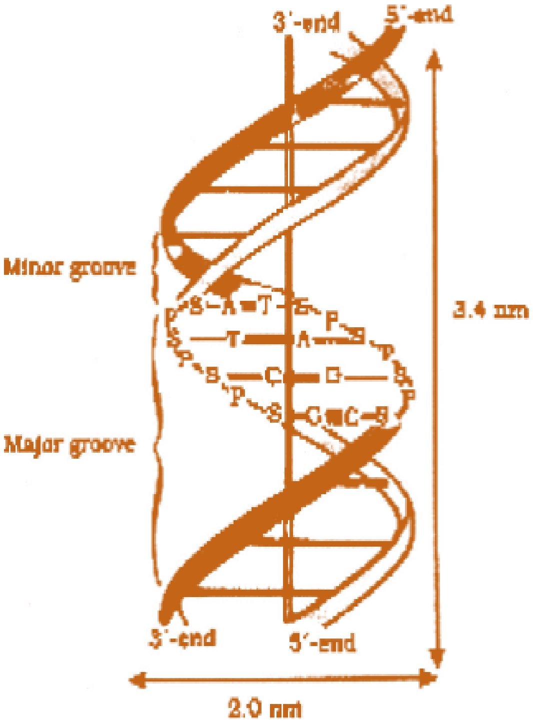


Fig. 31.4: *Watson and Crick's double helix structure of DNA*

Unlike DNA, RNA is a single stranded molecule, which may fold back on itself to form double helix structure by base pairing in a region where base sequences are complimentary. There are three types of RNA molecules which perform different functions. These are named as messenger RNA(m-RNA), ribosomal-RNA(r-RNA) and transfer RNA (t-RNA)

31.4.2 Biological Functions of Nucleic Acids

A DNA molecule is capable of self duplication during cell divisions. The process starts with the unwinding of the two chains in the parent DNA. As the two strands separate, each can serve as a master copy for the construction of a new partner. This is done by bringing the appropriate nucleotides in place and linking them together. Because the bases must be paired in a specific manner (adenine to thymine and guanine to cytosine), each newly built strand is not identical but complimentary to the old one. Thus when replication is completed, we have two DNA molecules, each identical to the original. Each of the new molecule is a double helix that has one old strand and one new strand to be transmitted to daughter cells (Fig. 3.15).

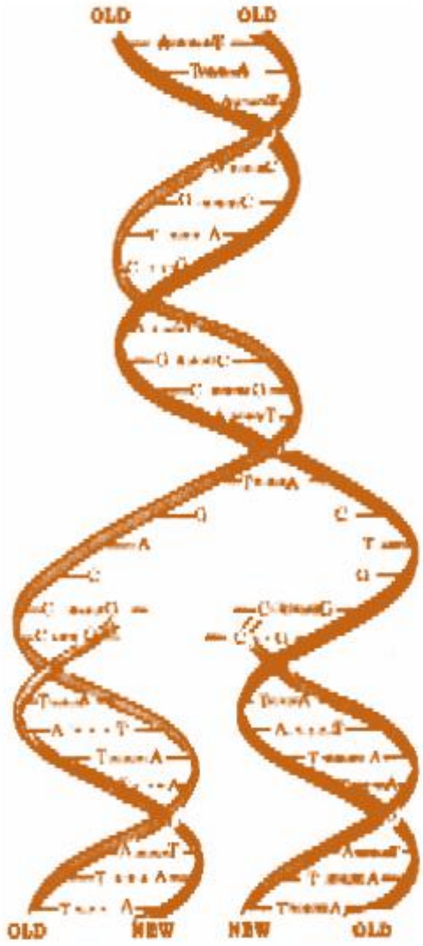


Fig. 31.5 : *Replication of DNA*

Another important function of nucleic acids is the protein synthesis. The specific sequence of bases in DNA represents coded information for the manufacture of specific proteins. In the process, the information from DNA is transmitted to another nucleic acid called messenger RNA, which leaves the nucleus and goes to the cytoplasm of the cell. Messenger RNA acts as template for the incorporation of amino acids in the proper sequence in protein. The amino acids are brought to the messenger RNA in the cell, by transfer RNA. Where they form peptide bonds. In short it can be said that DNA contains the coded message for protein synthesis whereas RNA actually carries out the synthesis of protein.

Intext Questions 31.4

1. What is a nucleotide?

....

2. Why structure DNA is called a “doublehelix”?

....

3. Write two main structural differences between DNA and RNA.

....

31.5 Enzymes

In a living system, many complex reactions occur at the temperature of about 310K. An example of this is the digestion of food, during which stepwise oxidation to CO_2 and water and energy production. These reactions are carried out under such mild conditions due to presence of certain chemicals which are called enzymes. They act as catalysts for biochemical reactions in living cells. Almost all the enzymes are globular proteins.

Enzymes are very selective and specific for a particular reaction. They are named after the compound or class of compounds upon which they work or after the reaction that they catalyze. The ending of an enzyme. name is ***-ase***. For example, maltase is an enzyme specifically catalyzes the hydrolysis of maltose into glucose. Similarly, an esterase is an enzyme which induces hydrolysis of ester linkage.

31.5.1 Mechanism of Enzyme Action

Just like chemical catalysts, enzymes are needed only in small quantities. Similar to the action of chemical catalysts, enzymes lower the energy barrier that reactants must over to form the products. For example, hydrolysis of the ester that needs boiling aqueous NaOH in the laboratory, whereas it occurs at nearly neutral pH and at moderate temperature when catalyzed by an enzyme.

There is a particular enzyme for each substrate and they are said to have lock and key arrangement. It is said that first the substrate molecule binds to the active site of the enzyme which results in the formation of an enzyme-substrate complex. In this complex the substrate is placed in the right orientation to facilitate a given reaction (Fig.31.6). This complex then breaks to give the molecule of the product and regenerates the enzyme for the next molecule of the substrate.

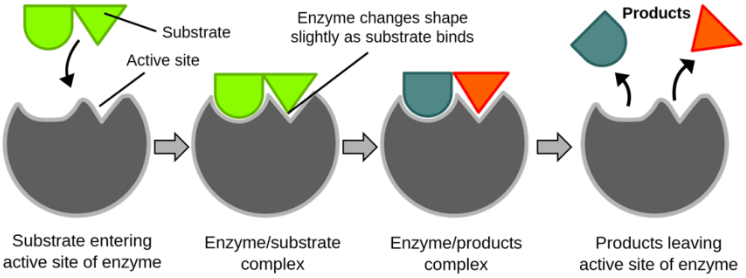


Fig. 31.6: Lock and Key arrangement of enzyme action

31.5.2 Characteristics of Enzymes

i. Enzymes speed up biochemical reactions up to ten million times compared to the uncatalysed reaction.
ii. Enzyme catalysed reactions rapidly attain equilibrium.
iii. Enzymes function in dilute aqueous solutions, at moderate temperatures and at a specific pH.
iv. They are very specific and selective in their action on substrates.
v. Enzymes are highly efficient and are needed in small amounts only.
vi. In addition to the protein structure, most active enzymes are associated with some non-protein component required for their activity, called co-enzymes. For example

nicotinamide adenine dinucleotide (NAD) is a co-enzyme which is associated with a number of dehydrogenation enzymes.

Intext Questions 31.5

1. How do enzymes increase the rate of a reaction?

....

2. What do you understand by lock and key arrangement?

....

What You Have Learnt

- Carbohydrates are polyhydroxy aldehydes or ketones or substances which provide such molecules on hydrolysis.
- They are classified as mono-, di-and polysaccharides.
- Proteins are the polymers of -amino acids which are linked by peptide bonds.
- All proteins are the polymers of twenty different -amino acids. Out of these 10 amino acids cannot be synthesized by our body and hence must form the part of our diet. These are called essential amino acids.
- Proteins are very important to us and perform many functions in a cell that are absolutely necessary for our survival.
- Chief sources of proteins are pulses, milk, meat, eggs, etc.
- Biomolecules which are insoluble in water and soluble in organic solvents are called lipids. They are classified as simple, compound and derived lipids.
- Nucleic acids are the compound which are responsible for the transfer of characters from parents to offsprings . .
- There are two types of nucleic acids- DNA and RNA. They are polymers composed of repeating units called nucleotides.
- DNA contains a five carbon sugar molecule called 2-deoxyribose whereas RNA contains ribose.
- The four bases present in DNA are adenine, cytosine, guanine and thymine whereas RNA contains uracil in place of thymine.
- DNA is a double strand molecule whereas RNA is a single strand molecule.
- DNA is present in the nucleus and have the coded message for proteins to be synthesized in the cell.
- Proteins are actually synthesized by RNA which are of three types - messenger-RNA (m-RNA), ribosomal-RNA (r-RNA) and transfer- RNA (t-RNA).
- Enzymes are biocatalysts which speed up the reactions in biosystems.
- Chemically all enzymes are proteins. They are very specific and selective in their action on substrates.

Terminal Exercises

1. How is excess glucose stored in our body?
2. What is a disaccharide? Give an example.
3. What are the products formed by the hydrolysis of lactose?
4. What are essential amino acids?
5. Differentiate between globular and fibrous proteins with suitable examples.
6. What are triglycerides? Mention one of its important uses.
7. What is a nucleotide?
8. Differentiate between the nucleotides of RNA and DNA.
9. What are different types of RNA found in the cell? Mention their functions.
10. What are enzymes?

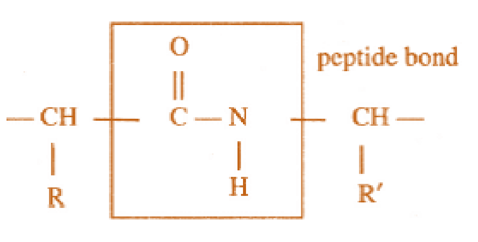
Answers to Intext Questions

31.1

1. Cereals, fruits and sugar.
2. Plants produce carbohydrates during photosynthesis.
3. Starch on hydrolysis gives glucose whereas sucrose on hydrolysis gives glucose and fructose.
4. Refer to section 31.1.2.

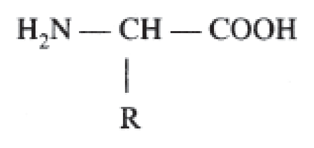
31.2

1. Information regarding the sequence of amino acids in a protein chain is called its primary structure.
2. Proteins are made up of many -amino acids which join together by the formation of an amide bond between NH_2 group of one amino acid and COOH group of another. When two amino acids combine in this way, the resulting product is called a dipeptide and the amide bond between them is called a peptide bond.



$$-\underset{\displaystyle R}{\underset{|}{CH}}-\boxed{\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{\underset{|}{N}}}-\underset{\displaystyle R'}{\underset{|}{CH}}-$$

3. An -amino acid may be represented as



$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$$

4. Refer to section 31.2.1.

31.3

1. Biomolecules which are insoluble in water and soluble in organic solvents like benzene, ether or chloroform are called lipids.
2. Oils on hydrolysis give glycerol and long chain fatty acids.

3. Two types of compound lipids are phospholipids and glycolipids.

4. A triglyceride which is solid at room temperature is called a fat and if it is liquid then it is called an oil.

31.4

1. A nucleotide consists of three subunits which are
    - (i) a nitrogen containing heterocyclic aromatic compound, also called a base;
    - (ii) a pentose sugar (ribose or 2-deoxy ribose) and
    - (iii) a molecule of phosphoric acid.
2. In DNA, two chains are wound around each other in the form of helix, hence the structure is called a double helix.
3. Two main structural differences between DNA and RNA are:
    - (i) DNA molecules are double stranded whereas RNA are single strand molecules.
    - (ii) In DNA,molecules, the sugar moity is 2-deoxyribose whereas in RNA molecules, it is ribose.

31.5

1. Refer to section 31.5.1
2. Refer to section 31.5.1

Transcription

Deoxy ribo Nucleic Acid (DNA) is greater than Ribo Nucleic Acid (RNA). DNA have double helical structure and RNA is single stranded.

RNA is of three types. They are 1. Messenger RNA (mRNA), 2. Ribosomal RNA (rRNA), 3. Transfer RNA (tRNA)

The synthesis of mRNA from a DNA blue print is called transcription. This takes place in the nucleus of the cell. The sequence of DNA base provides the blue print for the synthesis of mRNA.

In DNA Adenine, thymine, cytosine and guanine like nitrogen bases are present. The newly synthesized mRNA leave the nucleus and enters into the cytoplasm. Here, translation of this genetic information into proteins takes place.

The DNA a winds to give single strands exposing the bases. One of the strands is called sense or informational strand.

The other is antisense or template stand. The template strand is in 3’-5’ direction so that mRNA can be synthesized in 5’-3’ direction. Each guanine specifies incorporation of a cytosine into mRNA and each adenine to a uracil of mRNA. (RNA does not contain thymine).

Both sense strand and mRNA are complementary to the template strand. mRNA has a uracil wherever the sense strand has a thymine.

Some sites on DNA indicate that no more bases should be added to the growing strand of mRNA and then the synthesis stops.

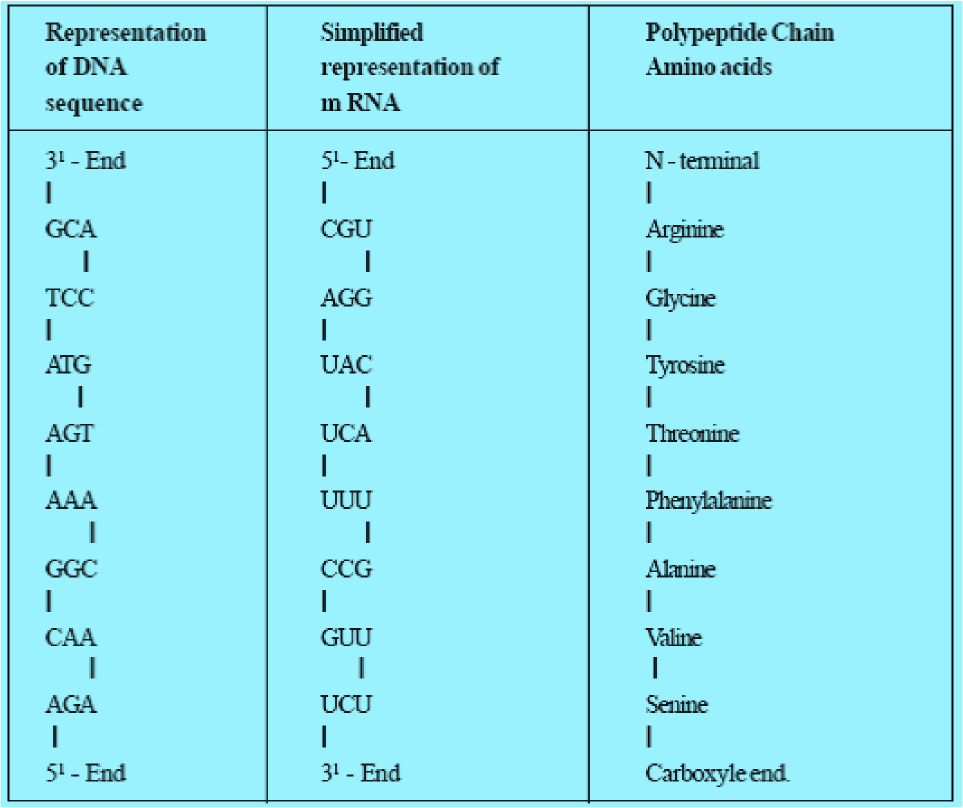
Protein Synthesis (Translation):

Translation is the process by which the genetic message in DNA that has been passed to mRNA is decoded and used to build proteins.

A protein is synthesized from its N-terminal end to its C-terminal end by the sequence of bases along mRNA strand in the 5'-3' direction.

A sequence of three bases, called codon specifies a particular amino acid that is to be incorporated into a protein.

e.g. - UCA on mRNA codes for the amino acid serine and CAG codes for glutamine. There are 64 codons, but 2^0 amino acids indicating that more than one codon can code for the same amino acid. A difference of simple base in the DNA molecule or a single error in the reading of the code can cause a change in the amino acid sequence which leads to mutation. Every t-RNA molecule is used for recognition of the triplets in mRNA.



Representation of DNA sequence	Simplified representation of m RNA	Polypeptide Chain Amino acids
3^1 - End	5^1- End	N - terminal
GCA	CGU	Arginine
TCC	AGG	Glycine
ATG	UAC	Tyrosine
AGT	UCA	Threonine
AAA	UUU	Phenylalanine
GGC	CCG	Alanine
CAA	GUU	Valine
AGA	UCU	Senine
5^1 - End	3^1 - End	Carboxyle end.

31.2.4.a Intext Question:

1. What are the Nitrogen bases present in R.N.A.

....

31.2.4.a Answer to Intext Question:

1. Adenine, uracil, cytosine and guanine Nitrogen bases are present in R.N.A.

31.3.3.a Vitamins

Carbon compounds which are required in minute quantities for the maintenance of normal health of organisms are called vitamins. The term vitamin was introduced by Dr. Funk. Their absence in the human body causes deficiency diseases. Plants can synthesise all vitamins. Animals can synthesise only few vitamins.

Vitamins in low concentrations catalyse biological reactions. Youngsters need higher quantities than elders.

Vitamins are designated by English alphabets A,B,C,D,E,K.

Classification:

Vitamins are classified based on their solubility into two groups.

They are:

1) Fat soluble vitamins,
2) Water soluble vitamins.

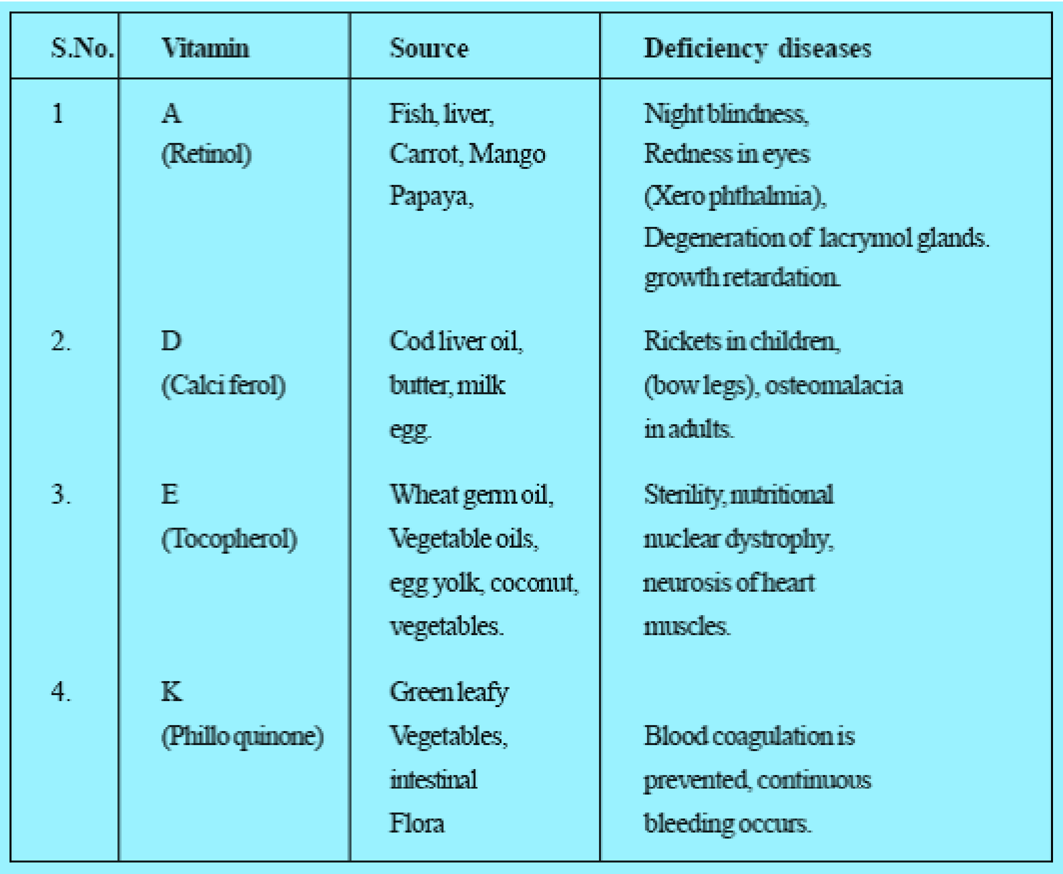
Fat Soluble Vitamins:

Vitamins A, D, E and K are fat soluble.

Water Soluble Vitamins:

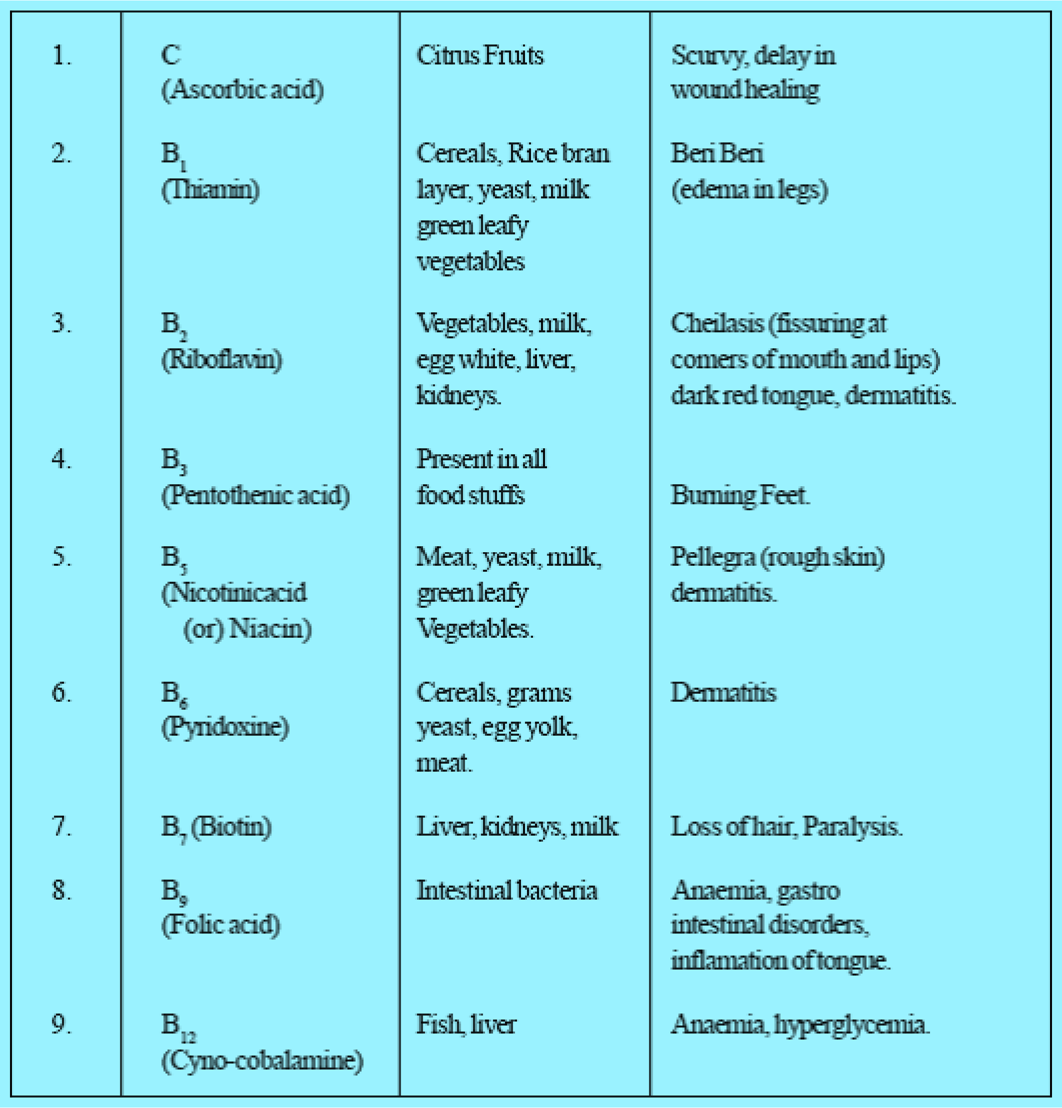
Vitamins C and B-Complex are water soluble.

Deficiency of vitamins causes diseases and they are tabulated as follows.



S.No.	Vitamin	Source	Deficiency diseases
1	A (Retinol)	Fish, liver, Carrot, Mango Papaya,	Night blindness, Redness in eyes (Xero phthalmia), Degeneration of lacrymol glands. growth retardation.
2.	D (Calci ferol)	Cod liver oil, butter, milk egg.	Rickets in children, (bow legs), osteomalacia in adults.
3.	E (Tocopherol)	Wheat germ oil, Vegetable oils, egg yolk, coconut, vegetables.	Sterility, nutritional nuclear dystrophy, neurosis of heart muscles.
4.	K (Phillo quinone)	Green leafy Vegetables, intestinal Flora	Blood coagulation is prevented, continuous bleeding occurs.

Fat Soluble Vitamins :



1.	C (Ascorbic acid)	Citrus Fruits	Scurvy, delay in wound healing
2.	B_1 (Thiamin)	Cereals, Rice bran layer, yeast, milk green leafy vegetables	Beri Beri (edema in legs)
3.	B_2 (Riboflavin)	Vegetables, milk, egg white, liver, kidneys.	Cheilasis (fissuring at corners of mouth and lips) dark red tongue, dermatitis.
4.	B_3 (Pentothenic acid)	Present in all food stuffs	Burning Feet.
5.	B_5 (Nicotinicacid (or) Niacin)	Meat, yeast, milk, green leafy Vegetables.	Pellegra (rough skin) dermatitis.
6.	B_6 (Pyridoxine)	Cereals, grams yeast, egg yolk, meat.	Dermatitis
7.	B_7 (Biotin)	Liver, kidneys, milk	Loss of hair, Paralysis.
8.	B_9 (Folic acid)	Intestinal bacteria	Anaemia, gastro intestinal disorders, inflamation of tongue.
9.	B_{12} (Cyno-cobalamine)	Fish, liver	Anaemia, hyperglycemia.

31.3.3.a Intext questions:

1. What are the diseases causes by deficiency of vitamin C and D.

....

31.3.3.a Answer to Intext Questions:

1. Deficiency of Vitamin ‘C’ Causes scurvy and deficiency of vitamin ‘D’ causes Rickets.