313

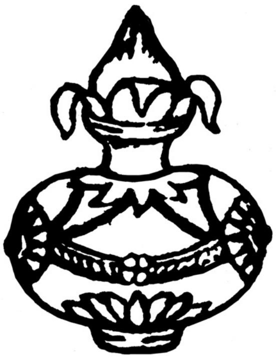
Intermediate (TOSS) Course
Senior Secondary Course

CHEMISTRY
2

(CORE MODULES)

Coordinator

Dr. Satya Prakash



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

Reprint : 2018 No of Copies : 1269

Published by the Director Telangana Open School Society, Hyderabad with the
Copyright Permission of NIOS, NOIDA.

COURSE DESIGN COMMITTEE

CHAIRPERSON
Prof. A. K Sharma
Former Director
NCERT, New Delhi

MEMBERS

Prof. N.K Jha
(Retd. From IIT Delhi
4192, Sector-B, Pocket 5&6,
Vasant Kunj,
New Delhi - 110070

Prof. B.S. Saraswat
(School of Sciences)
IGNOU, Maidan Garhi
New Delhi - 110067

Dr. K C. Trikha
Reader, Chemistry
ARSD, college, Dhaula Kuan
New Delhi

Prof. Sunita Malhotra
School of Sciences
IGNOU, Maidan Garhi
New Delhi - 110067

Dr. V.P. Singh
Principal, DIET (SCERT)
Delhi

Dr. Vijay Sarda
Reader, Chemistry
Zakir Hussain College
New Delhi - 110002

Dr. Vinod Kumar
Reader, Chemistry
Hansraj College
Delhi - 110 007

Ms. Vinita Sharma
PGT, Chemistry
Kendriya Vidyalaya No.3
Railway Colony, Mathura

Sh. KC. Saxena
Vice Principal
Govt. Sarvodaya Vidyalaya
New Delhi - 110 048

Dr. Satya Prakash
Course Co-ordinator,
NIOS New Delhi - 110 048

LESSON WRITERS

Prof. Sunita Malhotra
School of Sciences
IGNOU, Maidan Garhi
New Delhi - 110067

Dr. Sunita Bansal
Motilal Nehru College
Delhi University
New Delhi - 110021

Dr. K N. Upadhyaya
Former Reader, Ramjas
College, Delhi University,
New Delhi-110007

Dr. V. P. Singh
Principal
DIET (SCERT), Delhi

Dr. Sulekh Chandra
Reader, Zakir Hussian College
Delhi University, Delhi-110002

Dr. KK Arora
Reader, Zakir Hussian College
Delhi University, Delhi-110002

EDITORS TEAM

Prof. N. K Jha
Retired from IIT, 4192,
Sector B, Pocket 5&6,
Vasant Kunj, New Delhi-110070

Prof. Sunita Malhotra
School of Sciences
IGNOU, Maidan Garhi
New Delhi - 110 067

Dr. Satya Prakash
National Institute of
open Schooling
New Delhi - 110048

LANGUAGE EDITORS

Dr. Ranjana Rastogi
Reader, Hansraj College
Delhi University Delhi-110007

Dr. R.K Trikha
Reader, Hansraj College
Delhi University Delhi-110007

Dr. Satya Prakash
National Institute of open
Schooling, New Delhi - 110048

GRAPHIC ILLUSTRATORS

Vijay Computer
IE, Pocket-I, Mayur Vihar
Phase-I, Delhi

Sh. M.L. Jharotia
Sh. Mahesh Sharma
NIOS, New Delhi- 110 048

FORE WARD

Education plays an important role in the modern society. Many innovations can be achieved through Education. Hence the Department of Education is giving equal importance to non-formal education through Open Distance Learning (ODL) mode on 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 7,67,190 learners were enrolled in the Open Schools and 4,50,024 learners have successfully completed their courses.

With the aim of improving the administration at the grass-root level the Telangana Government re-organized the existing Districts and formed 31 new Districts. The formation of new Districts provide wide range of employment and Business opportunities besides self employment. Given the freedom and flexibilities available, the Open School system provides a second chance of learning for those who could not fulfill 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 2018-19 is being printed and supplied to all the learners throughout the state.

I 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.

With best wishes ....

S. Venkateshwara Sharma
DIRECTOR,
Telangana Open School Society,
Hyderabad

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

CHIEF EDITOR

Sri K. Ananda Kishore, M.Sc., M.Ed., PE Dip. in Edn (London)
Director,
Open School Society, Hyderabad.

EDITOR

Dr. P.E. Naga Lakshmi M.Sc., Ph.d.
Asso. Prof. in Chemistry
Sarojini Naidu Vanitha Mahavidyalaya
Exhibition grounds, Nampally, Hyderabad.

WRITERS

Dr. A. Vasundhara M.Sc., M.Phil., Ph.d.
Asso. Prof. in Chemistry
S.K.R College for women
Rajahmundry

Dr. D. Padmavathy M.Sc., M.Phil., Ph.d.
Asso. Prof. in Chemistry
S.K.R College for women
Rajahmundry

Mr. V. Muralidhar Reddy M.Sc., B.Ed
JL in Chemistry
T.S. SWR Junior College
Pargi, RR Dist.

Dr. D. Karunakar M.Sc., Ph.d.
Lecturer in Chemistry
NMGDC, Jogipet.

COORDINATION COMMITTEE

Sri. D. Narasimha Murthy M.Sc., B.Ed
Coordinator

Smt. M. Vijaya Lakshmi M.Sc., B.Ed
Coordinator

HOW TO USE THE STUDY MATERIAL

Your learning material has been developed by a team of physics 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 organisor 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 place using 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 center 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.

Overview of the Learning Material

①

Module I
Atoms, Molecules and Chemical Arithmatics

1. Mole Concept
2. Chemical Arithmatics

Module II
Atomic Structure and Chemical Bonding

3. Atomic structure
4. Periodic table and atomic properties
5. Chemical Bonding

Module III
State of Matter

6. The Gaseous State
7. The Liquid State
8. The Solid State
9. 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

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 Carboxylic Acids
30. Compounds of Carbon Containing Nitrogen
31. Biomlecules

③

Module VIIIA
Environmental Chemistry

32. Environmnetal 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 **Name of the Lesson** **Page No.**

VI. Chemistry of Elements

VII. Chemistry of Organic Compounds

MODULE- VI

CHEMISTRY OF ELEMENTS

1

MOLE CONCEPT

As you are aware, atoms and molecules are so small that we cannot see them with our naked eyes or even with the help of a microscope. Any sample of matter which can be studied consists of extremely large number of atoms or molecules. In chemical reactions, atoms or molecules combine with one another in a *definite number ratio*. Therefore, it would be pertinent if we could specify the total number of atoms or molecules in a given sample of a substance. We use may *number units* in our daily life. For example, we express the number of bananas or eggs in terms of 'dozen'. In chemistry we use a number unit called **mole** which is very large.

Objectives

After studying this lesson you will be able to :

- state the need of SI units;
- list base SI units;
- explain the relationship between mass and number of particles;
- define Avogadro's constant and state its significance;
- calculate the molar mass of different element and compounds and
- define molar volume of gases at STP.

1.1. SI Units (Revisited)

Measurement is needed in every walk of life. As you know that for every measurement a 'unit' or a 'reference standard' is required. In different countries, different systems of units gradually developed. This created difficulties whenever people of one country had to deal with those of another country. Since scientists had to often use each other's data, they faced a lot of difficulties. For a practical use, data had to be first converted into local units and then only it could be used.

In 1960, the 'General Conference of Weights and Measures." the international authority on units proposed a new system which was based upon the metric system. This system is called the "international System of Units' which is abbreviated as SI units from its French name, Le Systeme Internationale d'Unites. You have learned about SI units in your earlier classes also and know that they are based upon seven base units corresponding to seven base physical quantities. Units needed for various other physical quantities can be derived from these base SI units. The seven base SI units are listed in Table 1.1

Table 1.1 : SI Base Units

Physical Quantity	Name of SI Unit	Symbol of SI unit
Length	Metre	m
Mass	Kilogram	kg
Time	Second	s
Electrical current	Ampere	A
Temperature	Kelvin	K
Amount of substance	Mole	mol
Luminous intensity	Candela	cd

For measuring very large or very small quantities, multiples or sub-multiples of these units are used. Each one of them is denoted by a symbol which is **prefixed** to the symbol of the unit. For example, to measure long distances we use the unit **Kilometer** which is a multiple of metre, the base unit of length. Here **kilo is** the prefix used for the multiple 10^3. Its symbol is k which is prefixed to the symbol of metre, m. Thus symbol of kilometer is km and

$$1 \text{ km} = 1.0 \times 10^3 \text{ m} = 1000 \text{ m}$$

Similarly, for measuring small lengths we use centimetre (cm) and millimetre (mm) where

$$1 \text{ km} = 1.0 \times 10^{-2} \text{ m} = 0.01 \text{ m}$$

$$1 \text{ km} = 1.0 \times 10^{-3} \text{ m} = 0.001 \text{ m}$$

Some prefixes used with SI units are listed in Table 1.2.

Table 1.2 : Some Prefixes used with SI Units

Prefix	Symbol	Meaning	Example
Tera	T	10^{12}	1 terametre (Tm) = 1.0×10^{12} m
Giga	G	10^9	1 gigametre (Gm) = 1.0×10^9 m
Mega	M	10^6	1 megametre (Mm) = 1.0×10^6 m

Kilo	k	10^3	1 kilometre (km) = 1.0 x 10^3 m
Hecta	h	10^2	1 hectametre(hm) = 1.0 x 10^2 m
Deca	da	10^1	1 decametre (dam) = 1.0 x 10^1 m
Deci	d	10^{-1}	1 decimetre (dm) = 1.0 x 10^{-1} m
Centi	c	10^{-2}	1 centimetre (cm) = 1.0 x 10^{-2} m
Milli	m	10^{-3}	1 millimetre (mm) = 1.0 x 10^{-3} m
Micro	μ	10^{-6}	1 micrometre (mm) = 1.0 x 10^{-6} m
Nano	n	10^{-9}	1 nanometre (nm) = 1.0 x 10^{-9} m
Pico	p	10^{-12}	1 picometre (pm) = 1.0 x 10^{-12} m

Before proceeding further try to answer the following questions:

Intext Questions 1.1

1. Name the SI Unit of mass

   ....

2. What symbol will represent 1.0 x 10^{-6} g?

   ....

3. Name the prefixes used for (i) 10^2 and (ii) 10^{-9}

   ....

4. What do the following symbols represent ?

   i) Ms ii) ms

   i) ....

   ii) ....

1.2 Relationship between Mass and Number of Particles

Suppose you want to purchase 500 screws. How, do you think, the shopkeeper would give you the desired quantity? By counting the screws individually? No, he would give the screws by weight because it will take a lot of time to count them. If each screw weighs 0.8g, he would weight 400g screws because it is the mass of 500 screws (0.8 x 500 = 400g). You will be surprised to note that the Reserve Bank of India gives the desired number of coins by weight and not by counting. This process of *counting* by *weighing* becomes more and more labour saving as the number of items to be counted becomes large. We can carry out the reverse process also. Suppose we take 5000 very tiny springs (used in watches) and weigh them. If the mass of the springs is found to be 1.5g, we can conclude that mass of each spring is $1.5 \div 5000 = 3 \text{ x } 10^{-4}$ g.

Thus, we see that mass and number of identical objects or particles are inter-related. Since atoms and molecules are extremely tiny particles it is impossible to weigh or count them individually. Therefore we need a relationship between the mass and number of atoms and molecules (particles). Such a relationship is provided by 'mole concept'.

1.3 Mole - A Number Unit

Mass of an atom or a molecule is an important property. However, while discussing the quantitative aspects of a chemical reaction, the number of reacting atoms or molecules in more significant than their masses. Let us understand this with the help of the following activity.

Activity 1.1

Aim : To study whether during a reaction, the reactants react with each other in a simple ratio by mass.

What is required?

China dish, sulphur powder, iron powder, a magnet and a magnifying glass.

What to do?

Mix 1g each of iron and sulphur powders in china dish and heat them till the reaction is complete and the mixture becomes a hard mass. Now break it into small pieces. Repeat the procedure with a mixture of 2g of iron and 1g of sulphur powder.

What to observe?

- Pieces obtained from the '*reaction mixture containing iron and sulphur* in 1:1 *ratio by mass* (1g each) when observed through a magnifying glass show some yellowish particles of sulphur. When a magnet is brought near them, they are not attracted showing that there is no unreacted iron.
- Pieces obtained from the *reaction mixture containing iron and sulphur* in 2:1 *ratio by mass* (2g iron and 1g sulphur) do not show yellow particles of unreacted sulphur but are attracted by the magnet. This shows the presence of some unreacted iron.

Conclusion

You can conclude that iron and sulphur do not react with each other in a simple mass ratio. When taken in 1:1 ration by mass (Fe:S), some sulphur is left unreacted and when taken in 2:1 ration by mass (Fe:S) some iron is left unreacted.

Let us now write the chemical equation of this reaction

$$\mathrm{Fe + S \rightarrow FeS}$$

From the above chemical equation, it is clear that 1 atom of iron reacts with 1 atom of sulphur to form 1 molecule of iron (II) sulphide (FeS). It means that if we had taken equal *number* of atoms of iron and sulphur, both of them would have reacted completely. Thus we may conclude that *substances react in a simple ratio by number of atoms or molecules*.

From the above discussion it is clear that the *number* of atoms or molecules of a substance is more relevant than their masses. In order to express their number we need a number unit. One commonly used number unit is 'dozen', which, as you know, means a collection of 12. Other number units that we use are 'score' (20)) and 'gross' (144 or 12 dozens). These units are useful in dealing with small numbers only. The atoms and molecules are so small that even in the minute sample of any substance, their number is extremely large. For example, a tiny dust particle contains about 10^{16} molecules. In chemistry such large numbers are commonly represented by a unit known as **mole**. Its symbol is 'mol' and it is defined as.

A mole is the amount of a substance that contains as many elementary entities (atoms, molecules or other particles) as there are atoms in exactly 0.012 kg or 12g of the carbon-12 isotope.

The term mole has been derived from the Latin word '*moles*' which means a 'heap' or a 'pile'. It was first used by the famous chemist Wilhelm Ostwald more than a hundred years ago.

Here you should remember that one mole always contains the **same number of entities,** no matter what the substance is . Thus *mole* is a number unit for dealing with elementary entities such as atoms, molecules, formula units, electrons etc., just as *dozen* is a number unit for dealing with bananas or oranges. In the next section you will learn more about this number.

1.4 Avogadro's Constant

In the previous section we have learned that a mole of a substance is that amount which contains as many elementary entities as there are atoms in exactly 0.012 kilogram or 12 gram of the carbon-12 isotope. This definition gives us a method by which we can find out the amount of a substance (in moles) if we know the number of elementary entities present in it or *vice versa*. Now the question arises how many atoms are there in exactly 12g of carbon-12. This number is determined experimentally and its currently accepted value is 6.022045×10^{23}. Thus 1 mol = 6.022045×10^{23} entities or particles, or atoms or molecules.

For all practical purposes this number is rounded off to 6.022×10^{23}.

The basic idea of such a number was first conceived by an Italian scientist Amedeo Avogadro. But, he never determined this number. It was determined later and is known as Avogadro's constant in his honour.

This number was earlier known as *Avogadro's number*. This number alongwith the unit, that is, 6.022×10^{23} mol^{-1} is known as Avogadro constant. It is represented by the symbol N_A. Here you should be clear that mathematically a number does not have a unit. Avogadro's number 6.022×10^{23} will not have any unit but Avogradro's constant will have unit of mol^{-1}. Thus Avogradro's constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}.

Significance of Avogadro's Constant

You know that 0.012kg or 12g of carbon-12 contains its *one mole* of carbon atoms. A mole may be defined as the amount of a substance that contains 6.022×10^{23} elementary entities like atoms, molecules or other particles. When we say one mole of carbon-12, we mean 6.022×10^{23} atoms of carbon-12 whose mass is exactly 12g. This mass is called the *molar mass* of carbon-12. The ***molar mass*** *is defined as the mass (in grams) of 1 mole of a substance*. Similarly, a *mole of any substance* would contain 6.022×10^{23} particles or elementary entities. The nature of elementary entity, however, depends upon the nature of the substance as given below:

S.No.	Type of Substance	Elementary Entity
1.	Elements like Na, K, Cu which exist in atomic form	Atom
2.	Elements like O, N, H, which exist in molecular form (O_2, N_2, H_2)	Molecule
3.	Molecular compounds like NH_3, H_2O, CH_4	Molecule
4.	Ions like Na^+, Cu^{2+}, Ag^+, Cl^-, O^{2-}	Ion
5.	Ionic compounds like NaCl, $NaNO_3$, K_2SO_4	Formula unit

Formula unit of a compound contains as many atoms or ions of different types as is given by its chemical formula. The concept is applicable to all types of compounds. The following examples would clarify the concept.

Formula	Atoms / ions present in one formula unit
H_2O	Two atoms of H and one atom of O
NH_3	One atom of N and three atoms of H
NaCl	One Na^+ ion and one Cl^- ion
$NaNO_3$	One Na^+ ion and one NO_3^- ion
K_2SO_4	Two K^+ ions and one SO_4^{2-} ion
$Ba_3(PO_4)_2$	Three Ba^{2+} ions and two PO_4^{3-} ions

Now, let us take the examples of different types of substances and correlate their amounts and the number of elementary entities in them.

1 mole C = 6.022×10^{23} C atoms

1 mole O_2 = 6.022×10^{23} O_2 molecules

1 mole H_2O = 6.022×10^{23} H_2O molecules

1 mole NaCl = 6.022×10^{23} formula units of NaCl

1 mole Ba^{2+} ions = 6.022×10^{23} Ba^{2+} ions

We may choose to take amounts other than one mole and correlate them with number of particles present with the help of relation :

Number of elementary entities = number of moles x Avogadro's constant

1 mole O_2 = $1 \times (6.022 \times 10^{23})$ = 6.022×10^{23} molecules of O_2

0.5 mole O_2 = $0.5 \times (6.022 \times 10^{23})$ = 3.011×10^{23} molecules of O_2

0.1 mole O_2 = $0.1 \times (6.022 \times 10^{23})$ = 6.022×10^{22} molecules of O_2

Intext Questions 1.2

1. A sample of nitrogen gas consists of 4.22×10^{23} molecules of nitrogen. How many moles of nitrogen gas are there ?

   ....

2. In a metallic piece of magnesium, 8.46×10^{24} atoms are present. Calculate the amount of magnesium in moles.

   ....

3. Calculate the number of Cl_2 molecules and Cl atoms in 0.25 mol of Cl_2 gas.

   ....

1.5 Mole, Mass and Number Relationships

You know that 1 mol = 6.022×10^{23} elementary entities

and Molar mass = Mass of 1 mole of substance

= mass of 6.022×10^{23} elementary entities.

As discussed earlier the elementary entity can be an atom, a molecule, an ion or a formula unit. As far as mole - number relationship is concerned it is clear that one mole of any substance would contain 6.022×10^{23} particles (elementary entities). For obtaining the molar mass, i.e., mole-mass relationship we have to use atomic mass scale.

1.5.1 Atomic Mass Unit

By international agreement, a unit of mass to specify the atomic and molecular masses has been defined. This unit is called *atomic mass unit* and its symbol is 'amu'. The mass of one C-12 atom, is taken as exactly 12 amu. Thus, C-12 atom serves as the *standard*. The **Atomic mass unit** is defined as a mass exactly equal to the 1/12th of the mass of one carbon-12 atom.

$$1 \text{ amu} = \frac{\text{Mass of one C-12 atom}}{12}$$

Atomic mass unit also called **unified atomic mass unit** whose symbol is 'u'. Another name of atomic mass unit is **dalton** (symbol Da). The latter is mainly used in biological sciences.

1.5.2 Relative Atomic and Molecular Masses

You are aware that atomic mass scale is a *relative scale* with C-12 atom (also written as 12C) chosen as the standard. Its mass is taken as exactly 12. Relative masses of atoms and molecules are the number of times each atom or molecules is heavier than $^1/_{12}$th of the mass of one C-12 atom. Often, we deal with elements and compounds containing isotopes of different elements. Therefore, we prefer to use *average* masses of atoms and molecules. Thus

$$\text{Relative atomic mass} = \frac{\text{Average mass of 1 atom of the element}}{^1/_{12}\text{th of the mass of one C-12 atom}}$$

$$\text{and Rleative molecular mass} = \frac{\text{Average mass of 1 molecule of the substance}}{^1/_{12}\text{th of the mass of one C-12 atom}}$$

Experiemnts show that one O-16 atom is 1.333 times as heavy as one C-12 atom. Thus

$$\text{Relative atomic mass of O-16} = 1.333 \text{ x } 12 = 15.996 \simeq 16.0$$

The relative atomic masses of all elements have been determined in a similar manner. Relative molecular masses can aslo be determinsed experimentallty in a similar manner. In case we know the molecular formula of a molecule. we can calculate its relative molecular mass by adding the relative atomic masses of all its constituent atoms. Let us calculate the relative molecular mass of water, H_2O.

Relative molecular mass of water, H_2O = (2 x relative atomic mass of H) + (relative atomic mass of O)

= (2 x 1) + (16) = 2 + 16 = 18.

The relative atomic and molecular masses are just numbers and dimensionless, unit-less quantities.

1.5.3 Atomic, Molecular and Formula Masses

From the definition of atomic mass unit, we can calculate the atomic masses. Let us again take the example of oxygen-16 whose relative atomic atomic mass is 16. By definition.

$$\text{Relative atomic mass of O-16} = 16 = \frac{\text{mass of one O-16 atom}}{{}^{1}/_{12}\text{th of the mass of one C-12 atom}}$$

$$\text{Since 1 amu} = {}^{1}/_{12}\text{th the mass of one C-12 atom}$$

$$\therefore\ 16 = \frac{\text{mass of one O-16 atom}}{1\ \text{amu}}$$

Mass of one O-16 atom = 16 amu

Or Atomic mass of O-16 = 16 amu

From this example we can see that numerical value of the relative atomic mass and atomic mass is the same. Only, the former has no unit while the latter has the unit *amu*.

Molecular and formula masses can be obtained by adding the atomic or ionic masses of all the constituent atoms or ions of the molecule of formula unit respectively. Let us understand these calculations with the help of following examples.

Example 1.1 : Calculate the molecular mass of ammonia, NH_3.

Solution : One molecule of NH_3 consists of one N atom and three H atoms.

Molecular mass of NH_3 = (Atomic mass of N) + 3 (Atomic mass of H)

= [14+ (3x1)] amu

= 17 amu

Example 1.2 : Calculate the formula mass of sodium chloride (NaCl).

Solution : One formula unit of sodium chloride consists of one Na^+ ion and one Cl^- ion.

Formula mass of NaCl = (Ionic mass of Na^+) + Ionic mass of (Cl^-)

= 25 amu + 35.5 amu

= 58.5 amu

You would have noticed in the above example that ionic mass of Na^+ ion has been taken as 23 amu which is the same as the atomic mass of Na atom. Since loss or gain of few electrons does not change the mass significantly, therefore atomic masses are used as ionic masses. Similarly we havetaken ionic mass of Cl^- as 35.5 amu which is the same as the atomic mass of Cl^-.

1.5.4 Molar Masses

We know that molar mass is the mass of 1 mol of the substance. Also, 1 mol of any substance is the collection of its 6.022 x 10^{23} elementary entities. Thus

Molar mass = Mass of 6.022 x 10^{23} elementary entities.

i) Molar mass of an element

You know that the relative atomic mass of carbon-12 is 12. A 12g sample of it would contain 6.022 x 10^{23} atoms. Hence the molar mass of C-12 is 12g mol^{-1}. For getting the molar masses of other elements we can see relative atomic masses.

Since the relative atomic mass of oxygen -16 is 16, a 16g sample of it would contain 6.022 x 10^{23} oxygen atoms and would constitute its one mole. Thus, the molar mass of O-16 is 16g mol^{-1}. Relative atomic masses of some common elements have been listed the Table 1.3.

Table 1.3 : Relative atomic masses of some elements (upto 1st place of decimal)

Element	Relative Atomic Mass	Element	Relative Atomic Mass
Hydrogen, H	1.0	Phosphorus, P	31.0
Carbon, C	12.0	Sulphur, S	32.1
Nitrogen, N	14.0	Chlorine, Cl	35.5
Oxygen, O	16.0	Potassium, K	39.1
Sodium, Na	23.0	Iron, Fe	55.9

ii) Molar mass of a molecular substance

The elementary entity in case of a molecular substance is the molecule. Hence, *molar mass of such a substance would be the mass of its 6.022 x 10^{23} molecules*, whcih can be obtained from its relative molecular mass or by multiplying the molar mass of each element by the number of its moles present in one mole of the substance and then adding them.

Let us take the example of water, H_2O. Its relative molecular mass is 18. Therefore, 18g of it would contain 6.022 x 10^{23} molecules. Hence, its molar mass is 18 g mol^{-1}. Alternately we can calculate it as :

$$\begin{aligned}\text{Molar mass of water, } H_2O &= (2 \text{ x molar mass of H}) + (\text{molar mass of O}) \\ &= (2\text{x } 1 \text{ g mol}^{-1}) + (16\text{g mol}^{-1}) \\ &= 18\text{g mol}^{-1}\end{aligned}$$

Table 1.4 lists molecular masses and molar masses of some substances.

Table 1.4 : Molecular masses and molar masses of some substances

Element or Compound	Molecular mass / amu	Molar mass / (g mol^{-1})
O_2	32.0	32.0
P_4	124.0	124.0
S_8	256.8	256.8
H_2O	18.0	18.0
NH_3	17.0	17.0
HCl	36.5	36.5
CH_2Cl_2	85.0	85.0

iii) Molar masses of ionic compounds

Molar mass of an *ionic compound is the mass of its 6.022 x 10^{23} formula units.* It can be obtained by adding the molar masses of ions present in the formula unit of the substance. In case of NaCl it is calculated as.

Molar mass of NaCl = molar mass of Na^+ + molar mass of Cl^-

= (23g mol^{-1}) + (35.5g mol^{-1})

= 58.5 g mol^{-1}

Let us take some more examples of ionic compounds and calculate their molar masses.

Example 1.3 : Caclulate the molar mass of

i) K_2SO4 ii) $Ba_3(PO_4)_2$

Solution :

i) Molar mass of K_2SO_4 = (2 x molar mass of K^+) + (molar mass of SO_4^{2-})

= (2 x molar mass of K^+) +
(molar mass of of S + 4 x molar mass of O)

= [(2 x 39.1) + (32.1 + 4 x 16)] g mol^{-1}]

= (78.2 + 32.1 + 64) g mol^{-1} = 174.3 g mol^{-1}

ii) Molar mass of $Ba_3(PO_4)_2$ = (3 x molar mass of Ba^{2+}) + molar mass of PO_4^{3-})

= (3 x molar mass of Ba^{2+}) +
2 (molar mass of P + 4 x molar mass of O)

= [(3 x 137.3) + 2 (31.0 + 4 x 16.0)] g mol^{-1}]

= (411.9 + 190.0) g mol^{-1} = 601.9 g mol^{-1}

Now you have learned about the mole, mass and number relationships for all types of substances. The following examples would illustrate the usefulness of these relationships.

Example 1.4 : Find out the mass of carbon-12 that would contain 1.0×10^{19} carbon-12 atoms.

Solution : Mass of 6.022×10^{23} carbon-12 atoms = 12g

$$\text{Mass of } 1.0 \text{ x } 1019 \text{ carbon-12} = \frac{12 \times 1 \times 10^{19}}{6.022 \times 10^{23}} \text{ g}$$

$$= 1.99 \times 10^{-4} \text{ g}$$

Example 1.5 : How many molecules are present in 100g sample of NH_3 ?

Solution : Molar mass of $NH_3 = (14 + 3) \text{ gm mol}^{-1} = 17 \text{ g mol}^{-1}$

$\therefore$ 17g Sample of NH_3 contains 6.022×10^{23} molecules

$$\text{Therefore, 100g sample of } NH_3 \text{ would contain } \frac{6.022 \times 10^{23} \text{ molecule}}{17\text{g}} \times 100\text{g}$$

$$= 35.42 \times 10^{23} \text{ molecules}$$

$$= 3.542 \times 10^{24} \text{ molecules}$$

Example 1.6 : Molar mass of O is 16g mol^{-1}. What is the mass of one atom and one molecule of oxygen?

Solution : Mass of 1 mol or 6.022×10^{23} atoms of O = 16g.

$$\text{Mass of 1 atom of O} = \frac{16\text{g}}{6.022 \times 10^{23}}$$

$$= 2.66 \times 10^{-23}\text{g.}$$

Since a molecule of oxygen contains two atoms (O_2).

its mass = $2 \times 2.66 \times 10^{-23}\text{g} = 5.32 \times 10^{-23}\text{g}$.

Intext Questions 1.3

1. Calculate the molar mass of hydrogen chloride, HCl.

   ....

2. Calculate the molar mass of argon atoms, given that the mass of single atom is 6.634×10^{-26} kg.

   ....

3. Calculate the mass of 1.0 mol of potassium nitrate, KNO_3 (atomic masses : K = 39 amu; N = 14 amu, O = 16 amu).

   ....

4. The formula of sodium phosphate is Na_3PO_4. What is the mass of 0.146 mol of Na_3PO_4? (atomic masses : Na = 23.0 amu, P=31.0 amu; O = 16.0 amu)

   ....

1.6 Mass, Molar Mass and Number of Moles

Mass, molar mass number of moles of a substance are inter-related quantities. We know what :

Molar mass (M) = Mass of one mole of the substance.

Molar mass of water is 18g mol^{-1}. If we have 18g of water, we have 1mol of it. Suppose we have 36g water (18 x 2), we have 2 mol of it. In general in a sample of water of mass (n x 18) g, the number of moles of water would be n. We may generalize the relation as

$$\text{Number of moles (amount) of a substance} = \frac{\text{mass of the substance}}{\text{molar mass of the substance}}$$

$$n = \frac{m}{M}$$

$$m = n \times M$$

These relations are useful in calculations involving moles of substance.

Example 1.7 : In a reaction, 0.5 mol of aluminium is required. Calculate the amount of aluminium required in grams? (atomic mass of Al = 27 amu)

Solution : Molar mass of Al = 27g mol^{-1}

Required mass = no. of moles x molar mas.

= (0.5 mol) x (27g mol^{-1})

= 13.5 g

1.7 Molar Volume, V_m

Molar volume *is the volume of one mole of a substance*. It depends upon temperature and pressure. It is related to the density, by the relation.

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

In case of gases, we use thier volumes at **standard temperature and pressure (STP).** For the purpose **0^0C** or **273 K** temperature is taken as the **standard temperature** and **1 bar** pressure is taken as the **standard pressure**. At STP, the molar volume of an ideal gas is 22.7 litre*. You will study that gases do not behave ideally and therefore their molar volume is not exactly 22.7 L. However, it is very close to 22.7L and for all practical purposes we take the molar volume of all gases at STP as 22.7 L mol^{-1}.

Intext Questions 1.4

1. How many moles of Cu atoms are present in 3.05 g of copper (Relatine atomic mass of Cu = 63.5)

   ....

2. A piece of gold has a mass of 12.6 g. How many moles of gold are present in it ? (Relative atomic mass of Au = 197)

   ....

3. In a combustion reaction of an organic compound, 2.5 mol of CO_2 were produced. What volume would it occupy at STP (273K, 1 bar) ?

   ....

---

* Earlier 1 atmosphere pressure was taken as the standard pressure and at STP (273K, 1 atm) the molar volume of an ideal gas was taken as 22.4 L mol^{-1}. The difference in the value is due to the change in the standard pressure (1 bar) which is slightly less than 1 atm.

What You Have Learnt

- Mole is the amount of a substance which contains as may elementary entities as there are atoms present in 0.012 kg or 12g of C-12. Thus mole denotes a number.
- The number of elementary entities present in one mole of substance is 6.022×10^{23}.
- The mass of one mole of a substance is called its molar mass. It is numerically equal to relative atomic mass or relative molecular mass expressed in grams per mole (g mol^{-1}) or kilogram per mole (kg mol^{-1}).
- Molar volume is the volume occupied by one mole of a substance. One mole of an ideal gas at standard pressure and temperature, STP (273 K and 1 bar) occupies 22.7 litres.
- In ionic substances, molar mass is numerically equal to the formula mass of the compound expressed in grams.
- If the molar mass of a substance is known, then the amount of a substance present in a sample having a definite mass can be calculated. If M is the molar mass, then, the amount of substance n, present in a sample of mass m is expressed as $n = \frac{m}{M}$.

Terminal Exercise

1. How many atoms are present in a piece of iron that has a mass of 65.0 g / (atomic mass; Fe = 55.9 amu).
2. A piece of phosphorus has a mass of 99.2 g. How many moles of phosphorus, P_4 are present in it ? (atomic mass, P = 31.0 amu)
3. Mass of 8.46 x 10^{24} atoms of fluorine is 266.95g. Calculate the atomic mass of fluorine.
4. A sample of magnesium consists of 1.92 x 10^{22} Mg atoms. What is the mass of the sample in grams ? (atomic mass - 24.3 amu)
5. Calculate the molar mass in g mol^{-1} for each of the following.
   i) Sodium hydroxide, NaOH
   ii) Copper Sulphate $CuSO_4.5H_2O$
   iii) Sodium Carbonate, $Na_2CO_3.10H_2O$
6. For 150 gram sample of phosphorus trichloride (PCl_3), calculate each of the following:
   i) Mass of one PCl_3 molecule.
   ii) The number of moles of PCl_3 and Cl in the sample.
   iii) The number of grams of C1 atoms in the sample.
   iv) The number of molecules of $PC1_3$ in the sample
7. Find out the mass of carbon-12, that would contain 1 x 10^{19} atoms.
8. How many atoms are present in 100g sample of C-12 atom?
9. How many moles of $CaCO_3$ would weigh 5g ?
10. If you require 1.0 x 1023 molecules of nitrogen for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$.
    i) What is the mass (in grams) of N_2 required ?
    ii) How many moles of NH_3 would be formed in the above reaction from 1.0 x 10^{23} molecules of N_2 ?
    iii) What volume would NH_3 gas formed in ii) occupy at STP ?

Answers to Intext Questions

1.1

1. Kilogram
2. μg
3. i) h ii) n
4. i) Megasecond, 10^6 s

   ii) millisecond, 10^{-3} s.

1.2

1. Moles of N_2 gas = $\dfrac{4.22 \text{ x } 10^{23} \text{ molecules}}{6.022 \text{ x } 10^{23} \text{ molecules mol}^{-1}}$ = 0.70 mol

2. Amount of magnesium (moles = $\frac{8.46 \times 10^{24} \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}}$ = 14.05 mol

3. No. of Cl_2 molecules in 0.25 mol Cl_2 = 0.25 x 6.022 x 10^{23} molecules

= 1.5055 x 10^{23} molecules

Since each Cl_2 moecule has 2 Cl atoms, the number of Cl atoms = 2 x 1.5055 x 10^{23} = 3.011 x 10^{23} atoms.

1.3

1. Molar mass of hydrogen chloride = molar mass of HCl

= 1 mol of H + 1 mol of Cl

= 1.0 g mol^{-1} + 35.5 g mol^{-1}

= 36.5 g mol^{-1}

2. Molar mass of argon atoms = mass of 1 mol of argon

= mass of 6.022 x 10^{23} atoms of argon.

= 6.634 x 10^{-26} kg x 6.022 x 10^{23} mol^{-1}

= 39.95 x 10^{-3} kg mol^{-1}

= 39.95 g mol^{-1}

3. Molar mass of KNO_3 = mass of 1 mol of K + mass of 1 mol of N + mass of 3 mol of O.

Since molar mass of an element is numerically equal to its atomic mass but has the units of g mol^{-1} in place of amu = 39.1 g + 14.0 g + 3 x 16.0 g

∴ Molar mass of KNO_3 = 39.1 g + 14.0 g + 48.0 g = 101.1 g mol^{-1}

4. Mass of 1 mol of Na_3PO_4 = 3 x (mass of 1 mol of Na) + mass of 1 mol of P + 4 x (mass of 1 mol of oxygen)

= 3 (23.0 g) + 31.0 g + 4 (16.0) g

= 69.0 g + 31.0 g + 64.0 g = 164.0 g

∴ Mass of 0.146 mol of Na_3PO_4 = 0.146 x 164.0 g = 23.94 g

1.4

1. Moles of Cu atoms in 3.05 g copper = $\frac{3.05\text{g}}{63.5 \text{ g mol}^{-1}}$ = 0.048 mol

2. Moles of gold, Au = $\frac{12.6 \text{ g}}{197 \text{ g mol}^{-1}}$ = 0.064 mol

3. Molar volume of any gas at STP (298 K, 1 bar) = 22.7 L

∴ Volume occupied by 2.5 mol CO_2 at STP = 2.5 x 22.7 L = 56.75 L

2

CHEMICAL ARITHMATICS

We know that atoms of different elements combine in simple whole- number ratios to form molecules. For example, hydrogen and oxygen atoms combine in the mass ratio of 1:8 and form water, H_2O. However, it is impossible to deal with individual atoms because they are so tiny we can neither see nor weigh them. Therefore, we must increase the size of these quantities to the point where we can see them and weigh them. With the help of **mole concept** it is possible to take a desired number of atoms / molecules by weighing (please refer to lesson-1). Now, in order to study chemical compounds and reactions in the laboratory, it is necessary to have adequate knowledge of the quantitative relationship among the amounts of the reacting substances that take part and products formed in the chemical reaction. This relationship is know as stoichiometry. **Stoichiometry** (derived from the Greek *stoicheion* = element and *metron* = measure) is the term we use to refer to all the quantitative aspects of chemical compounds and reactions. In the present lesson, you will see how chemical formulae* are determined and how chemical equations prove useful in predicting the proper amounts of the reactants that must be mixed to carry out a complete reaction. In other words we can take reactants for a reaction in such a way that none of the reacting substances is in excess. This aspect is very vital in chemistry and has wide application in industries.

Objectives

After reading this lesson, you will be able to:

- Define empirical and molecular formulae;
- Differentiate between empirical and molecular formulae;
- Calculate percentage by mass of an element in a compound and also work out empirical formula from the percentage composition;
- Establish relationship between mole, mass and volume;
- Calculate the amount of substances consumed or formed in a chemical reaction using a balanced equation and mole concept, and
- Explain that the amount of limiting reagent present initially limits the amount of the products formed.

2.1. Molecular and Empirical Formulae

In your previous classes, you have studied how to write chemical formula of a substance. For example, water is represented by H_2O, carbon dioxide is represented by CO_2, methane is represented by CH_4, dinitrogen penta oxide is represented by N_2O_5, and so on. You are aware, formula for a molecule uses a symbol and subscript number to indicate the number of each kind of atoms present in the molecule (subscript 1 is always omitted). Such a formula is called **molecular formula** as it represents a molecule of a substance. A molecule of water consists of two hydrogen atoms and one oxygen atom. So its molecular formula is written as H_2O. Thus a **molecular formula shows the actual number of atoms of different elements in a molecule of a compound.**

There is another kind of formula, the empirical formula of a compound, which gives only relative number of atoms of different elements. These numbers are expressed as the simplest ratio. For example, empirical formula of glucose, which consists of carbon, hydrogen and oxygen in the ratio of 1:2:1 is CH_2O (empirical formulae are also called simplest formulae). Molecular formula = X_n where X is empirical formula and n is an integer). For example molecular formula of glucose is $C_6H_{12}O_6$ which is 6 x its empirical formula. Thus, while empirical formula gives only a ratio of atoms, the molecular formula gives the actual number of atoms of each element in an individual molecule. In some cases the ratio of atoms shown in a molecular formula cannot be reduced to smaller integers. In such cases molecular and empirical formulae are the same, for example, sucrose $C_{12}H_{22}O_{11}$ which is popularly known as cane-sugar. In case of certain elements, a molecule consists of several atoms for example P_4, S_8, etc. In such cases, empirical formula will be symbol of the element only.

As you know, common salt, which is chemically called sodium chloride is represented as NaCl. This salt is ionic in nature and does not exist in molecular form. Therefore, NaCl is its empirical formula which shows that sodium and chlorine atoms are present in NaCl in the ratio of 1:1. Similar is the case with all ionic substances. KCl, $NaNO_3$, MgO are examples of empirical formulae as these are all ionic compounds. Table 2.1 provides a few more examples.

Table 2.1 : Molecular and Empirical Formulae

Substance	Molecular formula	Empirical formula
Ammonia	NH_3	NH_3
Carbon dioxide	CO_2	CO_2
Ethane	C_2H_6	CH_3
Fructose	$C_6H_{12}O_6$	CH_2O
Sulphur	S_8	S
Benzene	C_6H_6	CH
Sodium chloride	-	NaCl
Calcium oxide	-	CaO

2.2. Chemical Composition and Formulae

How much carbon is present in one kilogram of methane whose molecular formula is CH_4? How much nitrogen is present in one kilogram of ammonia, NH_3 ? If we have prepared a substance that is made of 58.8% carbon, 28.4% oxygen, 8.28% nitrogen and 6.56% hydrogen, what is its empirical formula? You have studied **atomic masses**, **formulae**, and the **mole concept**. Can we solve the problem using these basic concepts? The answer is 'yes. Atomic masses, formulae and the mole concept are the basic tools needed to solve such problems. What is percentage composition? Let us take up this aspect in a little detail and try to understand.

2.2.1 Percentage Composition

If we know the formula of a compound, we can find out how much of each of the elements is present in a given quantity of the compound. Aluminium is obtained from its oxide. Al_2O_3 (which is found as the ore, bauxite). From the formula we can calculate how much aluminium can be obtained, at least in principle, frm a given amount of aluminium oxide. Calculation is done by making use of the idea of **percentage composition**.

Percentage mass of an element in a compound

$$\frac{\text{mass of element in one molecular formula or in one empirical formula}}{\text{molecular mass or empirical formula mass of compound}} = \text{x } 100$$

$$= \frac{\text{Mass of element in 1 mol of compound}}{\text{Molar mass of compound}} \text{ x } 100$$

Let us calculate percentage composition of aluminium oxide, Al_2O_3

$$\text{Percentage of Aluminium} = \frac{\text{Mass of aluminium in 1 mol } Al_2O_3}{\text{Molar mass of } Al_2O_3} \text{ x } 100$$

Molar mass of $A1_2O_3$ = (2 x 27.0) g + (3 x 16.0) g = 102.0 g

Since 1 mol of $A1_2O_3$ contains 2 mol of A1 atoms, the mass of Al is 2 x 27.0 g = 54.0 g Al

$$\text{Percentage of Aluminium} = \frac{54.0 \text{ g}}{102.0 \text{ g}} \text{ x } 100 = 52.9\%$$

We can calculate percentage of oxygen in the same way. One mole of $A1_2O_3$ contains 3 mole of O atoms, that is, 3 x 16.0g oxygen therefore

$$\text{Percentage of oxygen} = \frac{3 \text{ x } 16.0 \text{ g}}{102.0 \text{ g}} \text{ x } 100 = 47.1\%$$

Example 2.1 : Butanoic acid, has the formula $C_4H_8O_2$. What is the elemental analysis of butanoic acid ?

Solution : Molecular formula of the butanoic acid is $C_4H_8O_2$.

In one mole of butanoic acid there are 4 mol of carbon atoms. 8 mol of hydrogen atoms and 2 mol of oxygen atoms. Thus, 1 molar mass of butanoic acid will be equal to the sum of 4 x molar mass of carbon atoms, 8 x molar mass of hydrogen atoms, and 2 x molar mass of oxygen atoms.

Molar mass of butanoic acid = 4 x 12.0 g + 8 x 1.0 g + 2 x 16.0 g = 88.0 g

$$\text{Percentage of C by mass} = \frac{48.0 \text{ g}}{88.0 \text{ g}} \times 100 = 54.5\%$$

$$\text{Percentage of H by mass} = \frac{8.0 \text{ g}}{88.0 \text{ g}} \times 100 = 9.1\%$$

$$\text{Percentage of O by mass} = \frac{32.0 \text{ g}}{88.0 \text{ g}} \times 100 = 36.4\%$$

The percentage of O is butanoic acid can also be calculated as follows :

Percentage of O by mass = 100 - (Percentage of C by mass + Percentage of H by mass)

= 100 - (54.5 + 9.1) = 36.4%

2.2. Determination of Empirical Formulae - Formula Stoichiometry

We have just seen that if we know the formula of a compound we can calculate the percentage composition. Now the question arises, can we determine the formula of the compound if we know the percentage composition of compound. The answer will be 'yes', but this formula will not be molecular formula; instead it would be **empirical formula** as it would give simplest ratio of different atoms present in a compound. Normally we determine the percentag composition of different elements present in an **unknown compound** and determine its formula. Let us take a simple example of water. Water consists of 11.11% hydrogen and 88.89% oxygen by mass. From the data, we can determine empirical formula of water. Now if we assume that we have a 100.00 g sample of water, then the percentage composition tells us that 100.0 g of water contains 11.11 g of hydrogen atoms and 88.89 g of oxygen atoms.

From the atomic mass table, we find that 1 mol of hydrogen atoms has a mass of 1.0 g, and 1 mol of oxygen atoms has a mass of 16.0 g. Now we can write **unit conversion factors** so that the mass of hydrogen can be converted to moles of H atoms and the mass of oxygen can be converted to moles of O atoms. Since 1 mol of H atoms has a mass of 1.0g we get the conversion factor as

$$\frac{1 \text{ mol H atoms}}{1.0 \text{ g H}}$$

Therefore

$$11.11 \text{ g H} = (11.11 \text{ g H}) \frac{1 \text{ mol H atoms}}{1.0 \text{ g H}} = 11.11 \text{ mol H atoms}$$

Similarly conversion factor for oxygen will be

$$\frac{1 \text{ mol O atoms}}{16.0 \text{ g O}}$$

Therefore, $88.89 \text{ g O} = (88.89 \text{ g O}) \frac{1 \text{ mol O atoms}}{16.0 \text{ g O}} = 5.55 \text{ mol O atoms}$

Thus in water, the ratio of moles of hydrogen atoms to moles of oxygen atoms is 11.11:5.55.

Since a mole of one element contains the same number of atoms as a mole of another element, the ratio of moles of atoms in a compound is also the ratio of the number of atoms. Therefore, the ratio of hydrogen atoms to oxygen atoms is 11.1:5.55. Now by dividing each by the smaller of the two numbers we can convert both numbers to integers.

$$\frac{11.11}{5.55} = 2 \text{ and } \frac{5.55}{5.55} = 1.$$

Thus ratio hydrogen and oxygen atoms in water is 2:1 and empirical formula of water is H_2O.

Intext Questions 2.1

1. For the compound Fe_3O_4, calculate percentage of Fe and O.

   ....

2. State percent composition for each of the following :

   (a) C in $SrCO_3$ b) SO_3 in H_2SO_4

   ....

3. What are the empirical formulae of substances having the following molecular formulae ?

   H_2O_2, C_6H_{12}, Li_2CO_3, $C_2H_4O_2$, S_8, H_2O, B_2H_6, O_3, S_3O_9, N_2O_3

   ....

4. A compound is composed of atoms of only two elements, carbon and oxygen. If the compound contains 53.1% carbon, what is its empirical formula.

   ....

2.4 Chemical Equation and Reaction Stoichiometry

You have studied that a reaction can be represented in the form of a chemical equation. A balanced chemical equation carries a wealth of information qualitative as well as quantitative. Let us consider the following equation and learn what all information it carries.

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s) \qquad ...... (2.1)$$

(1) Qualitative Information

Qualitatively the equation (2.1) tells that iron reacts with oxygen to form iron oxide.

(2) Quantitative Information

Quantitatively a balanced chemical equation specifies numerical relationship among the quantities of its reactants and products. These relationships can be expressed in terms of :

i) **Microscopic quantities,** namely, atoms, molecules and formula units.

ii) **Macroscopic quantities,** namely, moles, masses and volumes (*in case of gaseous substances*) of reactants and products.

Now let us again take the reaction (2.1) given earlier and get the quantitative information out of it.

2.4.1 Microscopic Quantitative Information

The reaction (2.1)

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s) \qquad ...... (2.1)$$

tells that *4 atoms* of iron react with *3 molecules* of oxygen to form *2 formula units* of iron oxide. Often this information is written below each reactant and product for ready reference as shown below :

$$\underset{\textbf{4 atoms of Fe}}{4Fe(s)} + \underset{\textbf{3 molecules of }\mathbf{O_2}}{3O_2(g)} \longrightarrow \underset{\textbf{2 formula units of }\mathbf{Fe_2O_3}}{2Fe_2O_3(s)} \qquad ...... (2.1)$$

2.4.2 Macroscopic Quantitative Information

The microscopic quantitative information discussed in the previous section can be converted into macroscopic information with the help of mole concept which you have learnt in unit 1.

a) Mole Relationships

We know that Avogadro number of elementary entities like atoms, molecules, ions or formula units of a substance consitute one mole of it. Let us multiply the number of atoms, molecules and formula masses obtained in the previous section (Eq. 2.1a) by Avogadro's constant, N_A

$4Fe(s) \quad + \quad 3O_2(g) \quad \longrightarrow \quad 2Fe_2O_3(s)$ ...... (2.1)

4 atoms of Fe **3 molecules of O_2** **2 formula units of Fe_2O_3**

4 x N_A atoms of Fe 3 x N_A molecules of O_2 2 x N_A formula units of $Fe_2O_3(s)$

4 mol of Fe **3 mol of O_2** **2 mol of Fe_2O_3**

We may rewrite the above equation as

$4Fe(s) \quad + \quad 3O_2(g) \quad \longrightarrow \quad 2Fe_2O_3(s)$ ...... (2.1b)

4 mol of Fe **3 mol of O_2** **2 mol of Fe_2O_3**

The above equation (2.1b) gives us the mole relationship between reactants and products. Here *4 mol of Fe* react with *3 mol of O_2* and produce *2 mol of Fe_2O_3*.

b) Mass Relationships

The mole relationships which you have learnt in the previous section, can be converted into mass relationship by using the fact that mass of one mole of any substance is equal to its *molar mass* which can be calculated from its formula with the help of relative atomic masses of its constituent elements.

In the reaction that we are discussing, the relative atomic masses of iron and oxygen are 55.8 and 16.0 respectively. Therefore.

i) molar mass of Fe $= 55.8$ g mol^{-1}

ii) molar mass of O_2 $= 2 \times 16.0 = 32$ g mol^{-1}

iii) molar mass of $Fe_2\,O_3$ $= (2 \times 55.8 + 3 \times 16.0)$ g mol^{-1}

$= 159.6$ g mol^{-1}

Using these molar masses we can convert the mole relationship given by equation 2.1b into mass relationship as given below :

$4Fe(s) \quad + \quad 3O_2(g) \quad \longrightarrow \quad 2Fe_2O_3(s)$

4 mol Fe **3 mol O_2** **2 mol Fe_2O_3**

(4 x 55.8) g Fe (3 x 32) g O_2 $\longrightarrow$ (2 x 159.6) g Fe_2O_3

223.2 g Fe 96 g O_2 319.2 g FeO_3

Thus 223.2 g iron would react with 96g oxygen and produce 319.2 g iron oxide, We may rewrite the above equation as

$4Fe(s) \quad + \quad 3O_2(g) \quad \longrightarrow \quad 2Fe_2O_3(s)$ ...... (2.1c)

223.2 g Fe **96 g O_2** **319.2 g Fe_2O_3**

c) Volume Relationships

We know that one mole of *any gas* occupaies a volume of 22.7 L* at STP (standard temperature and pressure 0^0C and 1 bar pressure). We can use this information to arrive at volume relationships between gaseous substances. The reaction that we are considering involves only one gaseous substance, O_2. We may rewrite the equation (2.1b) as

$4Fe(s)$	+	$3O_2(g)$	$\longrightarrow$	$2Fe_2O_3(s)$	...... (2.1)
4 mol		**3 mol**		**2 mol**	
		(3 x 22.7) L at STP			
		68.1 L at STP			

Thus 4 mol of iron would react with 68.1 L of oxygen at STP to produce 2 mol of iron oxide. (The volume relationship becomes more useful for reactions involving 2 or more gaseous substances).

We can express microscopic as well macroscopic quantitative relationships involved in the above reaction as shown below.

$4Fe(s)$	+	$3O_2(g)$	$\longrightarrow$	$2Fe_2O_3(s)$
4 atoms		**3 molecules**		**2 formula units**
4 mol		3 mol		2 mol
223.2 g		96 g		319.2 g
-		68.1 L at STP		-

We may use even mixed relations. For example, we may say 4 mol of iron would react with 68.1 L (at STP) of oxygen to produce 319.2 g of iron oxide.

Let us understand these, relationships with two more examples.

a) Let us work out the mole, mass and volume relationships for the reaction involved in manufacture of ammonia by Haber's process.

Microscopic relationship	N_2 (g)	+	$3H_2$ (g)	$\longrightarrow$	$2NH_3$ (g)	..(2.2
Microscopic relationships	1 Molecules		3 Molecules		2 Molecules	
i) Moles	1 mol		3 mol		2 mol	
ii) Mass	28 g		(3x2.0) = 6.0g		(2x17.0) = 34 g	
iii) Wolume	1 x 22.7 L		(3 x 22.7)		(2 x 22.7)	
	= 22.7 L		= 68.1 L		= 45.4 L	
or	1 vol		3 vol		2 vol	

---

* Earlier, the standard pressure was taken as 1 atmosphere and the volume of one mole of gas at STP was taken as 22.4 L.

b) Let us take one more reaction, the combustion reaction of butane and work out the different types of relationships. The reaction is :

$2C_4H_{10}$ (g)	+	$13O_2$ (g)	$\longrightarrow$	$8CO_2$ (g)	+	$10H_2O$ (g)
2 molecues		13 molecules		8 molecules		10 molecules
2 mol		13 mol		8 mol		10 mol
2x(4x12+10x1g)		(13x32) g		8x(12+2x16) g		10x(2x1+16)g
116g		416g		352 g		180g
2x22.7=45.4L		13x22.7=295.1 L		8x22.7=181.6 L		10x22.7=227 L
2 vol		13 vol		8 vol		10 vol

Now let us use the mole, mass and volume reationships to make some calculations.

Eaxmple 2.2 In the manufacture of ammonia by Haber process, nitrogen reacts with hydrogen at high temperature and high pressure inthe presence of a catalyst and gives ammonia.

$$N_2\,(g) + 3H_2\,(g) \longrightarrow 2NH_3(s)$$

How much hydrogen would be needed to produce one metric ton of ammonia ?

Solution : We should first find out the mass relationships for the reaction.

N_2 (g)	+	$3H_2$ (g)	$\longrightarrow$	$2NH_3$(s)
1 mol		**3 mol**		**2 mol**
1x28g = 28 g		3x2g = 6.0 g		2x17g = 34 g

We know that :

1 metric ton = 1000 kg = 10^3 kg = 10^6 g

From the mass relationship 34 g NH_3 requires 6.0 g H_2 for its manufacture.

$\therefore$ 10^6g NH_3 would require $\dfrac{6.0\text{x}10^6}{34}$ g = 1.76 x 10^5g of H_2.

Thus 1 metric ton of ammonia will be obtained by using 1.176 x 10^5g of Hydrogen.

Example 2.3 In a rocket motor fuelled by butane, C_4H_{10}, how many kg of O_2 should be provided with each kg of butane to provide for complete combustion ?

Solution : The combustion reaction of butane is

$2C_4H_{10}$ (g)	+	$13O_2$ (g)	$\longrightarrow$	$8CO_2$ + $10H_2O$(s)
2 mol		**13 mol**		
2 x 58 = 116 g		**13 x 32 = 416 g**		

Thus, to completely burn 116g butane, exygen required is 416 g.

Therefore, to completely burn 1 kg (1000 g) butane, oxygen required will be

$$= \frac{416 \text{ x } 1000}{116} \text{ g } O_2$$

$$= 3586 \text{ g } O_2$$

$$= 3.586 \text{ kg } O_2 = 3.59 \text{ kg } O_2$$

Example 2.4 When lead sulphide; PbS and lead oxide, PbO, are heated together the product are lead metal and sulphur dioxide, SO_2.

$$PbS(s) \quad + \quad 2PbO(s) \xrightarrow{\text{heat}} 3Pb\,(1) \quad + \quad SO_2\,(g)$$

If 14.0 g of lead oxide reacts according to the above equation, how many (a) moles of lead (b) grams of lead, (c) atoms of lald and (d) grams of sulphur dioxide are formed?

(Atomic mass : Pb = 207.0, S = 32.1 ; O = 16.0

Solution : For each part of the question we well use the balanced equation

$$\underset{\textbf{1 mol}}{PbS(s)} \quad + \quad \underset{\textbf{1 mol}}{2PbO(s)} \xrightarrow{\text{heat}} \underset{\textbf{3 mol}}{3Pb\,(1)} \quad + \quad \underset{\textbf{1 mol}}{SO_2\,(g)}$$

Now formula mass of PbO = (207.0 + 16.0) = 223.0 amu

Thus, one mole of lead oxide formula units have a mass of 223.0 g. Therefore, 14.0 g of PbO is $\frac{14.0 \text{ g PbO}}{223.0 \text{ g mol}^{-1} \text{ PbO}} = 6.28 \text{ x } 10^{-2}$ mol PbO

a) The balanced equation show that 2 mol of PbO form 3 mol of Pb. Therefore, 6.28 x 10^{-2} mol of PbO form

$$6.28 \text{ x } 10^{-2} \text{ mol PbO x } \frac{3 \text{ mol Pb}}{2 \text{ mol PbO}} = 9.42 \text{ x } 10^{-2} \text{ mol Pb}$$

b) The atomic mass of Pb is 207.0; this tells us that one mol of lead has a mass 207.0g. Thus, 9.42 x 10^{-2} mol of Pb has a mass of

$$9.42 \text{ x } 10^{-2} \text{ mol Pb x } \frac{207.0 \text{ g Pb}}{1 \text{ mol Pb}} = 19.5 \text{ g Pb}$$

c) 9.42×10^{-2} mol of Pb is

9.42×10^{-2} mol of Pb x 6.022×10^{23} atoms mol^{-1} = 5.67×10^{22} Pb atoms

d) The balanced equation shows that 2 mol of PbO form 1 mol of SO_2.

$$6.28 \times 10^{-2} \text{ mol PbO} \times \frac{1 \text{ mol } SO_2}{2 \text{ mol PbO}}$$

$$= 3.14 \times 10^{-2} \text{ mol } SO_2$$

Now the relative molecular mass of $SO_2 = 32.1 + 2\,(16.0) = 64.1$

Molar mass of SO_2 = 64.1 g mol^{-1}

Therefore 3.41×10^{-2} mol of SO_2 molecules have a mass of 3.14×10^{-2} mol x 64.1 mol^{-1}

= 2.01 g

Intext Questions 2.2

1. How many grams of NH_3 can be made according to the reaction

   $N_2\,(g) \ + \ 3H_2\,(g) \ \longrightarrow \ 2NH_3(s)$

   from (a) 0.207 mol of N_2 (b) 22.6 g of H_2

   ....

2. In reaction

   $C_2H_4\,(g) \ + \ 3O_2\,(g) \ \longrightarrow \ 2CO_2\,(g) \ + \ 2H_2O(1)$

   How many (a) moles of O_2 are consumed and (b) moles of H_2O are formed when 4.16×10^{-2} mol of C_2H_4 react ?

   ....

2.5 Limiting Reagents

We generally find that substances which react with each other are not present in exactly the same proportionion a reaction mixture as stated by a balanced chemical equation. For example, if 2 mol each of hydrogen and oxygen are mixed and a spark is passed through the mixture, water is formed according to the equation.

$$\underset{\textbf{2 mol}}{2H_2} \quad + \quad \underset{\textbf{1 mol}}{O_2} \quad \longrightarrow \quad \underset{\textbf{2 mol}}{2H_2O}$$

Here, 2 mol of hydrogen react with only 1 mol of oxygen, and 1 mol of oxygen therefore remains unreacted. In this example hydrogen is said to be the limiting reagent or reactant because its amount becomes zero and the reaction therefore stops before the other reactant; that is, the oxygen is used up. The amount of hydrogen present initially limits the amount of product that is formed.

Example 2.5 3 mol of sulphur dioxide SO_2 is mixed with 2 mol of oxygen O_2, and after reaction is over sulphur trioxide, SO_3 is obtained.

i) Which is the limiting reagent ?

ii) What is the maximum amount of SO_3 that can be formed ?

Solution : i) We must first write the balanced equation

$$2SO_2 + O_2 \rightarrow 2SO_3$$

According to the above equation

a) 2 mol of SO_3 that can be formed from 3 mol of SO_2.

∴ Amount of SO_3 that can be formed from 3 mol of SO_2

$$= (3 \text{ mol } SO_2) \text{ x } \frac{2 \text{ mol } SO_3}{2 \text{ mol } SO_2} = 3 \text{ mol } SO_3$$

b) 2 mol of SO_3 can be formed from 1 mol of O_2. Therefore, the amount of SO_3 that can be formed from 2 mol of O_2.

$$= (2 \text{ mol } O_2) \text{ x } \frac{2 \text{ mol } SO_3}{1 \text{ mol } O_2} = 4 \text{ mol } SO_3$$

According to the definition, the limiting reactant is that reactant which gives the smallest amount. In this case SO_2 is the limiting reactant.

(ii) The maximum amount of product that can be obtained is the amount formed by the limiting reagent. Thus a the maximum amount of SO_3 that ca be obtained is 3 mol.

Example 2.6 2.3 g of sodium metal is introduced into a 2L flask filled with chlorine gas at STP (273 K, 1 bar). After reaction is over, find :

i) What is the limiting reagent in this reaction?

ii) How many moles of sodium chloride are formed ?

iii) Which substance is left unconsumed at the end of the reaction ? Find out its mass in grams.

iv) What percentage of the substance present in excess is converted into sodium chloride ?
(Given : Na = 23, Cl = 35.5)

Solution :

	2 Na (s)	+	Cl_2 (g)	$\rightarrow$	2NaCl
	2 mol		**1 mol**		**2 mol**
or			22.7 L at STP		

i) Moles of sodium introduced $= \dfrac{2.3 \text{ g}}{23 \text{ g mol}^{-1}} = 0.1$ mol

From the above equation, it is clear that 2 mol NaCl is formed from 2 mol Na

Therefore 0.1 mol Na can produce = $\frac{2 \text{ x } 0.1}{2}$ = 0.1 mol NaCl

Molar volume at STP = 22.7 L

Therefore moles of chlorine in 2 L volume at STP = $\frac{2\text{L}}{22.7\text{L mol}^{-1}}$ = 0.088 mol

From equation : 1 mol $C1_2$ can produce 2 mol NaCl

Therefore 0.088 mol Cl_2 can produce 2 x 0.088 = 0.176 mol NaCl.

ii) Sodium being the limiting reagent, as calculated in (i), the moles of NaCl produced = 0.1 mol

iii) From above equation, 2 mol NaCl is produced from 1 mol Cl_2

Therefore 0.1 mol NaCl is produced from $\frac{1 \text{ x } 0.1}{2}$ = 0.05 mol Cl_2

Initial moles of Cl_2 = 0.088 mol

Moles of Cl_2 left unconsumed = (0.088 - 0.05) mol = 0.038 mol

Therefore, mass of Cl_2 left unconsumed = 0.038 g x 71.0 g mol^{-1} = 2.698 g

(because molar mass of Cl_2 = 2 x 35.5 = 71.0 g mol^{-1})

iv) Moles of Cl_2 comsumed = 0.05 mol out of 0.088 mol

∴ Percent of Cl_2 consumed and converted into NaCl = $\frac{0.05}{0.088}$ x 100 = 56.8%

Eaxmple 2.7 : 2.0 g mixture of $MgCO_3$ and $CaCO_3$ are heated till no further loss of weight takes place. The residue weighs 1.04g. Find the percentage composition of the mixture. (Mg = 24, Ca = 40, C = 12, O = 16)

Solution : Mixture of $MgCO_3$ and $CaCO_3$ taken = 2.0 g

Let the mass of $MgCO_3$ be = *x* g

Therefore the mass of $CaCO_3$ = (2.0 - *x*) g

The decomposition reactions are

$$\underset{\substack{\textbf{(24+12+48) g}\\ \textbf{84 g}}}{MgCO_3\,(g)} \longrightarrow \underset{\substack{\textbf{(24+16) g}\\ \textbf{40 g (Residue)}}}{MgO\,(s)} + CO_2\,(g) \qquad \text{(i)}$$

$CaCO_3$ (g)	$\longrightarrow$	CaO (s)	+	CO_2 (g)	(ii)
(40+12+48) g		**(40+16) g**			
100 g		**56 g (Residue)**			

Form the equation (i)

84 g $MgCO_3$ leave a residue = 40 g

$$x \text{ g } MgCO_3 \text{ will leave residue } = \frac{40x}{84} \text{ g}$$

Form the equation (ii)

100 g $CaCO_3$ leave a residue = 56 g

$$(2.0 - x) \text{ g } CaCO_3 \text{ will leave residue } = \frac{56 \times (2.0 - x)}{100} \text{ g}$$

$$\text{Total mass of the residue} = \frac{40x}{84} + \frac{56 \times (2.0 - x)}{100} = 1.04 \text{ g (given)}$$

$$\begin{aligned} 40 \times 100x + 84 \times 56 \times 2 - 84 \times 56x &= 84 \times 100 \times 1.04 \\ 4000x + 9408 - 4704x &= 8736 \\ 9408 - 8736 &= (4704 - 4000)x \\ 672 &= 704x \end{aligned}$$

$$\text{Therefore, mass of } MgCO_3 \text{ in the mixture} = x = \frac{672}{704} = 0.96 \text{ g}$$

$$\text{Therefore, percentage of } MgCO_3 = \frac{0.96}{2.0} \times 100 = 48\%$$

and percentage of $CaCO_3$ = 100 - 48 = 52%

What You Have Learnt

- A chemical formula is used not only to represent the name of a compound but also to indicate its composition in terms (i) relative number of atoms and (ii) relative number of moles of atoms.
- A molecular formula of a substance shows (i) the number of atoms of different elements in one molecule. (ii) the number of moles of atoms of different elements in one mole of molecule.
- An empirical formula shows only a ratio of (i) number of atoms, and (ii) moles of atoms in a compound.

- Molecular formula is always an integral multiple of the empirical formula
- The empirical formula of a compound can be determined from its chemical analysis.
- In order to determine a compound's molecular formula, molecular mass also must be known.
- Stoichiometry is the quantitative study of the composition of chemical compounds (compound or formula stoichiometry) and of the substances consumed and formed in chemical reactions (reaction or equation stoichiometry).
- Chemical equations specify not only the identities of substances consumed and formed in a reaction, but also relative quantities of these substances in terms of (a) atoms, molecules and formula units and (b) moles of these entities.
- A balanced chemical equation demonstrates that all the atoms present in the reactants are accounted for in the product; atoms are neither created nor destroyed in a reaction.
- The stoichiometric rations among the moles of reactants shown in a balanced equation are useful for determining which substance is entirely consumed and which substance(s) is (are) left over.

Terminal Exercise

1. Write empirical formulae of the following compounds:

   CO, Na_2SO_3, C_4H_{10}, H_2O_2, KCl

   ....

2. The empirical formula of glucose is CH_2O which has a formula mass of 30 amu. If the molecular mass of glucose is 180 amu. Determine the molecular formula of glucose.

   ....

3. What is ratio of masses of oxygen that are combined with 1.0 gram of nitrogen in the compound NO and N_2O_3 ?

   ....

4. A compound containing sulphur and oxygen on analysis reveals that it contains 50.1% sulphur and 49.9% oxygen by mass. What is simplest formula of the compound?

   ....

5. Hydrocarbons are organic compound composed of hydrogen and carbon. A, 0.1647 g sample of a pure hydrocarbon on burning in a combustion tube produced 0.5694 g of CO_2 and 0.0845 g of H_2O. Determine the percentage of these elements in the hydrocarbon.

   ....

6. On combustion 2.4g of a compound of carbon, hydrogen and oxygen gave 3.52 of CO_2 and 1.44 g of H_2O. The molecular mass of the compound was found to be 60.0 amu.

   a) What are the masses of carbon, hydrogen and oxygen in 2.4 g of the compound ?

   ....

b) What are the empirical and molecular formulae of the compound ?

....

7. i) What mass of oxygen is required to react completely with 24g of CH_4 in the following reaction?

$C_2H_4 (g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2H_2O(1)$

....

(ii) How much mass of CH_4 would react with 96 g of oxygen.

....

8. Inthe reaction $H_2 + Cl_2 \longrightarrow 2HCl$

How many grams of chlorine, Cl_2 are needed to react completely with 0.245 g of hydrogen, H_2, to give hydrogen chloride, HCl ? How much HCl is formed ?

....

9. 3.65 g of H_2 and 26.7 g of O_2 are mixed and reacted. How many grams of H_2O are formed ?

....

10. Cuastic soda NaOH can be commercially prepared by the reaction of Na_2CO_3 with slaked lime, $Ca(OH)_2$. How many grams of NaOH can be obtained by treating 2.0 kg of Na_2CO_3 with $Ca(OH)_2$?

....

11. A potable hydrogen generator utilizes the reaction

$CaH_2 + H_2O \longrightarrow Ca(OH)_2 + 2H_2$

How many grams of H_2 can be produced by a 100 g cartridge of CaH_2 ?

....

12. The reaction $2Al + 3MnO \longrightarrow Al_2O_3 + 3Mn$ proceeds till the limiting substance is consumed. A mixture of 220g Al and 400g MnO was heated to initiate the reaction. Which initial substance remained in excess and by how much ? (Al = 27, Mn = 55).

....

13. $KClO_4$ may be prepared by means of following series of reactions

$Cl_2 + 2KOH \longrightarrow KCl + KClO + H_2O$

$3KClO \longrightarrow 2KCl + KClO_3$

$4KClO_3 \longrightarrow 3KClO_4 + KCl$

How much Cl_2 is needed to prepare 400 g $KClO_4$ by the above sequence ?

(K = 39, Cl = 35.5, O = 16, H = 1)

....

14. 2.0 g of mixture of Na_2CO_3 and $NaHCO_3$ was heated when its weight reduced to 1.876 g. Determine the percentage composition of the mixture.

....

15. Calculate the weight of 60% sulphuric required to decompose 150g of chalk (calcium carbonate). Given Ca = 40, C = 12, O = 16, S= 32)

....

Answers to Intext Questions

2.1

1. Molar mass of Fe_3O_4 $= 3 \times 56.0 + 4 \times 16.0$

$= (168.0 + 64.0) = 232.0 \text{ g mol}^{-1}$

Percentage of Fe $= \frac{168.0}{232.0} \times 100 = 72.41\%$

Percentage of O $= \frac{64.0}{232.0} \times 100 = 27.59\%$

2. a) Molar mass of $SrCO_3 = 87.6 + 12.0 + 48.0 = 147.6 \text{ g mol}^{-1}$

Percentage of carbon C in $SrCO_3 = \frac{12.0}{147.6} \times 100 = 8.13\%$

b) Molar mass of $H_2SO_4 = 2.0 + 32.1 + 64.0 = 98.1 \text{ g mol}^{-1}$

Molar mass of $SO_3 = 32.1 + 48.0 = 80.1 \text{ g mol}^{-1}$

Percentage of SO_3 in H_2SO_4 $= \frac{80.1 \times 100}{98.1} \times 81.65\%$

3.

Substance	**Empirical formula**
H_2O_2	HO
C_6H_{12}	CH_2
Li_2CO_3	Li_2CO_3
$C_2H_4O_2$	CH_2O
S_8	S
H_2O	H_2O
B_2H_6	BH_3
O_3	O_3
S_3O_9	SO_3
N_2O_3	N_2O_3

4. Percentage of carbon = 53.1%

Percentage of Oxygen = 46.9%

Suppose we take 100g of the substance then moles of carbon = $\frac{53.1}{12.0}$ g = 4.43 mol

mole of oxygen = $\frac{46.0}{16.0}$ = 2.93 mol

molar ration of C and O = $\frac{4.43}{2.93} : \frac{2.93}{2.93}$

= 1.50 : 1 or 3 : 2

Empirical formula of the compound is C_3O_2.

2.2

1. In equation

$$N_2\,(g) \quad + \quad 3H_2\,(g) \quad \longrightarrow \quad 2NH_3(s)$$

1 mol **3 mol** **2 mol**

0.207 mol N_2 gives 0.414 mol of NH_3

0.414 mol of NH_3 = 0.414 mol x 17.0 g mol^{-1} = 7.038 of NH_3

22.6 g of Hydrogen = $\frac{22.6}{2.0}$ = 11.3 mol of hydrogen

11.3 mol of hydrogen will give 2/3 x 11.3 mol of NH_3 = 7.53 mol

Therefore, Mass of NH_3 = 7.53 mol x 17.0 g mol^{-1} = 128.01 g

2. $C_2H_4\,(g) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O(g)$

1 mol **3 mol** **2 mol** **2 mol**

a) 4.16 x 10^{-2} mol of C_2H_4 will consume 3 x 4.16 x 10^{-2} mol of oxygen

= 12.48 x 10^{-2} = 1.248 x 10^{-1} mol of O_2

b) moles of H_2O formed = 2 x 4.16 x 10^{-2} mol

= 8.32 x 10^{-2} mol of H_2O

3

ATOMIC STRUCTURE

Chemistry has been defined as the study of matter in terms of its structure, composition and the properties. As you are aware, matter is made up of atoms, and therefore an understanding of the structure of atom is very important. You have studied in your earlier classes that the earliest concept of atom (smallest indivisible part of matter) was given by ancient (600-400 BC) Indian and Greek philosophers. At that time there was no experimental evidence. The origin of the concept of atom was based on their thoughts on 'What would happen if we continuously keep dividing matter'. John Dalton revived the concept of atom in the beginning of nineteenth century in terms of his atomic theory which successfully explained the laws of chemical combination. Later experiments showed that the atom is not indivisible but has an internal structure.

In this lesson you will learn about the internal structure of an atom which will help you to understand the correlations between is structure and properties. You would learn about these in the later lessons.

Objectives

After reading this lesson you will be able to:

- recognize the fundamental particles of atom;
- describe Rutherford's experiment and explain its results;
- define electromagnetic radiation;
- list and define the characteristic parameters of electromagnetic radiation;
- discuss line spectrum of hydrogen;
- explain Bohr's postulates and discuss his model;
- draw energy level diagram of hydrogen atom showing different series of lines in its spectrum;

- explain wave particle duality of matter and radiation;
- formulate Heisenberg's uncertainty principle;
- explain the need for quantum mechanical model;
- draw probability pictures of an electron in an atom;
- list quantum numbers and discuss their significance;
- draw the shapes of s,p and d orbitals;
- recognize nodal plane;
- explain Pauli's exclusion principle;
- define Aufbau principle and
- explain Hund's rule of maximum multiplicity.

3.1 Fundamental Particles of Atom

In 1897 J.J. Thomson discovered electron as a constituent of atom. He determined that an electron had a negative charge and had very little mass as compared to that of the atom. Since an atom was found to be electrically neutral it was inferred that some source of positive charge must be present in the atom. This soon led to the experimental discovery of the proton, which is a positively charged subatomic particle. Proton was found approximately 1840 times heavier than an electron. Further experiments revealed that the atomic masses were more than that expected from the presence of just protons and electrons in the atom. For example, the mass of helium atom was expected to be double that of hydrogen atom but was actually found to be almost four times the mass of hydrogen atom. This suggested the presence of neutral particles with mass comparable to that of protons in the atom. Sir James Chadwick discovered this neutral particle and called it **neutron** subsequently in 1932. Thus we may conclude that atoms are not indivisible but are made up of three fundamental particles whose characteristics are given in Table 3.1.

Table 3.1 Fundamental particles and their characteristics

Particle	Symbol	Mass / kg	Actual Charge / C	Relative charge
Electron	***e***	$9.109\ 389 \times 10^{-31}$	$-\ 1.602\ 177 \times 10^{-19}$	-1
Proton	***p***	$1.672\ 623 \times 10^{-27}$	$1.602\ 177 \times 10^{-19}$	+1
Neutron	***n***	$1.674\ 928 \times 10^{-27}$	0	0

Since atoms are made up of still smaller particles, they must have an internal structure. In the next section we shall take up some of the earlier ideas about the internal structure of atom.

Intext Questions 3.1

1. Compare the mass of an electron with that of the proton.

   ....

2. What is a fundamental particle?

   ....

3. What is the name given to neutral particles in the atom?

   ....

3.2 Earlier Models

Once it was established that the atom is not indivisible, the scientists made attempts to understand the structure of the atom. A number of models have been proposed for the internal structure of the atom. The first attempt to describe the structure of atom in terms of a model was made by J.J. Thomson.

3.2.1 Thomson's Model

On the basis of his experiments on discharge tubes. Thomson proposed that atoms can be considered as a large positively charged body with a number of small negatively charged electrons scattered throughout it. This model (Fig. 3.1) was called as plum pudding model of the atom.

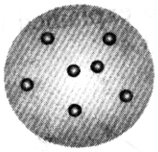
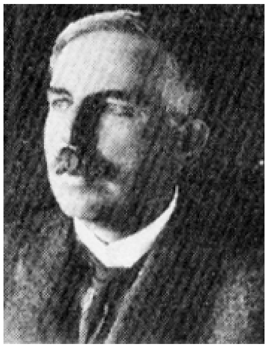


Fig 3.1 : *A pictorial representation of Thomson's plum-pudding model*

The electrons represent the plums in the pudding made of positive charge. It is sometimes also called as **watermelon model.** In this, the juicy pulp of the watermelon represents the positive charge and the seeds represent the electrons.

J.J. Thomson
(1856-1940)
Won Nobel Prize in Physics in 1906



Ernest Rutherford
(1871-1937)
Won Nobel Prize in Chemistry in 1908

3.2.2 Rutherford's Experiment

Ernest Rutherford performed an experiment called 'God Foil Experiment' or 'a- ray scattering experiment' to test the structure of an atom as proposed by Thomson. In this experiment a beam of fast moving alpha particles (positively charged helium ions) was passed through a very thin foil of gold. He expected that the alpha particles would just pass straight through the gold foil and could be detected by a photographic plate. But, the actual results of the experiment (Fig. 3.2) were quite surprising. It was observed that most of the α - particles did pass straight through the foil but a number of particles were deflected from their path. Some of these deflected slightly while a few deflected through large angles and about 1 in 10,000 α- particles suffered a rebound.

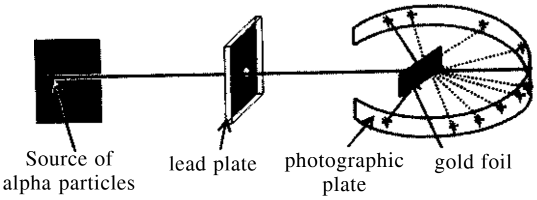


Fig. 3.2 *Schematic representation of Rutheford's α–ray scattering experiment.*

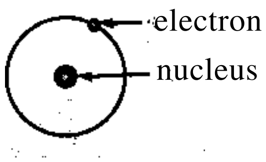


Fig. 3.3 *: Schematic representation of Rutherford's model*

These results led Rutherford to conclude that:

- the atom contained some dense and positively charged region located at the center of the atom that he called as **nucleus.**
- all the positive charge of the atom and most of its mass was contained in the nucleus.
- the rest of the atom must be empty space which contains the much smaller and negatively charged electrons (Fig. 3.3).

The model proposed by Rutherford explained the observation in the α–ray scattering experiments as shown below in Fig. 3.4.

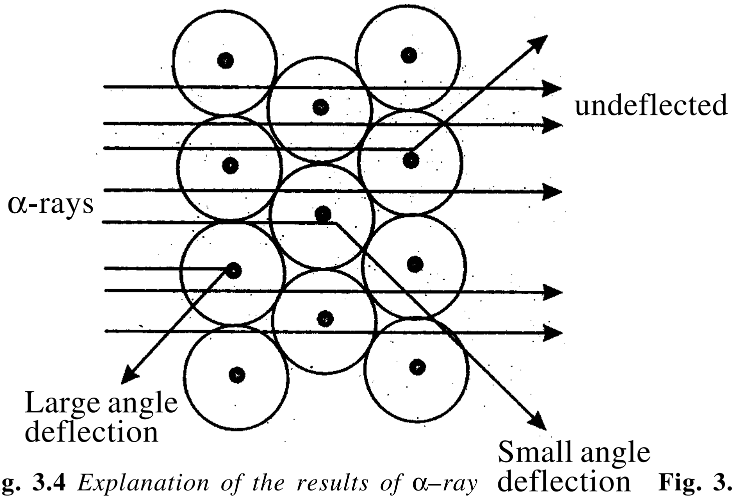


Fig. 3.4 *Explanation of the results of α–ray scattering experiment.*

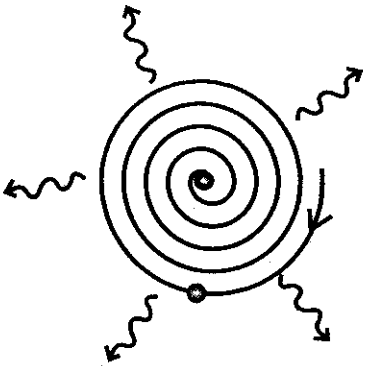


Fig. 3.5 *: Failure of Rutherford's model*

However, there was a problem with the Rutherford's model. According to the Maxwell's theory of electromagnetic radiation, a charged particle undergoing acceleration would continnously emit radiation and lose energy. Since the electron in the atom is also a charged particle and is under acceleration, it is expected to continuosly lose energy. As a consequence, the eletron moving around the nucleus would approach the nucleus by a spiral path (Fig. 3.5) and the atom would collapse. However, since it does not happen we can say that the Rutherford's model failed to explain the stability of the atom.

The next attempt to suggest a model for atom was made by Neils Bohr-a student of Rutherford. This model used the concept of quantisation of energy of electrons in the atom. Since this fact was suggested by line spectrum of hydrogen atom it is worthwhile to understand the meaning of a spectrum. For this we begin with the understanding of the nature of an electromagnetic radiation.

Intext Questions 3.2

1. List the three consituent particles of an atom.

   ....

2. What was the aim of Rutherford's a-rays scattering experiment ?

   ....

3. Briefly describe Rutherford's model of an atom.

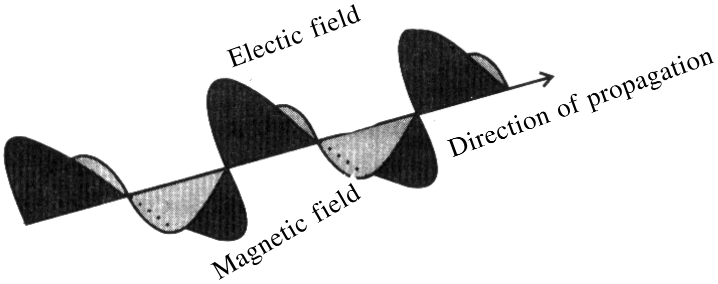
   ....

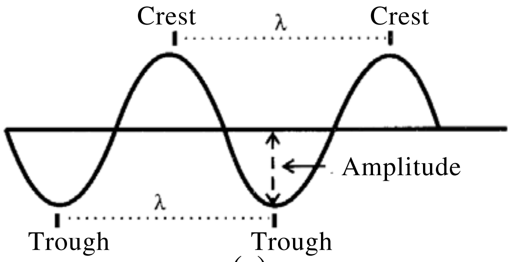
4. On what basis was the Rutherford's model rejected ?

   ....

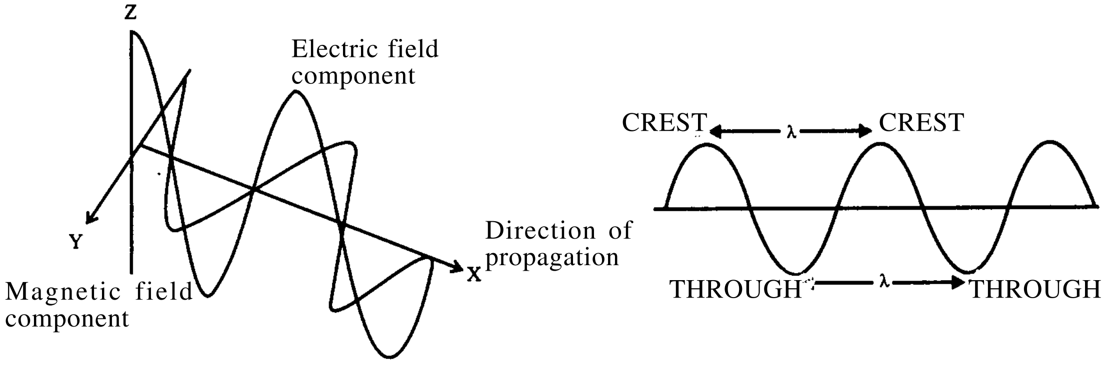
3.3 Electromagnetic Radiations

Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. These do not require any medium to propagate. Visible light, radiant heat, radio waves, X-rays and gamma radiation are some of the examples of electromagnetic radiations. According to the Maxwell's theory, an electromagnetic radiation can be visualised as oscillating electric and magnetic fields. These travel as waves in the planes perpendicular to each other and also the direction of propagation. (Fig. 3.6 (a)). These radiations travel with the velocity of light ($3.0 \times 10^8 ms^{-1}$).





(a)



(a) (b)

Fig. 3.6 : *(a) An electromagnetic wave showing electric and magnetic fields travelling in planes perpendicular to each other and also to the direction of propagation (b) Characteristics of electromagnetic wave*

3.3.1 Characteristic Parameters of Electromagnetic Radiations

The electromagnetic radiations are characterized by a number of parameters. These are

Amplitude : This is refers to the **maximum height to which the wave oscillates.** It equals the height of the crests or depth of the troughts.

Wavelength : It is the linear **distance between two consecutive wave-crests or wave-troughts** as shown in Fig. 3.6(b). It is represented by a Greek letter lambda (λ) and is expressed in terms of m, cm, nm or Angstrom ($1A^o = 10^{-10}$ m).

Frequency : It is defined as the **number of wave crests or wave troughs that pass through a given point per second.** It is represented by a Greek letter nu (ν) and is expressed in terms of s^{-1} (second inverse or per second). It is also called as Hz (Hertz).

Wave number : It equals **the number of waves per unit length.** It is denoted as $\bar{\nu}$ (nu bar) and is equal to the reciprocal of the wavelength. The SI of ν is m^{-1} (meter inverse). However, sometimes it is also expressed as cm^{-1} (centimeter inverse).

$$\bar{\nu} = \frac{1}{\lambda} \qquad .... (3.1)$$

Velocity : it is defined as the linear **distance travelled by the wave in one second.** The velocity in meters per second can be obtained by multiplying frequency in Hertz (s^{-1}) with wavelength in meters.

$$c = \nu \lambda \qquad \text{or} \qquad \nu = \frac{c}{\lambda} \qquad \text{.... (3.2)}$$

The velocity of a radiation depends on the medium. In vaccum the velocity is equal to 3.00 x 108 m s^{-1}.

The electromagnetic radiations also show the characteristics of particles. These are called as *quanta*. These quanta are actually bundles of energy. A quantum of visible light is called a photon. The energy of the quantum (or photon) is proportional to the frequency of the radiation. The two are related as

$$E = hv \qquad \text{.... (3.3)}$$

The energy of the quantum can also be related to the wavelength or wave number as

$$E = h\frac{c}{\lambda} \quad \text{or} \quad E = hc\bar{v} \qquad \text{.... (3.4)}$$

the energy of photon can be readily calculated from these equations if we know the frequency, wavelength or wave number.

Example 3.1 : A microwave radiation has a frequency of 12 gigahertz. Calculate the energy of the photon corresponding to this radiation. ($h = 6.626 \times 10^{-34}$ J s and 1 gigahertz = 10^9 Hz.)

Solution : The energy is given by the expression, $E = hv$
Substituting the values we get,

$$E = 6.626 \times 10^{-34} \text{ Js} \times 1.2 \times 10^{10} \text{ s}^{-1} = 7.95 \times 10^{-24} \text{ J}$$

Example 3.2 : The green light has a wavelength of 535 nm. Calculate the energy of a photon of green light.

Solution : We know that

$$E = hv = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js}) \times (3.0 \times 10^{8} \text{ ms}^{-1})}{535 \times 10^{-9} \text{ m}} = 3.71 \times 10^{-19} J$$

3.3.2 Electromagnetic Spectrum

Depending on their characteristics (wavelength, frequency and wave number) electromagnetic radiations are of many types and constitute what is called as an electromagnetic spectrum. (Fig. 3.7) The part of the spectrum that we can see is called visible spectrum and is a very small part of the overall spectrum.

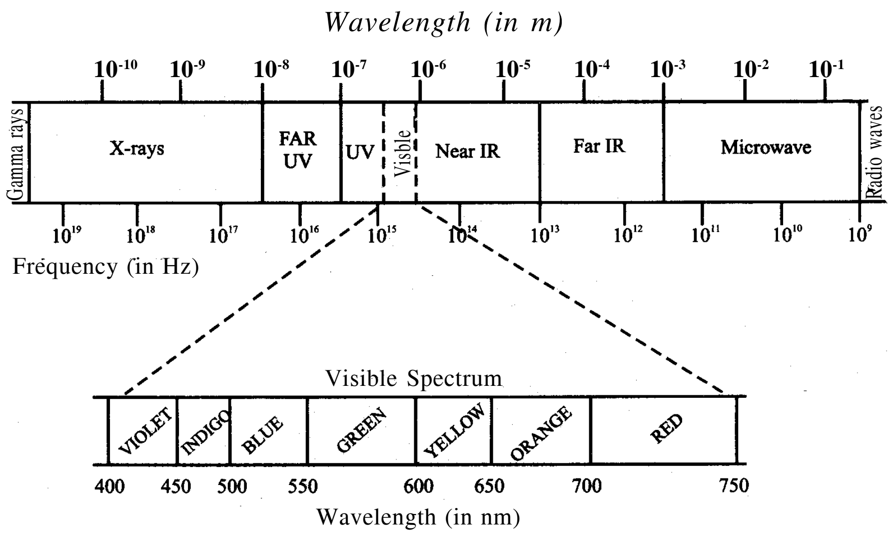


Fig. 3.7 : *The electromagnetic spectrum*

Intext Questions 3.3

1. What is an electromagnetic radiation ?

   ....

2. List any three characteristics of electromagnetic radiation.

   ....

3. What is wave number? How is it related to wave length ?

   ....

4. What is the difference between a ‘quantum’ and a ‘photon’ ?

   ....

3.4 Line Spectrum

You know that when we pass a beam of sunlight through a prism we get a range of colours from violet to red (VIBGYOR) in the form of a spectrum (like rainbow). This is called a ***continuous spectrum*** because the wavelengths of the light varies continuously that is without any break. Let us take another example. You are aware of the flame tests for identifying cations in the qualitative analysis. Compounds of sodium impart a bright yellow colour to the flame, copper gives a green flame while strontium gives a crimson red coloured flame. If we pass such a light through a prism it gets separated into a set of lines. This is called as *line spectrum*. Fig. 3.8 differentiates between a continuous and a line spectrum.

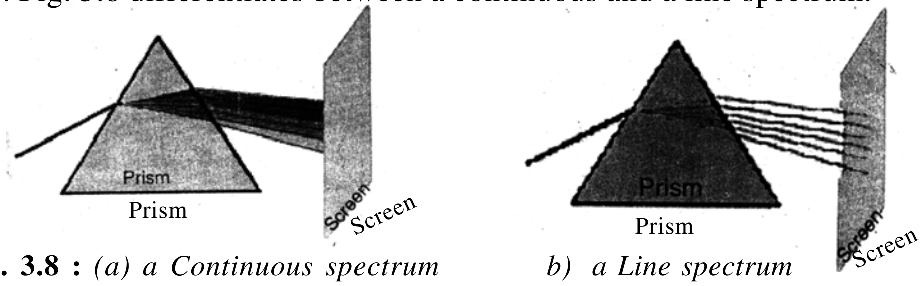
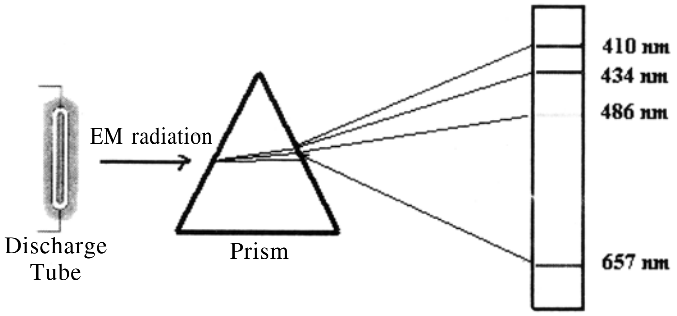


Fig. 3.8 : *(a) a Continuous spectrum* *b) a Line spectrum*

3.4.1 Line Spectrum of Hydrogen Atom

When an electric discharge is passed through a discharge tube containing hydrogen gas at low pressure, it emits some light. When this light is passed through a prism it splits up into a set of five lines. This spectrum is called the *line spectrum of hydrogen* (Fig. 3.9).




Johann Balmer
(1825-1898

Fig. 3.9 : *A schematic diagram showing line spectrum of hydrogen in the visible range*

On careful analysis of the hydrogen spectrum it was found to consist of a few sets of lines in the ultraviolet, visible and infrared regions. These sets of lines were observed by different scientists. These spectral emission lines could be expressed in the form of a general formula as :

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] cm^{-1}; R_H=109677cm^{-1} \qquad ...(3.5)$$

Where n_1 and n_2 are positive integers ($n_1 < n_2$) and R_H is called Rydberg's constant. The different sets of lines observed in the hydrogen atom spectrum, their discovers and the values of n_1 and n_2 are given in the Table 3.2.

Table 3.2 : Summary of the emission lines observed in hydrogen spectrum

Series	**n_1**	**n_2**	**Region of spectrum**
Lyman	1	2,3,4....	Ultraviolet
Balmer	2	3,4,5....	Visible
Paschen	3	4,5,6....	Infrared
Bracket	4	5,6,7....	Infrared
Pfund	5	6,7,8....	Infrared

The line Spectrum of hydrogen atom was explained by Bohr's model, which is discussed in section 3.5

Example 3.3 : Calculate the wavelength of the Balmer line corresponding to $n_2 = 3$.

Solution : According to Balmer series $^{=} = R_H\left[\frac{1}{2^2}-\frac{1}{n_2^2}\right]$

Where $R_H = 109{,}677\ cm^{-1}$

For $n_2 = 3$; $\bar{\nu} = 109{,}677\left[\frac{1}{2^2}-\frac{1}{3^2}\right] = 109{,}677\left(\frac{5}{36}\right)$

Since $\lambda = \frac{1}{\nu}; \lambda = \frac{36}{109{,}677x5}$

$= 6.56 \text{ x } 10^{-5}$ cm

= 656 nm

3.4.1.a Planck's Quantam Theory

The wave nature of light could explain the phenomenon of diffraction and interference. However, following are some of the observations which could not be explained with the help of electromagnetic theory. (called classical physics)

- The nature of emission of radiation from hot bodies.
- Reflection of electrons from metal surface when radiation strikes it.
- Variation of heat capacity of solids as a function of Temperature.
- Line spectra of atoms with special reference to hydrogen.

The First concrete explanation for the above observations was given by Max Planck in 1900.

According to his theory light is emitted or absorbed in small packets of energy called photons. Each photon has a definite amount of energy associated with it.

the photons travel with a velocity, equal to velocity of light. The Energy of radiation (E) is proportional to its frequency (ν).

$$E \alpha \nu \ ; E = h\nu$$

h is called the plank's constant.

$h = 6.6256 \text{ x } 10^{-34}$ Js $= 6.6256 \text{ x } 10^{-27}$ erg.s

Planck's theory successfully explains the emission of radiation from a hot body (black body radiations). When solids are heated they emit radiation over a wide range of wavelengths.

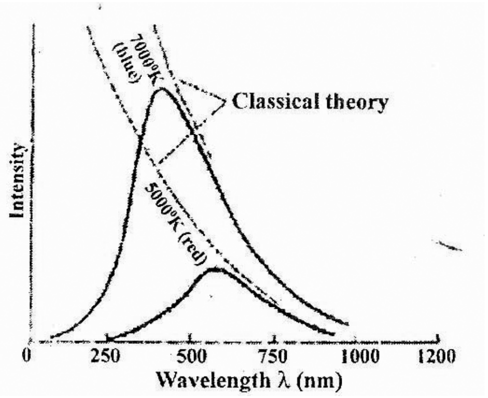


Fig. 3.9.a Radiations emitted by a black body at different temperatures

Example : When iron rod is heated in a furnace, it first turns to dull red and then becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white, then blue. In terms of frequency, it means that the radiation emitted goes from a lower frequency to higher frequency region of electromagnetic spectrum. The ideal body, which emits and absorbs all frequencies is called a black body and the radiation emitted by such a body is called black body radiation. A hallow sphere coated inside with platinum black and having a small hole in its wall acts as a near black body.

The exact frequency distribution of the emitted radiation i.e intensity of the radiation versus frequency give curves. Such curves obtained at different temperatures of the black body is shown in Fig. 3.4.1(a).

The study of the curves shows that the nature of the radiation depends on the temperature of the black body. If the energy emitted is continuous the curve should be as shown by the dotted lines, but it is not so.

The following conclusions are drawn from the study of the shape of the curves.

- At a given temperature, the intensity of the radiant energy increases with the wave length, reaches a maximum and then decreases.
- As the temperature increases, the peak of the curve shifts to lower wavelength.

The above experimental results could not be explained satisfactorily on the basis of the wave theory of light. The salient features of Planck's theory are

* The oscillating particle in the black body does not emit energy continuously.
* Radiation is emitted only in discrete quantities, Planck gave the name QUANTUM to the smallest quantity that can be emitted or absorbed in the form of electromagnetic radiation.
* The phenomenon of wave propagation of radiant energy in the form of quanta is called quantization of energy.
* Energy is emitted or absorbed in simple integral multiples of a quantum. It cannot be in fractional values.
* $E = n.h\nu$; where n = an integer.

3.4.1.b Explanation of Photo Electric Effect

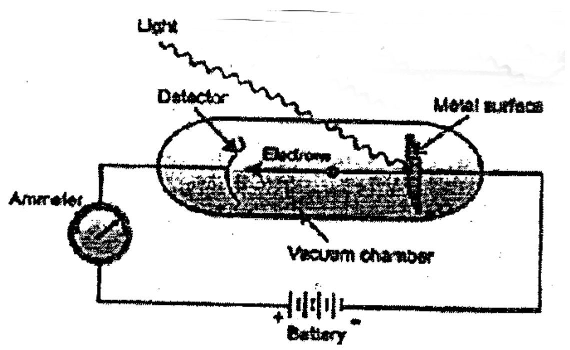


Fig. 3.9.b Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vaccum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.

When a clean surface of an alkali metal (Ex: Potassium, Rubidium etc) is exposed to a beam of light, ejection of electrons from the metal surface takes place. Only if the frequency of incident light is greater than a certain minimum value, characteristic of the metal. This phenomenon is known as photo electric effect.

It is observed that violet light is able to eject electrons from potassium but red light which is of lower frequency has no effect. The explanation from the frequency dependence of the photoelectric effect is given by ALBERT EINSTEIN. He could explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point.

Einstein argued that the wave model of light cannot explain the observed facts. However, if light is regarded as consisting of particles (called photons) such that the energy (E) of a photon is related to the frequency (ν) by the relation.

$E = h\nu$; where h = Planck's constant.

It is easy to understand photoelectric effect.

- When photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any timelog or delay.
- Greater the energy possessed by the photon, greater will be the transfer of energy to the electron and greater the kinetic energy of the ejected electron.
- When a photon strikes the surface of the metal, the energy ($h\nu$) of the photon is absorbed by the electron in the metal and a part of this energy is used to set free the electron from the attractive forces in the metal. The remaining energy of the photon appears in the form of the kinetic energy of the released electron.

  Thus we can write $h\nu = W + K.E$ where, $h\nu$ = Energy of the photon.

  W = Energy required to overcome the attractive forces on the electron in the metal. Also called work function.

  K.E = Kinetic energy of emitted electron.

  $\therefore h\nu = h\nu_o + 1/2\, m_e V^2$

  M_e = mass of electron; ν = velocity of ejected electron.

  ν_0 = Threshold frequency.

3.5 Bohr's Model

In 1913, Niels Bohr (1885-1962) proposed another model of the atom where electrons move around the nucleus in circular paths. Bohr's atomic model is built upon a set of postulates, which are as follows :

1. The electrons move in a definite circular paths around the nucleus (Fig. 3.10). He called these circular paths as **orbits** and postulated that ***as long as the electron is in a given orbit its energy does not change*** (or energy remains fixed). these orbits were therefore refered to as **stationary orbits** or **stationary states** or **non radiating orbits**.

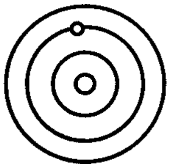


Fig. 3.10 : *Bohr's model*

Bohr won the Nobel Prize in Physics in 1922 for his work.

2. The ***electron can change its orbit by absorbing or releasing evergy***. An electron at a lower (initial) state of energy, E_i can go to a (final) higher state of energy, E_f by absorbing (Fig 3.11) a single photon of energy given by

   $E = hv = E_f - E_i$ ....(3.6)

   Similar, when electron changes its orbit from a higher initial state of energy E_i to a lower final state of energy E_f, a single photon of energy h_l is released.

Fig. 3.11 : *Absorption and emission of photon causes the electron to change its energy level.*

3. The **angular momentum of an electron** of mass m_e moving in a circular orbit of radius r and velocity v is an integral multiple of h/2π.

$$m_e v r = \frac{nh}{2\pi}$$

where *n* is a positive integer, known as the **principal quantum number**.

Bohr obtained the following expressions for the energy of an electron in stationary states of hydrogen atom by using his postulates.

Energy of the orbit, $E_n = -R_H\left(\frac{1}{n^2}\right)$ .... (3.8)

Bohr could correlate R_H to other properties as $R_H = \frac{mz^2e^4}{8h^2\varepsilon_0^2}$; .... (3.9)

where,

m = mass of the electron	h = Plank's constant
z = nuclear charge	ε_0 = permitivitty of the medium
e = electronic charge	

The negative sign in the energy expression means that the there is an attractive interaction between the nucleus and the electron. This means that certain amount of energy (called ionisation energy) would be required to remove the electron from the influence of the nucleus in the atom. You may note here that the energies of the Bohr orbits are inversely proportional to the square of the **quantum number** *n*. As *n* increase the value of the energy increases (becomes lesser negative or more positive). It means that as we go farther from the nucleus the enrgy of the orbit goes on increasing.

3.5.1 Bohr's Theory of Hydrogen atom:

Hydrogen atom contains a single proton in its nucleus with +e. An electron with –e revolve round the nucleus in a circular orbit of radius 'r'. As per coulomb's law, electrostatic force of attraction between the nucleus and the electron is given by

$$\text{Attractive force} = \frac{-e^2}{r^2}$$

This is columbic force of attraction of the electron towards the nucleus. For the atom to be stable an equal centrifugal force must act away from the nucleus. This centrifugal force arises as a result of the electron revolving around the nucleus in the circular orbit. It is equal to $\frac{mv^2}{r}$ where m is mass of electron revolving around the nucleus in the circular orbit and 'r' is the radius of the orbit.

Therefore altrative force of the electron revolving round the nucleus in a stationary orbit

$$\frac{-e^2}{r^2} = \frac{-mv^2}{r} \text{ or } \frac{e^2}{r} = mv^2 \qquad \text{---- (1)}$$

As per Bohr's quantum condition

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

$$\therefore V = \frac{nh}{2\pi mr} \text{ (or) } V^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \text{---- (2)}$$

Substitute the value of V^2 in equation (1) above

$$\frac{-e^2}{r^2} = \frac{mn^2h^2}{4\pi^2m^2r^2} \text{ (or) } r = \frac{n^2h^2}{4\pi^2me^2}$$

if r is represented as r_n for n^{th} orbit

Radius of nth orbit $(r_n) = \frac{n^2h^2}{4\pi^2me^2}$ ----- (3)

Substitute the values of $h=6.256 \times 10^{-27}$ erg.sec

$\pi = 3.14$

(mass of electron) $m = 9.1 \times 10^{-28}$ g

(Charge on electron) $e = 4.802 \times 10^{-10}$ e.s.u in equation (3)

we get Radius of n^{th} orbit $(r_n) = 0.529 \times 10^{-8} n^2$ cm

If n = 1 Bohr's orbit (r) = 0.529×10^{-8} cm = 0.529 A^0.

Since 'n' can have values 1,2,3…... a simple integer. It is obvious that orbits of only certain finite radii are possible and electron could occupy possibly only these permitted orbits. These simple whole numbers denoted by 'n' are called Principal Quantum numbers.

Energy of electron:

The total energy of electron revolving in an orbit is obtained by summing up its kinetic energy and potential energy.

Kinetic energy due to motion of an electron = $\frac{1}{2}mv^2$

(m is the mass of electron and v is its velocity)

Potential energy of electron due to position = $-e^2/r$

$$\text{Total energy of electron} = \text{K.E} + \text{P.E} = \frac{1}{2}mv^2 - \frac{-e^2}{r} = \frac{e^2}{2r} - \frac{e^2}{r} = \left[mv^2 = \frac{e^2}{r}\right]$$

Therefore total energy of electron (E) $= \frac{-e^2}{2r}$

Substituting the value of 'r' $= \frac{n^2h^2}{4\pi^2me^2}$

Energy of electron in nth orbit = $E_n = \dfrac{-e^2 4\pi^2 me^4}{2n^2h^2}$

$$E_n = \frac{-2\pi^2 me^4}{h^2} \text{ x } \frac{1}{n^2}$$

Except of 'n' all the other terms in the above equation are constant we can write

$$E_n = \frac{-K}{n^2} \text{ where } K = \frac{2\pi^2 me^4}{n^2}$$

Substituting the values of m,e,h and π we have

$$E_n = \frac{-21.72x10^{-12}}{n^2} \text{ erg} = \frac{-21.72x10^{-19}}{n^2} \text{ J or } \frac{-13.6}{n^2} \text{ eV.}$$

Thus, we can conclude that the energy of an electron (E) can have only certain discrete restricted values depending upon the value of 'n'. This is termed as quantization of energy of the electron. An electron revolves only in certain orbits of fixed radii and also it has only certain allowed energy levels. These orbits are also termed as main energy levels or the principal Quantum states.

In the equation energy of an electron $E_n = \dfrac{-K}{n^2}$

the energy of an electron is inversely proportional to the square of the principle quantum number n. As the value of n increases, radius of the orbit increase and the absolute value of energy of an electron also increases effectively.

As the value of n decrease, the radius of the orbit as well as the absolute value of its energy decreases. This increases the stability of the atom. When the electron of a hydrogen atom revolves in the first orbit, energy is at its lowest possible value and hence confers maximum stability to the hydrogen atom. This is termed as ground state of the hydrogen atom.

When the electron is free from the influence of nucleus the energy is taken as zero. The electron in this situation is associated with the stationary state of principle Quantum number.

(n) = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n the energy is emitted and it's energy is lowered. This is the reason for the presence of negative sign in the equation for energy and depicts its stability relative to the reference state of zero energy and n = ∞.

3.5.2 Explanation of Line Spectrum of Hydrogen Atom

As per the second postulate mentioned above, the energy emitted in the transition of a single electron from an initial stationary state of energy E_i to a final stationary state of energy E_f is given as hο = E_i - E_f. Substituting the expresisons for energy from Eq. 1.8 we can get the formula given in eg. 3.5. Thus Bohr's model providess an explanation for the observed line spectrum of hydrogen as summarized in Table 3.2 Fig. 3.12 shows the energy level diagram for hydrozen atom and the transitions responsible for the observed line spectrum.

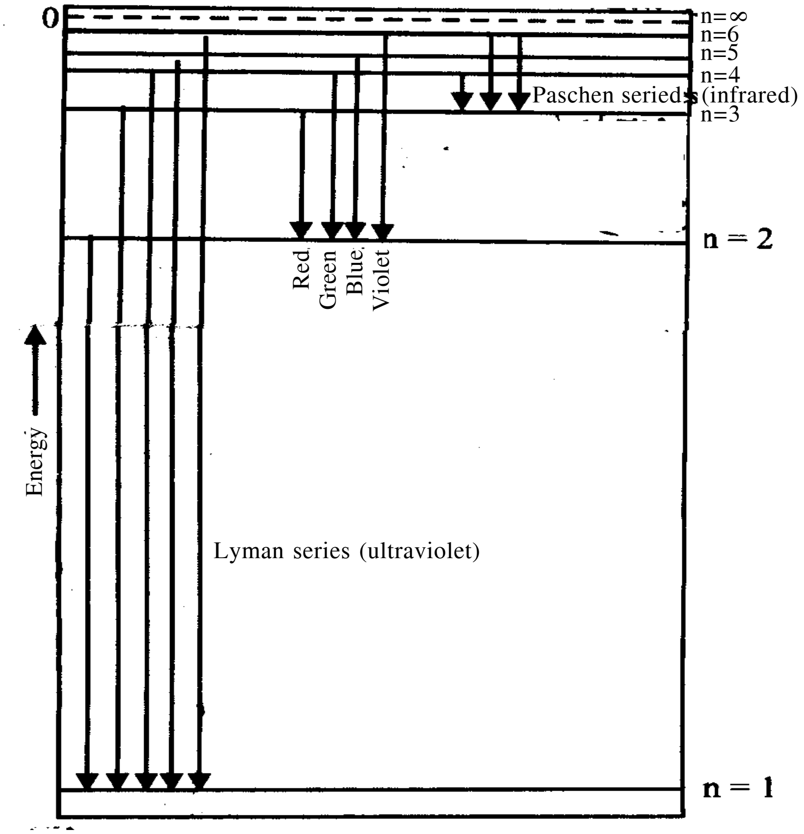


Fig. 3.12 : *Energy level diagram for H-atom, showing various transitions responsible for the observed line spectrum.*

Intext Questions 3.4

1. What is the difference between a line spectrum and a continous spectrum ?

    ....

2. What are the main postulates of Bohr's model ?

    ....

3. How does the energy of a Bohr orbit vary with the principle quantum number 'n'.

    ....

4. What is 'Quantum'?

    ....

5. Give the value of Planck's constant in S.I. system

    ....

6. State photoelectric effect.

....

7. Define threshold energy.

....

3.6 Wave - Particle Duality

In section 3.3 you have learnt about the wave nature of light. As you are aware that some of the properties of light e.g. diffraction and interference can be explained on the basis of its wave nature. On the other hand some other properties like photoelectric effect and scattering of light can be explained only on the basis of particle nature of light. Thus light has a dual nature possessing the properties of both a wave and a particle, i.e., light could under some conditions behave like a particle and other conditions behave as a wave.

In 1923 a young French physicist, Louis de Broglie, argued that if light can show wave as well as particle nature, why should particles of matter (e.g., electron) not posses wave like characteristics ? He proposed that matter particles should indeed have a wave nature and said that a particle of mass *m* moving with a velocity *v* has an associated wavelength, *e* (some times called *de Broglie wavelength*) given by the formula;

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \lambda = \frac{h}{p} \qquad \text{.... (3.10)}$$

Where p (=mν) is the momentum of the particle. The de Broglie wavelength of a body is inversely proportional to its momentum. Since the magnitude of *h* is very small, the wavelength of the objects of our everyday world would be too small to be observed. Let us make a calculation to see this.

Example 3.4 : Calculate the de Broglie wavelength associated with a cricket ball weighing 380g thrown at a speed of 140 km per hour.

Solution : Mass of the cricket ball = 380g = 380 x 10^{-3} kg = 0.38 kg

Speed or Velocity = 140 km/hr = (140 x 1000) / 3600

= 38.89 m s^{-1}

The wavelength associated with the cricket ball will be

$$\lambda = \frac{\text{h}}{\text{mv}} = \frac{6.626\text{x}10^{-34}\,\text{JS}}{(0.380\text{kg})(38.89\text{ms}^{-1})}$$

= 4.48 x 10^{-35} m (J = kg m^2 s^{-2})

dr-Broglie
(1892-1987)
de-Broglie proposed the theory of wave-particle dualism as a part of his PhD thesis in 1924. He got the physics Nobel Prize in 1929

If the electrons show wave nature then a beam of these electrons is expected to show diffraction which is a property of waves. In 1927 G.P. Thomson and C.J. Davidson demonstrated the diffraction of electron waves by the crystal lattice of nikel (Fig. 3.13). Thus electrons also show a dual nature. That is, sometimes these show particle nature while at some other times they show wave nature.

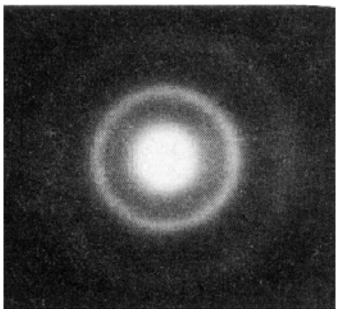


Fig. 3.13 : *Electron diffraction pattern from nickel crystal*

Werner Heisenberg
(1901-1976)
Heisenberg got the phys. Nobel prize in 1932

3.7 Heisenberg's Uncertainty Principle

An important consequence of the wave-particle duality of matter and radiation was discovered by Werner Heisenberg in 1927 and is called the **uncertainty principle**. According to this principle it is not possible to simultaneously measure both the position and **momentum** (***or velocity***) of an electron accurately. In simple words we may state that more accurately you measure a particle's position, the less accurately you're able to measure its momentum, and vice versa. Mathematically, the Heisenberg principle can be expressed in terms of an inequality.

$$\Delta x \ \Delta p \ \geq \ \frac{h}{4\pi} \qquad \text{....(3.11)}$$

Where Äx and Äp are the uncertainities in the measurements of position and momentum respectively. If the position of an object is known exactly (i.e., Ä$x = 0$), then the uncertainly in the momentum must be infinite, meaning that we cannot say anything about the velocity. Similarly, if the velocity is known exactly, then the position would be entirely uncertain and the particle could be anywhere. It means that we cannot say anything about the position of the particle. In actual practice none of the two properties can be measured with certainly. Due to the small value of the Planck's constant, h (6.626 x 10^{-34} J s) this principle is not relevant while making measurements of large objects like car, bus or aeroplane etc. It is relevant, only when you are making measurements on very small objects such as electrons.

Heisenberg's principle questioned the validity of Bohr's model. It is so because according to Bohr's model we can precisely calculate the radius of the orbit (i.e., the position of the electron) and the velocity of electron in it. But it is not possible according to Heisenberg's principle. It motivated many scientists to develop newer models of the atom using the dual nature of the electron. This resulted into the development of a Quantum mechanical or *Wave Mechanical Model* of the atom discussed in the next section.

Intext Questions 3.5

1. What do you understand by wave-particle duality ?

   ....

2. Name the experiment that established the wave nature of electron.

   ....

3. Compute the de-Broglie wavelength associated with an electron moving which a velocity of 100 km / second? ($m_e = 9.1 \times 10^{-31}$ kg)

   ....

4. State Heisenberg's Uncertainty Principle ?

   ....

3.8 Wave Mechanical Model of atom

Wave Mechanical Model of atom was proposed by Erwin Schrodinger - an Austrian physicist in 1926. This model is basically a formalism or a mathematical recipe, which is based on some postulates that have no foundation in classical physics. The correctness of these postulates can be justified in terms of the correctness of the results predicted by them. According to this Model, the motion of electron inside the atom could be described in terms of a mathematical function called, **wave function**, ϕ (Greek letter, psi). The wave functions are assumed to contain all the information about the electron and are obtained by solving a differential equation called Schrodinger wave equation (SWE). The square of the wave function ϕ^2 is a measure of the probability of finding an electron in a three dimensional space around the nucleus.

On solving the SWE for hydrogen atom we get a number of wave functions, which are characterized by three quantum numbers viz.,

- Principal quantum number, n
- Azimuthal quantum number, l
- Magnetic quantum number, m_l

These quantum numbers arise in the process of logically solving the wave equation. Every electron in an atom has a unique (different) set of quantum numbers which help to describe the three dimensional region where there is maximum probability of finding the electron. This region is called as ***atomic orbital*** or simply ***orbital***.

3.8.1 Significance of Quantum Numbers

The three quantum numbers describe the size, shape, and orientation of the atomic orbitals in space. There is an additional quantum number which does not follow from the Schrodinger wave equation but is introduced to account for electron spin. The fourth quantum number thus help in designating the electrons present in the atom. Let us understand the significance of each of these quantum numbers.

Principal quantum number, *n*

The principal quantum number, *n* describes the energy level (or principal shell) of the electron within the atom. *n* can have only positive non zero integral values (i.e., *n* = 1,2,3,4.....). This means that in an atom, the electron can have only certain energies. Thus we may say that n quantizes energy of the electron. The principal quantum number also determines the mean distance of the electron from the nucleus, i.e., its size. Greater the value of *n* farther is the electron from the nucleus.

Each principal shell can accommodate a maximum of $2n^2$ electrons, i.e.

n = 1	number of electrons : 2
n = 2	number of electrons : 8
n = 3	number of electrons : 18 and so on...

Azimuthal quantum number, *l*

The azimuthal quantum number, *l* is related to the geometrical shape of the orbital. The value of *l* may be zero or a positive integer less than or equal to n-1 (n is the principal quantum number), i.e., *l* = 0,1,2,3....... (n-1). Different values of *l* corrrespond to different types of **subshells** and each subshell contains orbitals of a given shape.

***l* = O,** corresponds to **s**-subshell and contains the orbital with **spherical shape** called as ***s*-orbital**.

***l* = 1,** corresponds to **d**-subshell and contains the orbitals with a **dumb-bell shape** called as as ***p*-orbitals**. Therer are three p-orbitals in each p-subshell.

***l* = 2,** corresponds to **p**-subshell and contains the orbitals with a **cloverleaf shape** called as as ***d*-orbitals**.

***l* = 3,** corresponds to **f**-subshell and contain **f orbitals.** There are seven *f*-orbitals in each *f*-shubshell.

The shapes of s, p and d orbitals will be discussed in the next subsection.

Magnetic quantum number, m_l

The quantum number, m_l describes the direction or orientation of the orbital in space. The quantum number m_l may have any intergral value from - *l* to + *l*. For example, for *l* = 1; m_l can have the values as -1,0 and 1.

Magnetic quantum number, m_s

The quantum number, m_s describes the spin of the electron i.e., whether it is clockwise or anticlockwise. The quantum number, m_s does not arise while solving SWE. The clockwise and anticlockwise direction of electron spin has arbitrarily been assigned the value as + 1/2 and -1/2 respectively.

To sumup, let us take an example of an electron belonging to the third shell (n=3). This electron can be in as *s*-subshell (l = 0) or a *p*-subshell (l = 1) or a *d*-subshell (l = 2). If it happens to be in a *p*-shell it may be in any of the three possible *p*-orbitals (corresponding to m_l = -1, 0 + 1 directed along *x*, *y* or *z* - axis. And within the orbital it may have clockwise ($m_s = +{}^1/_2$) or anti-clockwise ($m_s = -{}^1/_2$) direction of electron spin. The possible values of different quantum numbers for an electron belonging to the third shell are given in Table 3.3.

Table 3.3 : The quantum numbers for an electron belonging to the third shell

Principal quantum number, *n*	**Azimuthal quantum number, *l***	**Magnetic quantum number, m_l**	**Magnetic spin quantum number, m_s**
3	0	0	+1/2
			-1/2
	1	-1	+1/2
			-1/2
		0	+1/2
			-1/2
		+1	+1/2
			-1/2
	2	-2	+1/2
			-1/2
		-1	+1/2
			-1/2
		0	+1/2
			-1/2
		+1	+1/2
			-1/2
		+2	+1/2
			-1/2

You may note here that the third shell can contain a maximum of 18 electrons and each of them, has a distinct set of four quantum numbers.

Intext Questions 3.6

1. What do you understand by a Wave Function ?

   ....

2. What is the difference between an orbit and an orbital ?

   ....

3. What are quantum numbers? List different quantum numbers obtained from Schrodinger Wave Equation ?

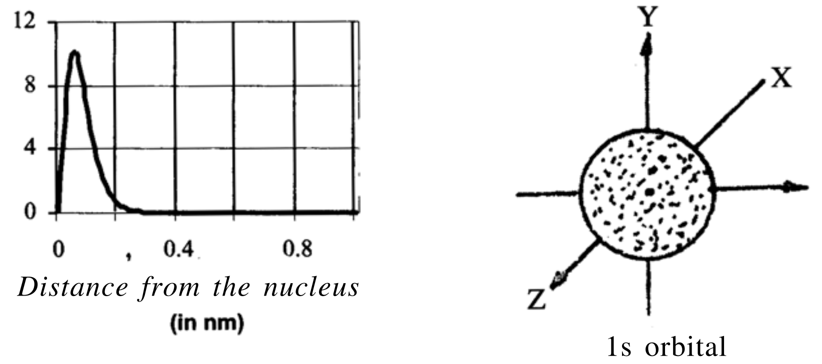
   ....

4. Give the significance of the Principal, azimuthal and magnetic quantum numbers ?

   ....

3.8.2 Shapes of Orbitals

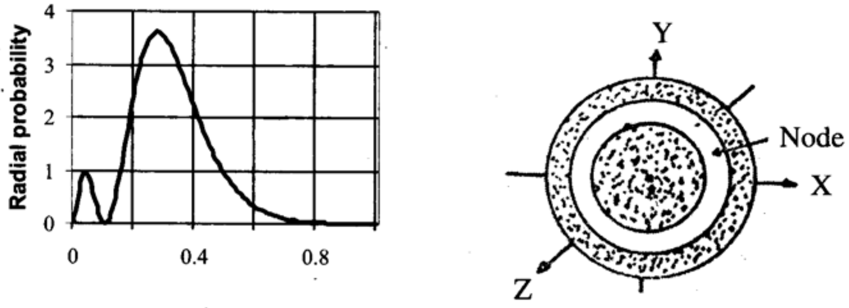
We have defined an orbital as "***the three dimensional region of space around the nucleus where there is maximum probability of finding the electron***". Lets us try to understand the meaning of an orbital by taking the example of 1s orbital ($n = 1$; $l = 0$). This can be understood in terms of a radial probability curve. Such a curve gives the variation of the probability of finding the electron as a function of distance from the nucleus. For 1s orbital the radial probability curve (Fig. 3.14 (a)) shows that the probability of finding the electron in 1s orbital increase as we move away from the nucleus and reaches a maximum at a certain distance (=0.0529 nm or 52.9 pm for hydrogen atom) and then decreases as we go further away from it and at a certain distance it becomes close to zero. The curve shows the radial probability for a given direction. The probability would be same for all possible directions. if we put all such curves together it would give a spherical distribution of the electron probability. Since the radial probability



(a) (b)

Fig. 3.14 : *(a) Radial probability curve for 1s orbital (b) Boundary surface diagram for 1s orbital*

does not become zero at any distance, we cannot specify the size of the sphere. Therefore, the orbital is represented as a boundary surface diagram, which may be thought as a region of space, which contains 95% of the probability of finding the electron, as indicated in Fig. 3.14 (b). Thus the 1s orbital is represented as a sphere.



Distance from the nucleus (nm)
(a)

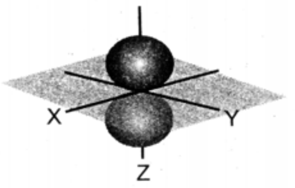
2s orbital
(b)

Fig. 3.15 : *(a) Radial probability curve for 2s orbital (b) Boundary surface diagram for 2s orbital*

Similarly, the Fig 3.15 (a) gives the radial probability curve for a 2s orbital while the Fig 3.15 (b) shows the boundary surface diagram for the same. You can note two things here. First you may note that for a 2s orbital the boundary surface diagram is bigger as compared to a 1s orbital. Secondly, the radial probability curve shows two maxima. The probability initially increases, reaches a maxima then it decreases and comes close to zero. It increases again and decreases as we move further away from the nucleus. The region where the probability comes close to zero (before increasing again) is called a ***spherical node***. There are n-1-1 spherical nodes in an orbital.

A node is a region in space where the probability of finding the electron is close to zero.

p*- orbital:** Now when we draw the shape of a p orbital ($n = 1$; $l = 1$) we get a shape as shown in the Fig. 3.16. This picture shows the shape of one of the three possible p orbitals which is directed towards the z-axis; P_z. You may note that the probability picture for a P_z orbital consists of two lobes; one along the positive z-axis and the other along the negative z-axis. Another important feature of a p-orbital is the absence of the electron probability in the XY-plane. Such a plane is called a ***nodal plane. The shapes of the three p-orbitals are given in Fig. 3.17



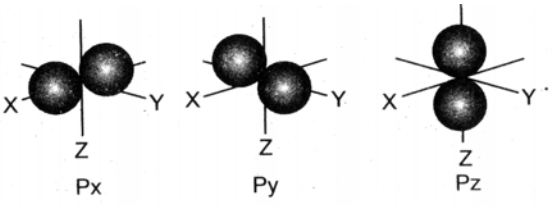


Fig. 3.16 : *A p-orbital surface diagrams (shapes)*

Fig. 3.17 : *The boundary showing a nodal plane of the p-orbitals*

The Fig. 3.18 gives shapes of five possible d-orbitals. The d-orbitals also contain nodal planes. The five d-orbitals have different shapes but they all have same energies i.e., these are degenerate.

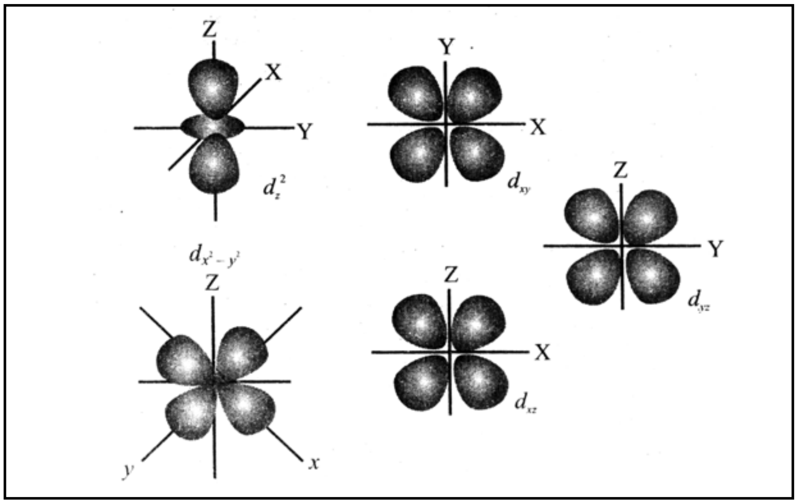


Fig. 3.18 : *The boundary surface diagrams (shapes) of the five d-orbitals*

Intext Questions 3.7

1. What are the shapes of s, p and d orbitals ?

....

2. Describe the shape of a 2s orbital. How is it different from that of a 1s orbital ?

....

3. What do you understand by

   i) a spherical node ?

   ii) a nodal plane ?

....

4. How many spherical nodes will be there in 3s orbtial ?

....

3.8 Electronic Configuration of Elements

You have so far learn that an atom consists of a positively charged nucleus surrounded by electrons present in orbitals of different shapes and sizes. These orbitals are part of different shells and sub-shells and are characterized by the three quantum numbers viz. n, l and m_l. Let us now take up the distribution of electrons in these shells and sub-shells. Such a distribution of electrons is called **Electronic Configuration** and is governed by three basic rules or principles.

3.9.1 Aufbau (or building up) Principle

This principle is concerned with the energy of the atom and states that the electrons should occupy. The electrons occupy the orbitals in such a way that the energy of atom is minimum. In other words **the electrons in an atom are filled in the increasing order of their energies**. Now, how does one know the increasing order of the orbital energies? You have learnt above that the principal quantum number determines the energy of the orbitals. Higher the value of *n* higher the energy. This is true only for hydrogen atom. For other atoms, we need to consider both *n* and *l*. This means that **different sub-shells in a given shell have different energies**. The order of orbital energies can be determined by the following $(n + l)$ rules.

Rule 1 : An orbital with a lower value for $(n + l)$ has lower energy. For example, the 4s orbital $(n + l = 4 + 0 = 4)$ will fill lbefore a 3d orbital $(n + l = 3 + 2 = 5)$.

Rule 2 : If the value of $(n + l)$ is same for two orbitals then the orbital with lower value of *n* will be filled first. For example, the 3d orbital $(n + l = 3 + 2 = 5)$ will fill before a 4p orbital $(n + l = 4 + 1 = 5)$.

Following these rules the increasing order of the orbital energies comes out to be

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

3.9.2 Pauli's Exclusion Principle

This principle concerns the spin of electrons present in an orbital. According to the Pauli's principle, **no two electrons can have all the four quantum numbers to be same.** For example, if a given electron in an atom has the set of four quantum numbers as $n = 2$, $l = 1$, $m_l = 1$ and $m_s = +1/2$ then no other electron in the atom can have the same set of quantum numbers.

As you know that an orbital is characterized by three quantum numbers so the electrons occupying a given orbital would have same values of these three quantum numbers. These electrons are distinguished in terms of their spin quantum number, m_s. Since the spin quantum number can have only two values so ***only two electrons can occupy a given orbital***. In fact this fourth quantum number was introduced through Pauli's principle only.

3.9.3 Hund' Rule

This rule concerns the distribution of electrons in a set of orbitals of the same energy, i.e. constituents of a subshell. According to this rule if a number of orbitals of the same sub-shell are available then the electrons distribute in such a way that each orbital is first singly occupied with same spin. For example, the six electrons in carbon distribute as

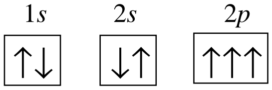
$1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^0_z$ and not as $1s^2\ 2s^2\ 2p^2_x\ 2p^0_y\ 2p^0_z$

Since electrons repel each other, they remain as far as possible from one another by occupying different orbitals.

The rules discussed above can be used to write the electronic configuration of different elements. There are two common ways of representing the electronic configurations. These are

a) Orbital notation method : In this method the filled orbitals are written in the order of increasing energies. The respective electrons in them are indicated as superscripts as shown in the example given below. For example, the electronic configuration of nitrogen atom (atomic number 7) is written as $1s^2\ \ 2s^2\ \ 2p^1_x\ 2p^1_y\ 2p^1_z$.

b) Orbital diagram method : In this method the filled orbitals are represented by circles or boxes and are written in the order of increasing energies. The respective electrons are indicated as arrows whose direction represents their spin. For example, the electronic configuration of nitrogen in the orbital diagram notation can be written as



Electonic configuration can also be written in a short hand form. In this method the last **completed orbital shell** is represented in terms of a noble gas. For example, the electronic configuration of lithium and sodium can be written as

Li	$[He]2s^1$
Na	$[Ne]2s^1$

The electrons in the noble gas configuration are termed as ***core electrons*** while the ones in the outer shell are called ***valence electrons***.

Intext Questions 3.8

1. What do you understand bythe electronic configuration of an atom ?

   ....

2. What is Pauli's exclusion principle ?

   ....

3. What is Aufbau principle ? What are $(n + l)$ rules ?

   ....

4. Which of the following orbitals wil be filled first ?
   i) 2*p* or 3s
   ii) 3*d* or 4*s*

   ....

What You Have Learnt

- Atoms are made up of three fundamental particles namely, electrons, protons and neutrons.
- J.J. Thomson made the first attempt to describe the structure of an atom in terms of a model called **plum pudding model**. According to this atoms can be considered as a large positively charged body (pudding) in which a number of small negatively charged electrons (plums) are scattered..
- According to the Rutherford's model, the positive charge of the atom and most of its mass is contained in the nucleus and the rest of the atom is empty space which contains the much smaller and negatively charged electrons.
- Electromagnetic radiation is a kind of energy, which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.
- The electromagnetic radiations are characterized by a number of parameters like, amplitude, wavelength, frequency, wave number and velocity.
- In 1913, Niels Bohr proposed 'Planetary Model for atom. According to the model the electrons move in definite circular paths of fixed energy around a central stationary nucleus. The electrons can change their orbits by absorbing or emitting a photon of energy (= hl) equal to the difference of the energies of the orbits.
- Bohr's model did explain for the stability of atom and the line spectrum of hydrogen. The model however was unable to explain the spectra of atoms other than hydrogen.
- Louis de Broglie, argued for the dual nature of electron and proposed that matter particles should have a wave nature. The associated wave length, is given by the formula; $\lambda = \frac{h}{mv}$ or $\lambda = \frac{h}{p}$
- This was experimentally verified by Thomson and Davisson by diffraction of electron waves by the crystal lattice of nickel.
- The wave-particle duality of matter led Werner Heisenberg to propose the **uncertainty principle**. According to which it is not possible to measure simultaneously both the ***position*** and ***memontum*** of a particle with a infinite precision.
- The dual nature of electron and Heisenberg's uncertainy principle led to the development of wave mechanical model.
- According tot he Wave Mechanical Model, the motion of electron inside the atom can be described in terms of a mathematical function called, wave function, ϕ. This wave function contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.

- The square of the wave function, ψ^2 is a measure of the probability of finding the electron in a certain three dimensional space around the nucleus. This region is called as ***atomic orbital*** or simply ***orbital***.

- These wavefunctions are characterized by three quantum numbers. These quantum numbers describe the size, shape and orientation of the atomic orbitals in space. Every electron in an atom has a unique set of quantum numbers.

- The principal quantum number *n* concerns the quantisation of the energy of the electron while the Azimuthal quantum number, *l* is related to the shape of the orbital. The magnetic quantum number m_l describes the direction or orientation of the orbital in space.

- An additional quantum number, m_s is introduced to account for electron spin. This quantum number does not follow from the wave mechanical model and describes the spin of the electron.

- Different orbitals have different shapes. An s orbital is spherical; p orbitals are dumb-bell shaped; *d* orbitals have cloverleaf shape while *f* orbitals have a eight lobed shape.

- The distribution of elections in the shells and subshells is called **Electronic Configuration**. If is governed by three rules which are Aufbau principle; Pauli's exclusion principle and Hund's Rule of maximum multiplicity.

- According to Aufbau principle the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + 1)$ rules.

- According to the Pauli's exclusion principle, no two electrons can have all the four quantum numbers to be same.

- While filling electrons in the orbitals of same subshell, according to Hund's rule, each orbital is first singly occupied with same spin then the pairing up takes place.
- The photons travel with a velocity equal to the velocity of light. The energy of radiation (E) is proportional to its frequency (ν)

  $E \alpha \nu$; $E = h\nu$

  h is a Planck's constant

  $h = 6.6256 \times 10^{-34}$ JS

- The phenomenon of ejection of electrons from the metal surface when light is exposed on it is called photo electric effect.

Terminal Exercise

1. a) What are the three fundamental particles that constitute an atom ?

   b) Compare the charge and mass of an electron and of a proton.

2. What do you think is the most significant contribution of Rutherford to the development of atomic structure ?

3. What experimental evidence shows the dual nature of light?

   a) Compute the energy of FM radio signal transmitted at a frequency of 100 MHz.

   b) What is the energy of a wave of red light with λ = 670 nm?

4. In what way was the Bohr's model better than the Rutherford's model ?

5. What are the drawbacks of Bohr's Model ?

6. What led to the development of Wave Mechancial Model of the atom ?

7. What do you understand by an orbital ? Draw the shapes of s and p-orbitals.

8. Explain the Hund's rule of maximum multiplicity with the help of an example.
9. Explain Planck's Quantum theory.

10. The threshold energy (work function) of a metal is 4.2 ev. If radiation of 2000 A^0 falls on the metal, what is the kinetic energy of the fastest photoelectron?

Answers to Intext Questions

3.1

1. Proton is heavier than electron. The ratio of their masses is

$$= m_p/m_e = \frac{1.672\ 623 \times 10^{-27}\ \text{kg}}{9.109\ 389 \times 10^{-13}\ \text{kg}}$$

$$= 1836$$

2. Main constituent particles like proton, neutron and electron etc. present in the atom come in the category of fundamental particles.

3. Neutron

3.2

1. Electron, proton and neutron

2. The aim of Rutherford's experiment was to test the Thomson's plum-pudding model.

3. According to Rutherford's model for atom, the positive charge of the atom and most of its mass is contained in the nucleus. The rest of the atom is empty space which contains the much smaller and negatively charged electrons.

4. Rutherford's model was rejected because it could not explain the stability of the atom.

3.3

1. Electromagnetic radiation is a kind of energy which is transmitted through space in the form of electric and magnetic fields. It travels with the speed of light and does not need any medium to travel.

2. The different characteristics of electromagnetic radiation are

   i) Ampliture

   ii) Wavelength,

   iii) Frequency,

   iv) Wave number and

   v) Velocity

3. The wave number is defined as the number of waves per centimeter. It is equal to the reciprocal of the wavelength.

4. A quantum of visible light is called photon. The energy of the quantum (or photon) is proportional to the frequency of radiation.

3.4

1. A line spectrum consists of a series of discrete lines of characteristic wavelengths while a continuous spectrum contains a broad band of radiations containing all possible wavelengths in the range i.e., wavelengths of the radiation varies continuously.

2. The main postulates of Bohr's model are

   i) The electrons move in a definite circular paths called as **stationary orbits or stationary state** around a central stationary nucleus.

   ii) The electrons can change their orbits by absorbing or emitting a photon of energy (= *hl*) equal to the difference of the energies of the orbits.

   iii) The angular momentum of the electron is quantised.

3. The energy of a Bohr's orbit increases with an increase in the value of the principal quantum number, n. In fact it becomes lesser and lesser negative.
4. The smallest packet of energy is called quantum.

5. 6.625 x 10^{-34} Joules – second

6. When light is exposed to clean metallic surface, electrons are ejected from the surface. This effect is called as photo electric effect.

7. The minimum energy required for emission of photo electrons is called threshold energy.

3.5

1. The wave-particle duality refers to the fact that light and the material particles like electrons could sometimes behave as a particle and as a wave at other times.

2. The wave nature of electron was established by the diffraction of electron waves by the crystal lattice of nickel.

3. Mass of the electron = 9.1×10^{-31} kg

   Speed or Velocity = 100 km s^{-1} = 105 m s^{-1}

   Using equation, the wavelength associated with the electron will be

$$\lambda = \frac{h}{mv} = \frac{6.626x10^{-34}\,Js}{(9.1x10^{-31}kg)(105ms^{-1})} = 7.28x10^{-9}\,m$$

4. According to Heisenberg's Uncertainty Principle it is not possible to measure both the *position* and *momentum* of a particle with any degree of certainity. More accurately we measure a particle's position, the less accurately we are able to measure it's momentum and vice versa.

3.6

1. It is a mathematical fucntion that describes the motion of an electron inside the atom. It contains all the information about the system and can be found by solving a wave equation called Schrodinger wave equation.

2. An orbit refers to definite cirular paths of fixed energy around a central stationary nucleus while an orbital refers to the three dimensional region of space around the nucleus where there is a probability of finding the electron.

3. The quantum numbers are integers that characterize the wavefunctions. These are obtained in the process of solving Schrodinger wave equation and every electron in an atom has a different set of quantum numbers. The three quantum numbers obtained from Schrodinger Wave Equation are

   i. The principal quantum number, n

   ii. Azimuthal quantum number, l and

   iii. The magnetic quantum number m_l

4. The principal quantum number, n is concerned with the energy of the electron in a shell. The quantum number l is related to the geometrical shape of the orbital and the quantum, number, m_l describes the orientation of the orbital in space.

3.7

1. *s*-orbital : spherical;

   p-orbitals : dumb-bell shaped ;

   d-orbitals : cloverleaf shaped.

2. The 2s orbital is spherical in shape similar to the 1s orbital. However there are two differences. Firstly, the size of a 2s orbital is bigger as compared to a 1s orbital and secondly, it contains a spherical node.

3. i) It is a spherical region of zero probability in an s orbital (other than 1s).

   ii) It is a planar region in an orbital (other than s orbitals) where the probability or finding the electron is zero.

4. The 3s orbtial will have **two** spherical nodes.

3.8

1. The distribution of electrons in the shells and subshells of an atom is called *Electronic Configuration*.

2. Pauli's principle states that an atom no two electrons can have same set of the four quantum numbers.

3. Aufbau principle states that the electrons in an atom are filled in the increasing order of their energies which is determined by $(n + l)$ rules.

   There are two $(n + l)$ rules. These are

   An orbital with a lower value for $(n + l)$ is filled first.

   If the value of $(n + l)$ is the same for two orbitals then the orbital with lower value of n will be filled first.

4. i) 2p : $(n + l)$ for 2p = 2 + 1 = 3; for 3s $(n + l)$ = 3 + 0 = 3 ; Rule 2

   ii) 4s : $(n + l)$ for 4s = 4 + 0 = 4; for 3d $(n + l)$ = 3 + 2 = 5 ; Rule 1

4

PERIODIC TABLE AND ATOMIC PROPERTIES

We have seen different heaps of onions & potatoes at vegetable shop. Imagine, they are lying mixed and you want to buy 1kg of onion. What will happen? You will have to wait for long to sort that and then weight them. When you possess a variety of material substances, you have to keep them classified for an easy access and quick use. You cannot afford to mix clothes with eatables, cosmetics or books. Classification assures you that your eatables are in the kitchen, books on the study table or rack and your cosmetics are on the dressing table. Shopeekers, business houses, storekeepers, administrators, managers, information technology experts and scientists etc. have to keep their materials duly classified.

Chemists faced a similar problem when they were to handle a large number of elements. The study of their physical and chemical properties and keeping a systematic record of them had been a great challenge to chemists. Classification of elements finally could be possible due to pioneering work of a few chemists. In the present lesson we shall discuss the need, genesis of classification and periodic trends in physical and chemical properties of elements.

Objectives

After reading this lesson you will be able to:

- recognise the need for classification of elements;
- recall the earlier attempts on classification of elements;
- define modern periodic law;
- name the elements with atomic number greater than 100 according to IUPAC nomenclature;
- co-relate the sequence of arrangement of elements in the periodic table with the electronic configuration of the elements.
- recall the designations of the groups (1-18) in the periodic table;
- locate the classification of elements into s-, p-, d- and f- blocks of the periodic table and

- explain the basis of periodic variations of

a) atomic size	b) ionic size
c) ionization enthalpy	d) electron gain enthalpy within a group or a period.

4.1 Early Attempts

Attempts were made to classify elements ever since the discovery of metals or may be even earlier. J.W. Dobereiner in 1817 discovered that when closely related elements are grouped in a set of three, the atomic weight of the middle element was almost the arithmetical mean of the two elements in the group e.g.,

Element	Lithium	Sodium	Potassium
Atomic weight	6.94	22.99	39.10
mean atomic weight	--------	23.02	--------

He called such a group of three elements a triad. He could group only a few elements due to lack of knowledge of correct atomic weights of the elements at that time.

In 1863, J.A.R. Newlands, developed a system of classification of elements and entitled it as **Law of Octaves**. He arranged the elements is such a way that every eighth element had similar properties, like the notes of music. The law could not apply to a large number of known elements. However, the law indicated very clearly the recurrence of similar properties among the arranged elements. Thus the periodicity was visualised for the first time in a meaningful way.

Periodicity : Re-occurrence of properties after regular intervals.

More signifcant results were obtained when Lother Meyer’s work reflecting the periodicity was found to be based on physical properties of the elements. He clearly showed that certain properties showed a periodic trend.

4.2 Mendeleev’s Periodic Table

In 1869, Mendeleev’s a Russain Chemist made a thorough study of the relation between the atomic weights of the elements and their physical and chemical properties. He then constructed a table in which elements were arranged in order of their increasing atomic weights. It was also found that every eighth elements had properties similar to that of the first element. Thus, there was a periodic occurrence of elements with similer properties.

One of the most striking application of Mendeleev’s classification of elements was that in his periodic table (Table 4.1) he left gaps for elements which were yet to be discovered. He also predicted the properties of these elements. However, Mendeleev’s periodic table did not provide any place for isotopes and noble gases which were discovered later on.

Table 4.1 Mendeleev's Table of 1871

	I		II		III		IV		V		VI		VII		VIII		
Oxide	R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7			RO_4	
Hydride	RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH				
Periods ↓	A	B	A	B	A	B	A	B	A	B	A	B	A	B		Transition series	
1	H 1,008																
2	Li 6.939		Be 9.012		B 10.81		C 12.011		N 14.007		O 15.999		F 18.998				
3	Na 22.99		Mg 24.31		Al 29.98		Si 28.09		P 30.974		S 32.06		Cl 35.453				
4 First series:	K 39.102		Ca 40.08			Sc 44.96		Ti 47.90		V 50.94		Cr 50.20		Mn 54.94	Fe 55.85	Co 58.93	Ni 58.71
Second series:		Cu 63.54		Zn 65.37	Ga 69.72		Ge 72.59		As 74.92		Se 78.96		Br 79.909				
5 First series:	Rb 85.47		Sr 87.62			Y 88.91		Zr 91.22		Nb 92.91		Mo 95.94		Tc 99	Ru 101.07	Rh 102.91	Pd 106.4
Second series:		Ag 107.87		Cd 112.40	In 114.82		Sn 118.69		Sb 121.75		Te 127.60		I 126.90				
6 First series:	Cs 132.90		Ba 137.34			La 138.91		Hf 178.49		Ta 180.95		W 183.85			Os 190.2	Ir 192.2	Pt 195.09
Second series:		Au 196.97		Hg 200.59	Tl 204.37		Pb 207.19		Bi 208.98								

The extent of knowledge regarding the chemical properties of the elements and his insight into the system of periodicty possessed by the elements under certain arrangement have no parallel in the history of chemistry. This work laid strong foundation of the fundamental principles of the periodic law. One of his most important conclusions was that the elements if arranged according to their atomic weights, exhibit an evident systematic reoccurence of properties (periodicity of properties) and even the properties of some elements were listed much before their discovery. Mendeleev's periodic Table (Table 4.1) was quite useful till the discovery of atomic number there existed certain inherent defects which opposed the system.

4.3 Modern Approach

Atomic number was discovered in 1913 by a team lead by Moseley. The periodic table based on atomic number is termed as Modern Periodic Table. Moseley arranged all the elements according to increasing atomic number and showed that the properties of elements are periodic function of their atomic numbers.

Modern periodic law : The properties of the elements are periodic function of their atomic numbers.

4.4 Long Form of Periodic Table

The arrangement of elements in the long form of periodic table is a perfect matching of electronic configuration of the elements on one hand and physical and chemical properties of the elements on the other. Some important considerations of the modern atomic structure applied to the clasffication of elements are discussed below :

i) An atom loses electrons from or gains electrons in the outermost shell of an atom during a chemical reaction.

ii) The sharing of an electron or electrons by an atom with other atom or atoms is largely through the outer most shell. Thus the electrons in the outermost shell of an atom largely determine the chemical properties of the elements.

We may therefore conclude that the elements possessing identical outer electronic configuration should possess similar physical and chemical properties and therefore they should be placed together for an easy and systematic study.

Keeping in mind the reasoning given above, when all the known elements are arranged in a table according to their increasing atomic number, the properties of the elements show periodicity (reappear at definite intervals). The periodicity is shown in Table in 4.2

4.5 Structural Features of the Long Form of Periodic Table

i) In this table there are 18 vertical columns called **GROUPS**. They are numbered from 1 to 18. Every group has a unique configuration.

ii) There are seven horizontal rows. These rows are called **PERIODS**. Thus the periodic table has seven periods, numbered from 1 to 7.

iii) There are a total of 114 elements known to us till today. Of all the known elements 90 are naturally occurring and others are made through nuclear transformations or are synthesised artificially. Either way they are **Manmade Elements**, but you will find the term specifically applied to transuranic elements (elements listed after uranium) only.

iv) First period consists of only two elements (very short period). Second and third periods consists of only eight elements each (short periods). Fourth and fifth periods consist of 18 elements each (long periods). Sixth period consists of 32 elements (long period). Seventh period is yet incomplete and more and more elements are likely to be added as the scientific research advances.

v) There are also nick names given to the groups or a cluster of groups on the basis of the similarly of their properties, as given below :

Group 1 elements except hydrogen, are called **Alkali Metals**

Group 2 elements are called **Alkaline Earth Metals**

Group 3 to 12 elements are called **Transition Metals.**

Group 16 elements are called **Chalcogens**

Group 17 elements are called **Halogens**

Group 18 elements are called **Noble Gases.**

Apart from what has been said above elements with atomic numbers 58 to 71 are called *Lanthanoids* - or Inner Transition elements (First series). Elements from atomic numbers 90 to 103 are called actinoids - Inner Transition elements (Second series). All elements except transition and inner transition elements are also collectively called **Main Group Elements**.

Atomic number (Z)
Name of element

Symbol of element
Atomic weight or mass number (A)

TRANSITION ELEMENTS

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

4.6 Position of Metals, Non-Metals and Metalloids

In order to locate the position of metals, non-metals and metalloids in the periodic table, you may draw a diagonal line joining the elements boron (At. no. 5) with that of tellurium (At. no. 52) and passing through silicon and arsenic. Now we are in a position to make the following observations.

i) The elements above the diagonal line and to the far right are non-metals (except selenium which shows slightly metallic character also). The non-metallic character is more marked the farther an element is from the diagonal line and up.

ii) The elements below the diagonal line and to the left are metals. (Hydrogen is a non-metal and is an exception) The metallic character is more marked the farther an element is from the diagonal line and down. All lathanoids and actinoids are metals.

iii) The elements along the diagonal line are metalloids and possess the characteristics of metals as well as of non-metals. In addition germanium, antimony and selenium also show the characteristics of metalloids.

Intext Questions 4.1

1. Classify the elements of group 14, 15 and 16 into metlas, non-metals and metalloids.

   ....

2. Compare the metallic character of aluminium and potassium.

   ....

3. Name the group number for the following types of elements.
   i) Alkaline earth metals
   ii) Alkali metals
   iii) Transition metals
   iv) Halogens
   v) Noble gases.

   ....

4. Name five man made elements.

   ....

4.7 Catagorisation of Elements into *'s'*, *'p'*, *'d'*, and *'f'* Blocks

Grouping of elements in the periodic table can be done in another way also, which is more related to their electronic configuration. Under this categorisation, the location of the **differentiating electron** (the last electron) is most important. If, for example, the electron has gone to 's-subshell', the elements will fall in 's-block' and if the last electron goes to 'p-subshell', then the element will belong to p-block. Similarly if the defferentiating electron enters the d-subshells of an atom, then the elements comprising all such atoms will belong to d-block.

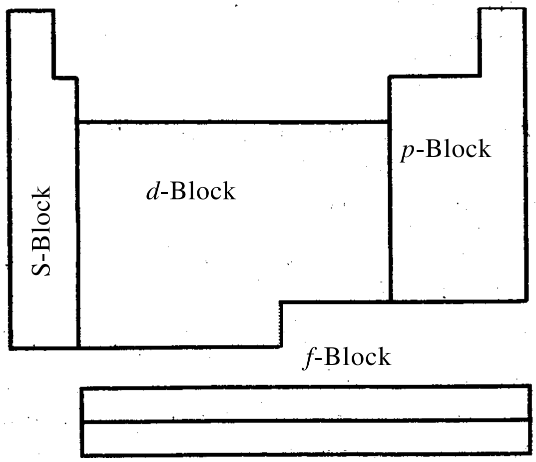


Fig. 4.1 : *Blockwise categorization of elements*

There are minor exceptions in Mn and Zn configurations. You will study more about the reasons for such exceptions in Lesson 23.

The grouping of elements explained above can be related to the type of elements disussed earlier.

i) s-block elements : All alkali metals and, alkaline earth metals.

ii) p-block elements : All elements of group no. 13 to group no. 18.

iii) d-block elements : All elements from group no. 3 to group no. 12 except Lanthanoids and Actinoides.

iv) f-block elements : Lanthanoids (at no 58 to 71) and Actinoids (at no. 90 to 103)

This is shown in Fig. 4.1

Nomenclature of Elements with Atomic Numbers greater than 100

The naming of the new elements was earlier left entirely to its discoverer. The suggested names were then later ratified by IUPAC. But due to certain disputes that arose over the original discoverer of some of the elements of atomic numbers greater than 104, the IUPAC in 1994 appointed a Commission on Nomenclature of Inorganic Chemistry (CNIC). After consultation with the Commission and the chemists around the world, the IUPAC in 1997 recommended a nomenclature to be followed for naming the new elements with atomic numbers greater than 103 until their names are fully recognised.

- The names are derived directly from the atomic number of the element using the following numerical roots for 0 and number 1-9.

0 = nil
1 = un
2 = bi
3 = tri
4 = quad
5 = pent
6 = hex
7 = sept
8 = oct
9 = enn

- The roots are put together in the order of the digits which make up the atomic number and 'ium' is added at the end.
- Names, thus derives, and the IUPAC approved names of some elements with atomic numbers greater than 103 are listed in Table 4.3

Table 4.3 Nomenclature of elements with atomic numbers greater than 103

Atomic Number	Name	Symbol	IUPAC approved Name	IUPAC Symbol
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnillium	Uun		
111	Unununnium	Uuu		
112	Ununbium	Uub		
113	Ununtrium	Uul		
114	Ununquadium	Uuq		
115	Ununpentium	Uup		

4.8 Periodicity in Atomic Properties

The term periodicity is used to indicate that some characteristic propeties occur in the periodic table after definite intervals, however with a varying megnitude. Thus after starting from a certain point on the periodic table, we are almost certain that the movement in particular direction will show steady increase or decrease of a said property.

4.9 Atomic Size

In homonuclear diatomic molecules the distance from the centre of one nuclus to the centre of another nucleus gives the bond length and half of this bond length is atomic radius. (Fig. 4.2). The first number of each period is the largest in size. Thus we can say that the group 1 atom are the largest in their respective horizontal rows. Similarly, atoms of group 2 elements are large but are definitely smaller than the corresponding atoms of group 1. This is due to the reason that the extra charge on the nucleus draws the electrons inward resulting in smaller size for the atoms under reference. This trend of decrease in size of atoms, continues from left to right. An example is shown in Fig. 4.3. However there may be some exceptions and there will be other reasons to explain them.

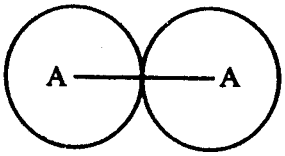


Fig. 4.2 : *Atomic radium* = *1/2* $d_{AA} = r$

Fig. 4.3 : *From left to right, size of atoms decrease in the periodic table*

In going down the group of elements (in any particular column) the atomic size increases at each step.

This increase may be explained in terms of a new electron shell being added, when we pass from one element to another in a group.

4.9.a Types of atomic radius

The atomic radius cannot be determined exactly. But the inter-nuclear distance of the bonded atoms can be measured using x-ray difraction or other methods.

The atomic radius depends on many factors like the number of bonds formed by the atom, nature of bonding, oxidation state etc.

The types of atomic radius are considered based on nature of bonding. They are

1. Crystal radius or Atomic radius
2. Vander waal's radius.
3. Covalent radius .

Crystalline Radius :

This type of radius is applicable for metal atoms.

Half of the distance between the centres of the nuclei of two adjacent metal atoms in the metallic crystal is called crystal radius or atomic radius.

It is measured in $1A^0 = 10^{-8}$ cm $= 10^{-10}$ m = 0.1 m

$1 \text{ nm} = 10^{-9} \text{ m}$

Example : The distance between two Na Atoms = 3.72 A^0
Crystal radius of Na = 3.72/2 = 1.86 A^0

Vander Waal's radius :

This type of radius is used only for molecular substances present in the solid state.

'Vander Waal's radius is distance between the centres of two atoms of different molecules which are closest to each other.

These atoms which approach closest to one another do not form chemical bond. But remain together due to Vander waal's forces of attractions.

For example the distance between two adjacent Chlorine atoms of different molecules is 3.6A^0 – Then the Vander Waal's radius of Chlorine is 3.6/2 = 1.80 A^0

Vander Waal forces of attraction are weak so it is found that Vander Waal's radius is 40% more than half of the distance between two nuclei of chemically bonded atoms.

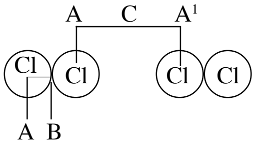
Covalent radius :

This radius is generally used while referring to non-metals.

It is half of the distance between the nuclei of two atoms held together by a covalent bond.

For Example the inter nuclear distance between Chlorine atoms in a molecule is 1.98A. The covalent radius of chlorine is one half of the inter nuclear distance.

ie. 1.98/2 = 0.99A^0



Vander waal and Covalent radii in chlorine.

Vander waal's radius = $AC = A'C = r = 1.8A^0$
Covalent radius = $AB = r = 0.99\ A^0$
The inter nuclear distance = AA_1 distance = $3.6A^0$
vander waal's radius = $AA_1\ 1/2 = 3.6/2 = 1.80\ A^0$

Intext Questions 4.2

1. Give the order of penetration of orbitals toward, nucleus for a given principal quantum number.
   ....
2. Define shielding effect.
   ....
3. Define covalent radius of elements.
   ....

4.10 Ionic Size

An ion is formed when an atom undergoes a loss or gain of electron.

$$M(g) \longrightarrow M^+(g) + e^- \qquad \text{(cation formation)}$$

$$M(g) + e^- \longrightarrow M^-(g) \qquad \text{(anion formation)}$$

A cation is formed when an atom loses the most loosely bound electron from its outermost shell. The atom acquires a positive charge and becomes an ion (a cation). A cation is smaller than its atom. On the removal of an electron, the positive charge of the nucleus acts on lesser number of electrons than in the neutral atom and thus greater pull is exerted by the nucleus, resulting in a smaller size of the cation.

An anion is bigger than its atom because on receipt of an electron in the outermost orbit the number of negative charges increase and it out weights the positive charges. Thus the hold of the nucleus on the shells decrease resulting in an increase in the size of the anion.

A cation is always smaller than its atom and an anion is always bigger than its atom e.g. Na^+ is smaller than Na, Cl^- is bigger than Cl.

- In the main groups, the ionic radii increase on descending the group e.g., $Li^+ = 0.76$ A°, $Na^+ = 1.02$ A°, $K^+ = 1.38$ A°, etc. it is due to the addition of extra shell at each step.
- There is a decrease in the ionic radii of the positive ions on moving from left to right across a period in the periodic table. $Na^+ = 1.02$ A°, $Mg^{2+} = 0.72$ A°, $Al^{3+} = 0.535$ A°, etc. It is due to the increase in the number of charges on the nucles and also due to the increase in the charge on the ion.
- The ionic radii of the negative ions, also decrease on moving from left to right across a period. e.g. $O^{2-} = 1.40$ A°, $F^- = 1.33$ A°, etc. This is partly due to increase in the number of charges on the nucleus and also due to the decreasing change on the ion.

Intext Questions 4.3

1. Write the names of the elements with atomic numbers 105, 109, 112, 115 according to IUPAC nomenclature.

   ....

2. Arrange the following in the order of increasing size.

   Na^+, Al^{3+}, O^{2-}, F^-

   ....

3. How does the size of atoms vary from left to right in a period and on descending a group in the periodic table ?

   ....

4.11 Ionization Enthalpy

Ionization Enthalpy is the energy required to remove the most loosely bound electron from an isolated atom inthe gaseous state for one mole of an element. It is expressed in kJ mol^{-1} (kilo joules per mole)

$$M(g) + IE \longrightarrow M^{+}(g) + e^{-}$$

As we move from left to right in the periodic table, there is a nearly regular increase in the magnitude of the ionization enthalpy of elements.

Similarly, on moving down a group the magnitude of the ionization enthalpy indicates a regular decline. The ionization enthalpy of the first member of any group is the highest within that group and the ionization enthalpy of the last member in the same group, is the least. This is shown an table 4.4

Table 4.4 : First ionization enthalpies of the elements (in kJ mol^{-1})

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H • 1311																	He • 2372
2	Li • 520	Be • 899											B • 801	C • 1086	N • 1403	O • 1410	F • 1681	Ne • 2081
3	Na • 496	Mg • 737											Al • 577	Si • 786	P • 1012	S • 999	Cl • 1255	Ar • 1521
4	K • 419	Ca • 590	Se • 631	Ti • 656	V • 650	Cr • 652	Mn • 717	Fe • 762	Co • 758	Ni • 736	Cu • 745	Zn • 906	Ga • 579	Ge • 760	As • 947	Se • 941	Br • 1142	Kr • 1351
5	Rb • 403	Sr • 549	Y • 616	Zr • 674	Nb • 664	Mo • 685	Te • 703	Ru • 711	Rn • 720	Pd • 804	Ag • 731	Cd • 876	In • 558	Sn • 708	Sb • 834	Te • 869	I • 1191	Xe • 1170
6	Cs • 376	Ba • 503	La • 541	Hf • 760	Ta • 760	W • 770	Re • 759	Os • 840	Ti • 900	Pt • 870	Au • 889	Hg • 1007	TI • 589	Pb • 1007	Bi • 589	Po • 715	At • 703	Rn • 813
7	Fr	Ra 912	Ac 1037															

The variation in the magnitude of ionization enthalpy of elements in the periodic table is mainly dependent on the following factors :

a) The size of the atom
b) The magnitude of the nuclear charge on the atom,
c) The extent of screening
d) The type of orbital involved (s, p, d or f)

- In small atoms, the electrons are tightly held whereas in large atoms the electron are less strongly held. Thus, the ionization enthalpy decreases as the size of the atom increases.
- When an electron is removed from an atom, the effective nuclear charge, i.e., the ratio of the number of charges onthe nucleus to the number of electrons, increases. As a result the remaining electrons come closer to the nucleus and are held more tightly. The removal of a second electron, therefore, requires more energy. e.g., Mg^+ is smaller than the Mg atom. The remaining elctrons in Mg^+ are more tightly held. The second ionisation enthalpy is, therefore, more than the first ionisation enthalpy.
- Since the orbitals (*s, p, d* and *f*) have different shapes, the ionization enthalpy depends on the types of electrons removed. e.g. an electron in an *s* orbital is more tighly held as compared to an electron in a *p* orbital. It is because an *s* electron is nearer to the nucleus as compared to a *p* electron. Similarly a *p*-electron is more tightly held than a *d*-electron, and a *d*-electron is more tightly held than a *f*-electron. If all other factors are equal, the ionization enthalpies are in the order $s > p > d > f$.

These factors taken together contribute largely to decid the extent of the force of attraction between the nucleus and the electrons around it. The resultant of these factos thus determine the magnitude of ionization enthalpy of any element. You can see the variation in the magnitude of the ionization enthalpy of elements with atomic number in the Fig. 4.4.

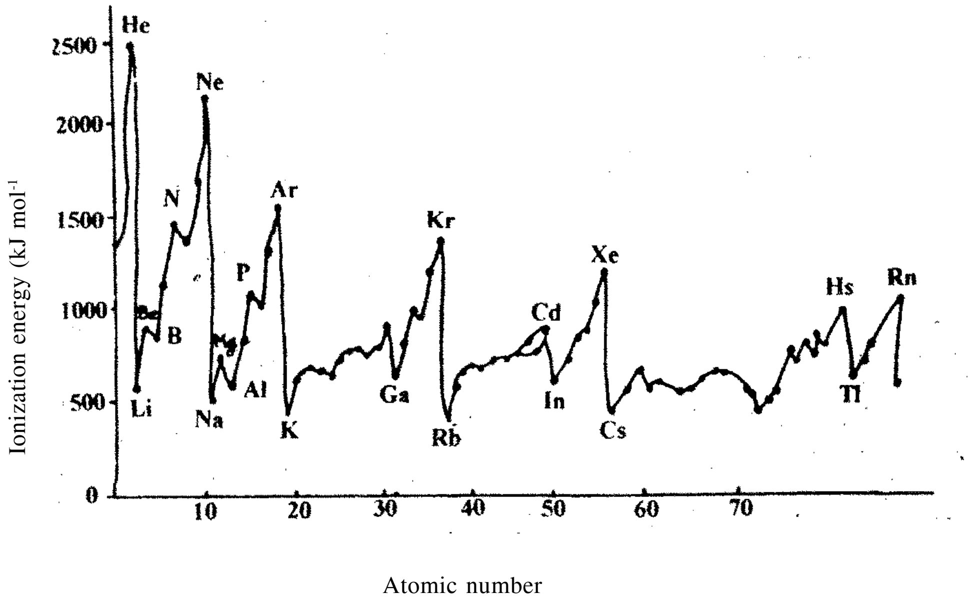


Fig. 4.4 : *Variation of ionization enthalpy of elemetns.*

It is clear from Fig. 4.4 that

i) The metals of group 1 (Li, Na, K, Rb, etc.) have the lowest ionization enthalpies in their respective periods.

ii) The noble gases (He, Ne, Ar, Kr, Ze and Rn) have the highest ionization enthalpies in their respective periods. It is because the energy required to remove an electron from a stable fully filled shell is very large.

iii) The values of ionization energies do not increase smoothly. e.g. the first ionization enthalpy of B (boron) is lower than that of Be (beryllium); the ionization enthalpy of Al (aluminium) is lower than that of Mg (magnesium); the first ionization enthalpy of O (oxygen) is lower than that of N (nitrogen). it can be explained as follows.

- The first ionization enthalpies of Be and Mg are higher than those of their preceding elements because the electrons are removed from the fully filled s-orbitals.
- The first ionization enthalpy of N is higher than that of O because from N, the electron is to be removed from a half-filled p-orbitals.

Ionization enthalpy is the energy required to remove the most loosely bound electron form an atom (in the gaseous state) for one mole of an element. It is an absolute value and can be determined experimentally.

Factors effecting Ionization energy

The magnitude of Ionization potential of an atom depends on the following factors :

1. Atomic radius
2. Nuclear Charge
3. Screening or shielding effect on the outer electrons
4. Extent of penetration of orbitals of valence electrons.
5. The nature of sub shells; Whether half filled or completely filled with electrons or not.

1. **Atomic radius:** As the atomic size increases valence electrons move farther from the nucleus and so are held by weak nuclear attraction. So less energy is enough for the removal of the outer most electron of an atom. Hence, as the atomic radius increases, the Ionization energy decreases.

2. **Nuclear Charge :** The Number of electronic shells remain same, as the nuclear charge increase, the outer electrons are more strongly held by the nucleus due to attractive forces As a result, the energy required to remove the most loosely held electron from the atom is more. Hence IP increases, as the nuclear charge increases.

Element	Li	Be	C	N	F
Nuclear Charge	3	4	6	7	9
Ionization Potential ev$^-$	5.39	9.32	11.25	14.52	17.42

3. **Screening effect:** In an atom having more than one electron, the valance electrons are attracted by the nucleus and at the same time repelled by the inner core of electrons. The electrons present in the inner orbits screen the electrons present in the outer most orbit from being attracted by the nucleus. Hence, the nuclear attraction on the outer most electron decreases. This influence of the inner core of electrons on the attraction of the nucleus towards outer electrons is referred screening effect.

   $$\text{Screening Effect} \;\alpha\; \frac{1}{1p}$$

   The screening efficiency of orbitals falls off in the order s>p>d>f

4. **Extent of penetration of Orbitals of valence electrons:** For a given quantum number the s-orbital penetrates more towards nucleus because of its spherical and symmetrical shape. So an electron of an s-orbital requires large amount of energy to be removed. In the same shell P-electrons require less energy to remove. Hence the Ionization energy follows the sequence of the extent of penetration of the orbitals s>p>d>f.

5. **Completely filled or half filled sub shells:** Completely filled or half filled electronic sub energy levels impart greater stability to the atom ie. the element. Such atoms required more energy for Ionization. Hence, they have more Ionization energy values.

4.12 Electron Gain Enthalpy

Every atom, in general, has a tendency to gain or loose electrons in order to acquire a noble gas configuration. The atom which have five, six or seven electrons in their outermost shell show tendency to accept electrons and attain the nearest noble gas configuration. Halogens, for example, have seven electrons in their outermost orbit. Thus they show a tendency to accept, one more electron and attain the nearest noble gas configuration. The energy change (ΔE) for this process is called **electron gain enthalpy** of that atom.

Electron gain enthalpy is the energy released or adsorbed for one mole of neutral atoms in a gaseous state when electron is accepted by each atom.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

Where X represents an atom.

$$Cl\,(g) + e^- \longrightarrow Cl^-(g):\ \Delta E = -349\ kJ\ mol^{-1}$$

The negative value shows release of energy and hence tendency to greater stabilisation. The eletron gain enthalpy becomes more in negative from left to right in a period. This is because it is easier to add an electron to a smaller atom since the added electron would be closer to the positvely charged nucleus. Halogens release maximum energy when they accept an electron. On the otehr hand, metals do not accept electrons and show a high positive value for ΔE. Thus electron enthalpy can be positive or negative.

Electron gain enthalpies becomes less in negative as we go down the group showing that the electropositive character of the atoms increases. This is because the size of the atom increases down the group and the electron added goes to the higher shells. Electron affinity values for some elements are shown in table 4.5, along with their position in the periodic table. The electron gain enthalpy of chlorine is more in negative value as compared to that of fluroine. This is due to the small size of the F atom. As the electron approaches the small F atom, it expriences a repulsion from other electrons.

Table 4.5 : Electron gain enthalpy in kJ mol^{-1}

	1	2	13	14	15	16	17	18
1	H							He
	-73							+98
2	Li	Be	B	C	N	O	F	Ne
	-59.6	(0)	-26.7	-154	-7	-111	-328	+116
3	Na						Cl	Ar
	-53						-349	+96
4	K						Br	Kr
	-48						-325	+96
5	Rb						I	Xe
	-47						-295	+77
6								Rn
								+68

4.13 Electronegativity

It is an indicator of the extent of attraction by which electrons of the bond pair are attracte by an atom linked by this bond. The value of electronegativity is assigned arbitrarily to one atom such as hydrogen. Then the value of electronegativity is assigned to all other atoms with respect to hydrogen. One such scale is the **Pasuling Scale of electronegativity** (Table 4.6).

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

In a homonuclear diatomic molecule such as hydrogen (H_2) or fluorine (F_2), the electron pair of the covalent bond in each molecule experiences equal attraction by each atom. Thus non of the two atoms is able to shift the bond pair of electrons to itself. However in a heteronuclear diatomic molecule, the bond pair electrons get shifted towards the atom which is more electronegative than the other. For example, in HF or HCl the bond pair of electrons are not shared equally but the more electronegative atom F or Cl is able to shift the bond pair towards itself, resulting in the polarization of the molecule.

A large difference between electronegativities of the two atoms indicates highly ionic character of the bond between them. For example Cs^+F^-. On the other hand, zero difference in the electronegativities between the two atoms indicates that the percentage ionic character is zero. Therefore the molecule is purly covalent e.g. H_2, Cl_2, N_2 etc.

Table 4.6 : Electronegativities of elements on Pauling Scale.

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Se	Ge	As	Sc	Br
0.8	1.0	1.3	1.7	1.8	2.1	2.5
Cs	Ba					
0.7	0.9					

The most electronegative elements have been placed on the farthest right hand upper corner (noble gases are not included). The value of electronegativity decreases as we go down in any group and increases from left to right in the period. Thus fluorine is the most electronegative and caesium is the least electronegative element. (We have not considered Francium being radioactive).

Intext Questions 4.4

1. What is the correlation between atomic size and ionization enthalpy.

   ....

2. Which species, in each pair is expected to hav higher ionization enthalpy.

   i) $_{3}Li$, $_{11}Na$ ii) $_{7}N$, $_{15}P$

   iii) $_{20}Ca$, $_{12}Mg$ iv) $_{13}Al$, $_{14}Si$

   v) $_{17}Cl$, $_{18}Ar$ vi) $_{18}Ar$ and $_{9}K$

   vii) $_{13}Al$, $_{14}C$

   ....

3. Account for the fact that there is a decrease in first ionization enthalpy from Be to B and Mg to Al.

   ....

4. Why is the ionization enthalpy of the noble gases highest in their respective periods ?

   ....

5. Name the most electronegative element.

   ....

What You Have Learnt

- The classification of elements makes their systematic.
- The arrangement of elements in the long form of the periodic table depends on their electronic configuration.
- The properties of the elements are periodic function of their atomic number.
- All the known elements are arranged in 18 groups in the long form of periodic table
- There are seven horizontal rows (periods) in the long form of the periodic table.
- Elements of groups 1 and 2 are known as alkali metals and alkaline earth metals respectively.
- *s, p, d* and *f* are the four blocks in the periodic table classified on the basis of their outer most electrons residing in *s, p, d* and *f* sub-shell.
- The elements can be classififed into metals, non-metals and metalloids on the basis of their properties and their position in the periodic table.
- The atomic size, ionic size, ionization enthalpy, electron gain enthalpy and electronegativity show regular trends along a group and a period.
- Various type of atoms radius possible for atoms
- Factors which effect the Ionization potential of different atoms.

Terminal Exercise

1. Define modern periodic law.
2. Refer the periodic table in Table 4.2 and answer the following questions.
   i) The elements placed in group number 18 are called ....
   ii) Alkali and alkaline earth metals are collectively called .... block metals.
   iii) The general configuration for halogens is ....
   iv) Name a *p*-block elements which is a gas other than a noble gas or a halogen.
   v) Name the groups that comprise the ‘s’ block of elements.
   vi) Element number 118 has not yet been established, to which block, will it belong?
   vii) How many elements should be there in total if all the 7s, 7p, 6d and 5f blocks are to be full ?
3. Describe the variation of Electron Affinity and Ionization Enthalpy in the periodic table.

4. Define the following :

   a) Electron gain enthalpy   b) Ionization enthalpy

   c) Ionic radius   d) Electronegativity

5. What is electronegativity ? How is it related to the type of bond formed ?

6. Why is the electron gain enthalpy of Cl more in negative value as compared to that of F ?
7. Name the different types of atomic radius
8. What is shielding effect?
9. Explain 3 factors which influence the Ionization energy.

Answers to Intext Questions

4.1

1.

Metals	Non metals	Metalliods
Sn, Pb	C	Si, Ge
Sb, Bi	N, P	As
Te, Po	O, S	Se

2. Potassium is mroe mettalic than aluminum.

3. i) 2   ii) 2   iii) 3-12   iv) 17   v) 18

4. Np,   Lw,   No,   Rf,   Hs.

4.2

1) s>p>d>f
2) Protection of outer electrons from nuclear attraction by electrons present in inner shells of an atom.
3) Covalent radius is half of the distance between the nuclei of two atoms held together by a covalent bond.

4.3

1. i) Unnilpentium

   ii) Unnilennium

   iii) Ununbium

   iv) Unnunpentium

2. Al^{3+}, Na^{+}, F^{-}, $O2^{-}$

3. The atomic size decreases from left to right across a period and increases on moving down the group.

i) s>p>d>f

ii) Protection of outer electrons from nuclear attraction by electrons present in inner shells of an atom.

iii) Covalent radius is half of the distance between the nuclei of two atoms held together by a covalent bond.

4.4

1. Ionization enthalpy decreases with increase in atomic size and vice-versa.

2. i) $_{3}Li$ ii) $_{7}N$ iii) $_{12}Mg$ iv) $_{14}Si$

   v) $_{12}Ar$ vi) $_{18}Ar$ vii) $_{6}C$

3. The electronic configuration of Be is $1s^2\,2s^2$ whereas that of B is $1s^2\,2s^2\,2p^1$. In case of Be, the electron is to be removed from completely filled s orbital whereas in case of B it is to be removed from a singly occupied p orbital. Fully-filled orbitals are more stable. Hence, ionization enthalpy decreases from be to B. Similarily it decreases from Mg to Al.

4. The nole gases have fully filled and are stable. Hence, they have the highest ionization enthalpies in their respective periods.

5. Fluorine.

SENIOR SECONDARY COURSE
CHEMISTRY
Student's Assignment - 1

Maximum Marks : 50 Time : 2.30 Hrs.

INSTRUCTIONS :

- Answer all the questions on a separate sheet of paper.
- Give the following information on your answer sheet.
  - Name
  - Enrolment Number
  - Subject
  - Assignmnet Number
  - Address
- Get your assignment checked by the subject teachmer at your study centre so that you get positive feedback about your performance.

Do not send your assignment to APOSS

1. a) Write down symbols for prefixes micro and mega.
   b) Write the empirical formula of C_2H_2 and C_3H_8.
   c) State charles' law and given mathematical expression for it.
   d) Express 4.6 x 10^{-10} m in terms of pico metre.
   e) What is the SI unit for measuring electric potential.
   f) Atomic mass of C-12 is 12. What is the mass of one C-12 atom ?
   g) Write down the names of four quantum numbers.
   h) State Heisenberg's uncertainly quantum numbers.
   i) How many moles of oxygen atoms are present in 2 moles of $CuSO_4.5H_2O$?
   j) Define Orbital. (1x10=10)

2. a) Calculate the mass of one molecule of benzoic acid, C_6H_5COOH (Atomic masses; C=12, H = 1, O = 16).
   b) Write the empirical formulae of the following C_6H_6,N_2O_4,$C_6H_{12}O_6$,NH_3.
   c) What are anode rays ? Give their two important properties.
   d) Given values of *n, l* and *m* quantum numbers of an electron which is present in $3p_x$ orbital
   e) Write electronic configuration of chromium (atomic number = 24)
   f) Which of the following orbitals is not possible *3p, 4s, 2d, 5f.*

g) Write two differences between atom and ion.

h) What are electromagnetic radiations.

i) A solution of ferric sulphate containing 0.280 g of ferric ions is treated with an excess of a solution of Ba $(OH)_2$. Calculate the weight of the precipitate formed if they react as

$Fe_2 (SO_4)_3 + 3Ba (OH)_2 (aq) \longrightarrow 2Fe (OH)_3 (s) + 3BaSO_4 (s)$

(Atomic Masses : Fe = 56, Ba = 137, O = 16, H = 1, S = 32)

j) Calculate and compare the energies of two radiations having wavelengths λ_1 = 4000A and λ_2 = 8000A. (2x10=20)

3. a) Using de Broglie expression, calculate the momentum of a moving particle whose wave length (λ) is 200 pm. (pm = picometers)

b) Determine the molecular formula of a compound which contains 2.19%H; 12.8% C and 85.1% Br. 1g of the compound in gaseous state occupies 119 mL volume at STP. (Atomic masses : C = 12, H = 1, Br = 80)

c) Calculate the wave length and frequency of the spectral line in Lyman series of hydrogen spectra which has minium frequency.

d) 1.84 g of a mixture of $CaCO_3$ and $MgCO_3$ are heated strongly to decompose (as given below) till no forther loss of weight occurs.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$\text{and } MgCO_3 \longrightarrow MgO + CO_2$$

The residue weighs 0.96g. Find the percentage composition of mixture (Atomic masses : Mg = 24, Ca = 40, C = 12, O = 16) (3x4=12)

4. a) What is the uncertainty in the velocity of a moving cricket ball having mass 150g if its uncertainty in position is 1A.

b) A naturally occuring mineral was found to contain 42% $MgCO_3$ and 55% $CaCO_3$ and the rest was in purity. What volume of CO_2 measured at 15^0C and 745 mm Hg pressure will be evolved by heating 10g of the mineral hydrochloric acid if the reation occurs as follows:

$$MCO_3 + 2HC \longrightarrow MCl_2 + CO_2 + H_2O$$

Where M = mg or Ca (4x2=8)

5

CHEMICAL BONDING

In lesson 1 you have learnt about the structue of atom while in the lesson 2 you studied about the classfication of elements and the variation in atomic properites. You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine ?
- What are the different ways in which the atoms can combine ? and
- What are the shapes of different molecules ?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.

Objectives

After reading this lesson you will be able to:

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- list the charateristics of ionic compounds;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulson (VSEPR) theory;
- predict the geometry of molecules with the help of VSEPR thoery;

- explain the hybridisation of atomic orbitals involving s, p and d orbitals and illustrate with examples;
- tabulate the geometry of some molecules showing sp, sp^2, sp^3, dsp^2 and dsp^3 hybridisation;
- explain the formation of σ and π bonds in CH_4, CH_2H_4 and C_2H_2;
- explain molecular orbital theory;
- write the molecular orbital configuration of H_2, N_2, O_2 and F_2 molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

5.1 What is a Chemical Bond

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a chemcial bond. Thus *a chemical bond may be visualised as an effect that leads to the decrease in the energy*. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the consituent atoms.

A question arises, "How do atoms achieve the decrease in energy to form the bond." The answer lies in the electronic configuration. As you are aware, the noble gases do not react with other elements to form compounds. This is due to their stable electronic configuration with eight electrons (two in case of helium) in their outermost shells. The formation of a bond between two atoms may be visualised in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

5.2 Ionic or Electrovalent Bond

Accordingt to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

The electronic configuration of sodium atom (atomic number 11) is 2, 8, 1. Since it is highly electropositive, it readily loses an electron to attain the stable configuation of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process

$$\underset{\mathbf{2,\,8,1}}{Na} \longrightarrow \underset{\mathbf{2,8}}{Na^+} + e^- \; ; \qquad \Delta H = 493.8 \text{ k J mol}^{-1}$$

(ΔH is enthalpy change)

On the other hand, a chlorine atom (electronic configuration: 2, 8, 7) requries one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl^-) in the process.

$$\underset{\mathbf{2,\,8,7}}{Cl} + e^- \longrightarrow \underset{\mathbf{2,8,8}}{Cl^-} \; ; \qquad \Delta H = 397.5 \text{ k J mol}^{-1}$$

According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.

$$\underset{\mathbf{2,\,8,1}}{Na} + \underset{\mathbf{2,8,7}}{Cl} \longrightarrow \underset{\mathbf{2,8}}{Na^+} + \underset{\mathbf{2,8,8}}{Cl^-}$$

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic atrractions. The bond so formed is called an **electrovalent** or an **ionic bond**. *Thus the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

Factors favour the Ionic bond formation :

a) Cation formation

1) **Lower ionization energy :** Lower the ionization energy of an atom, greater is the case of formation of cation.

   The IP of sodium is 519.82 kJ. mol^{-1} and that of Potassium is 495.57 kj. mol^{-1} so K^+ ion can readily form than Na^+ ion.

2) **Large size of the atom :** Large atom can easily lose the valence electrons. If the size is large, the distance between the nucleus and the valence electrons is more

and therefore nuclear attraction is less. Therefore the electron can be removed easily from the atom forming cation.

3) **Ion with lower change :** Small magnitude of the change favours the formation of ions easily. eg. : the case of ion formation increases in the order $Na^+ > Mg^{+2} > Al^{+3}$.

4) **Cations with inert gas configuration :** Ions pocessing eletronic configuration similar to zero group elements are more stable than those ions which do not have such configuration.

   e.g. Ca^{+2} (2,8,8) in more stable than Zn^{+2} (2,8,18) because Ca^{+2} has inert gas configuration.

b) **Anion formation :**

1) **High Electron affinity :** If the electron affinity of an element is high its anion can be easily formed.

   e.g. $Cl^- > O^{2-} > N^{3-}$

2) **Smaller size of atom :** Smaller the atom lesser is the distance between the nucleus and the valance orbit. Hence the nuclear attraction on incoming electron is more So the anion is readily formed.

3) **Lower change :** Ions with lower change are more readily formed than those with higher charges. (like O^{-2} and N^{-3}).

   $Cl + e^- \longrightarrow Cl^- > O^{2-} > N^{3-}$

c) **Electro Negativity Values :**

If the two bonded atoms differ by more than 1.70 in their EN values, the bond between them is ionic in nature.

5.2.1 Energetics of Ionic Compounds Formation

We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when more **energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy ? Your questions is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

a) **Sublimation** of solid sodium to gaseous sodium atoms.

$Na(s) \longrightarrow Na(g)$; $\Delta H = 108.7\ kJ\ mol^{-1}$

b) **Ionization** of gaseous sodium atom to give sodium ion.

$Na(s) \longrightarrow Na^+(g) + e^-$; $\Delta H = 493.8\ kJ\ mol^{-1}$

c) **Dissociation** of gaseous chlorine molecule into chlorine atoms

$^1/_2\ Cl_2(g) \longrightarrow Cl(g)$; $\Delta H = -120.9\ kJ\ mol^{-1}$

d) Conversion of gaseous chlorine atom to chloride ion (**addition of electron**)

$Cl(g) + e^- \longrightarrow Cl^-(g)$; $\Delta H = -379.5\ kJ\ mol^{-1}$

e) Formation of NaCl from sodium and chloride ions. (**Crystal or lattice formation**).

$Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$; $\Delta H = -754.8\ kJ\ mol^{-1}$

The energy released in this step is **lattice energy.**

The net reaction would be

$Na(s) + {}^1/_2Cl_2(g) \longrightarrow Na^+Cl^-(s)$; $\Delta H = -4109.\ kJ\ mol^{-1}$

The overall energy change can be computed by taking the sum of all the energy changes;

$\Delta H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9\ kJ\ mol^{-1}$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Of the five different types of energies involved, two (sublimation and dissociation energies) are generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic configuration the basis of the above discussion we can say that the formation of an nion compound formed by

i. Low ionisation energy of the metal,

ii. High electron affinity of the other element (non-metal), and

iii. High lattice energy

5.2.2 Characteristic Properties of Ionic Compounds

- These exist as crystalline solids in which the ions are arranged in regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.
- These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.
- These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.

- These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explain bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly eletronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2, etc. For example in case of O_2, there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalnet bonding.

Properties of ionic compounds :

1) **Physical State :** Due to close packing of ions, ionic compounds are crystalline solids.

2) **Melting and Boiling points :** In ionic crystals the oppositely charged ions are bound by strong electrostatic force of attraction. To overcome these attractive force between ions, more thermal energy is required. Hence the melting and boiling points of ionic compounds are high.

3) **Solubility :** Ionic compounds are soluble in polar solvents like water, liquid ammonia etc. But are insoluble in non-polar solvents like benzene, carbondisulphide etc.

4) **Reactivity :** Reaction between ionic compounds in aqueous solution are very fast due to strong attraction among ions.

   e.g. When $AgNO_3$ solution is added to NaCl solution, a white precipitate of AgCl is formed.

$$\overset{+}{Ag}+\overset{-}{NO_3}+\overset{+}{Na}\overset{-}{Cl} \longrightarrow AgCl + \overset{+}{Na}\overset{-}{NO_3}$$

5) **Isomerism :** Ionic bond is non directional so ionic compounds cannot exhibit isomersim.

6) **Electrical, conductivity :** Ionic substances conduct electricity in molten state and in aqueous solution. The ionic compounds are, therefore, electrolytes.

5.3 Covalent Bond

Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration is achieved, is different. Lewis proposed that this is achieved by "sharing of pair of electrons" between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shows as

$$H. \;+\; .H \longrightarrow H:H \longrightarrow H-H$$

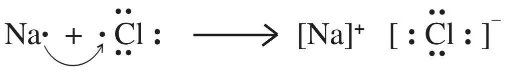
This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds. In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecues. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol.** This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the eletrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as :

$$\cdot\text{Li}\ ;\ \cdot\text{Be}\cdot\ ;\ \cdot\underset{\cdot}{\text{B}}\cdot\ ;\ \cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot\ ;\ :\overset{\cdot}{\underset{\cdot}{\text{N}}}\cdot\ ;\ :\overset{\cdot\cdot}{\underset{\cdot}{\text{O}}}\cdot\ ;\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}\cdot\ ;\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Ne}}}:$$

You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols.

In terms of Lewis symbols the ionic bond formation in NaCl can be represented as



$$\text{Na}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow [\text{Na}]^{+}\ [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:]^{-}$$

and the covalent bond formation in HCl is represented as

$$\text{H}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}: \longrightarrow \text{H}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:$$

Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as

$$\text{H}_{\text{x}} + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}: \longrightarrow \text{H}{}^{\cdot}_{\text{x}}\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:$$

In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no differece between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}: \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}:$$

Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

You may have noticed that in the process of bond formation the elements of second period acquire eight electrons in their valence shell.. This is called **'Octet rule'**. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding Electrons the pair of electrons is called '*bond pair*' and the pairs of electrons not involved in the bonding process are called '*lone pairs*'. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 5.4.

Valency Bond Theory

VSEPR theory gives the geometry of simple molecules but it does not explain them. Also it has limited applications. To overcome these limitations, the Valence Bond Theory (VBT) and the Molecular Orbital Theory (MOT) are introduced. Both the theories are based on quantum mechanical principles.

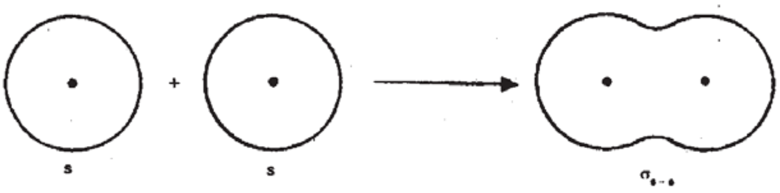
Many attempts were made to apply this theory for the formation of covalent bonds. One such theory, valence bond theory (VBT) was postulated by Heitler and London. This was extended later by pauling and slater to explain the shapes of the molecules as well as the directions of the bonds in them. The important postulates of this theory are as follows :

1) A covalent bond is formed by the overlap of two atomic orbitals.
2) The overlaping orbitals contain unpaired electrons of opposite spins.
3) Each of the bonded atoms retains its own atomic orbitals. But the electron pair in the overlapping orbitals is shared by both atoms.
4) Greater the extent of over of orbitals, stronger is the bond formed.
5) As the atomic orbitals are directional in nature (except 's' orbitals) the bonds that result due to the overlap of orbitals are also directional. This gives the definite geometry to the covalent molecule.
6) The increased electron density due to the overlap of atomic orbitals of the two combining atoms, is along the internuclear axis and keeps two atoms attracted to each other. This gives stability to the molecule.

Examples :

i) Formation of H_2 molecules :

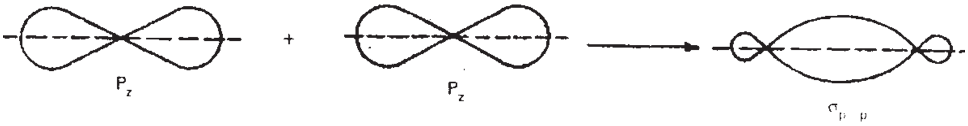
Hydrogen molecule is formed due to overlapping of s-s orbitals. When two hydrogen atoms come together, 1s orbitals of the Hydrogen atoms overlap to form a strong "σ" bond this is σ s-s.



Formation of H_2

Formation of Cl_2 molecule :

The electronic configuration of chlorine atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2_x\ 3p^2_y\ 3p^1_z$. It has one half filled $3p_z$ orbital. The Pz orbital of one chlorine atom overlaps the Pz orbital of the chlorine atom and the two electrons of opposite spins pair up to form covalent bond. As the overlap along the internuclear axis is maximum a strong bond is formed. The bond is formed due to σ P-P overlap.



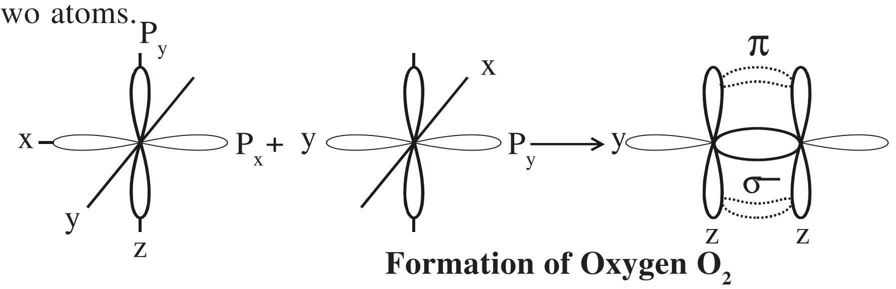
Formation of Cl_2

Formation of O_2 molecule :

Th electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z$. It has two half filled 2p orbitals i.e., $2p_y$ and $2p_z$.

The Py orbital of one atom overlaps the P_y orbital of the second atom to form a 'σ' bond σ P_y - P_y.

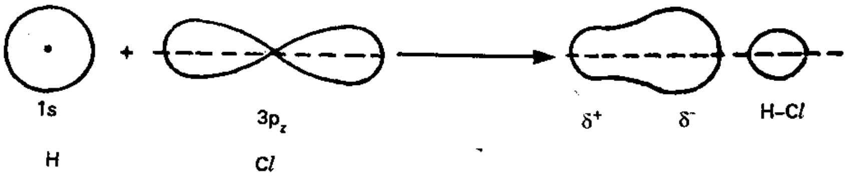
The Pz orbital in the two atoms will be at right angles to the internuclear axis. These two have lateral overlap. The electron density of the bonded pair is distributed in two banana like regions lying on either side of the internuclear axis. Thus the oxygen molecule has a double bond. The molecule has one σ P-P and one π P-P between the two atoms.



Formation of Oxygen O_2

Formation of HCl molecule :

The electronic configuration of chlorine atom is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2 3p_y^2 3p_z^1$. It has one half filled $3p_z$ orbital. The $3P_z$ orbital of chlorine overlaps 1s orbital of hydrogen atom and two electrons of opposite spins pair up to form covalant bond. As overlap along the inter nuclear axis is maximum a strong bond is formed. The bond is formed due to σ s-p overlap.



HCl formation

5.3.1 Polar Covalent Bond

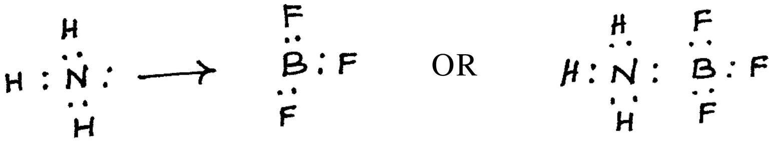
In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule the shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more toward more electronegative chlorine atom. As a result of this unequal sharing of the electron pair, the bond acquires polarity or partial ionic character.

$$H\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \qquad H^{\delta+}\quad Cl^{\delta^-}$$

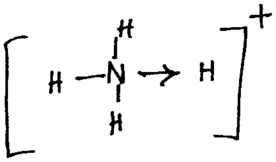
In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus, though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

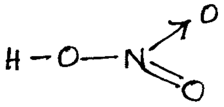
5.3.2 Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A common example is the formation of a bond between boron trifluoride (BF_3) and ammonia (NH_3). BF_3 is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electron on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electron to electron deficient BF_3. Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.



A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is idential to a covalent bond in terms of its polairty and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO_3 and NH_4^+ ion are some more common examples of formation of a coordinate bond.





Intext Questions 5.1

1. Define, electrovalent bond.

   ....

2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.

   ....

3. What do you understand by a polar covalent bond? Give two example.

   ....

4. What is a coordinate covalent bond ? How is it different from a covalent bond ?

   ....

5. What are the factors which favour the formation of cation.

   ....

6. Ionic compounds do not exhibit isomerism why ?

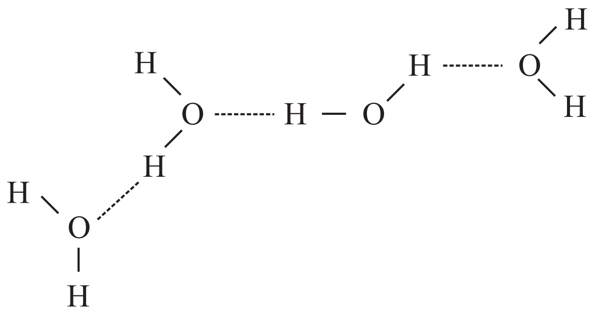
   ....

5.3.3 Characteristic Properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like bebzene, carbon tetrachloride etc.

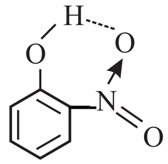
5.3.4 Hydrogen Bonding

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol^{-1}. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol^{-1} of energy to break. However, it is strong enough to be responsible for the high boiling points of H_2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.

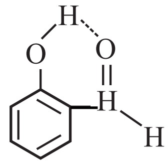


$$H - F \cdots\cdots H - F \cdots\cdots H - F$$

Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hyrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding**. Salicyldehyde and o-nitrophenol are two common examples of the moelcules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



O-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecule like proteins and nucleic acids.

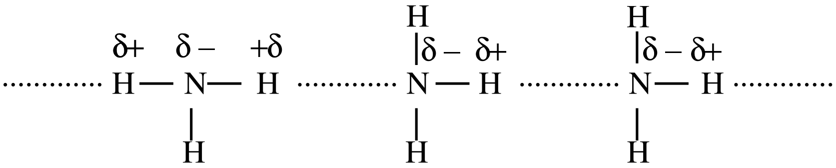
Effects of Hydrogen bond on some properties with example :

Ring formation or chelaton through intramolecular H-bonding results in greater volatility lower boiling points and lower solubility in water. These properties can be utilized in the separation of the compounds with intramolecular hydrogen bonding.

The solubility of lower alcohols (ex. CH_3OH ; C_2H_5OH etc.) is due to H-bonding between molecules of alcohols and the molecules of water.

Intermolecular H-bonding has striking effect on the physical properties like metling points, boiling points, enthalpies of vapourization and sublimation.

Comparision of boiling points of NH_3 and HCl : NH_3 has higher boiling points has HCl even though nitrogen and chlorine have nearly same electronegatie values. NH_3 formsH-bonds while HCl does not. This is because of smaller size of Nitrogen atom compared to the chlorine atom.

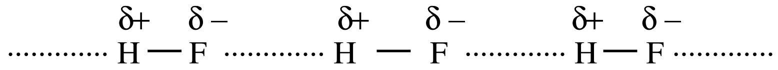


NH_3 as associated molecule

Comparision of boiling points of H_2O and HF :

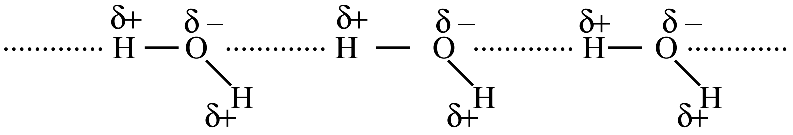
The boiling point of H_2O is higher than that of HF even though both the compounds form associated molecules through intermolecular hydrogen bonding. They differ in the number of hydrogen atoms. The number of hydrogen bonds are more in case of water due to the presence of two hydrogen atoms. But HF exists as $(HF)_6$ even in vapour state while water molecules exist as simple H_2O molecules in vapour state.

It means energy is not utilized to break the H-bonding in HF. But H-bonds in H_2O consume energy for their cleave. Hence, the boiling point of water is higher than that of hydrogen flouride.



$$\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{F}\cdots\cdots$$

HF as associated molecule



H_2O as associated molecule

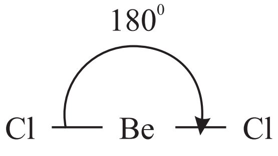
5.4 Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a molecule the constituent atoms have definite positions relative to one another ie. the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in 1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be started in terms of two postulates.

POSTULATE 1

The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

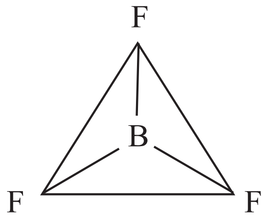
$BeCl_2$ is one of the simple triatomic molecules. In this molecules, the central atom, beryllium has an electronic configuration of $1s^2\ 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180^0 which gives the molecule a linear shape.



linear molecule

Other molecules of this type would also have a similar shape.

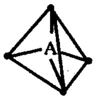
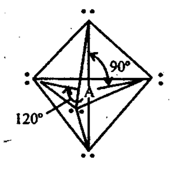
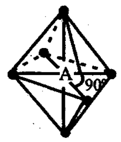
BF_3 : In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2$ $2s^2$ $2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120^0 which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 5.1.

Table 5.1 : Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative Structure	Example
AX_2	2	Linear		$HgCl_2$, BeH_2
AX_3	3	Planer trigonal		BF_3, BCl_3
AX_4	4	Tertahedral		CCl_4, CH_4, $SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

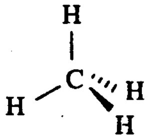
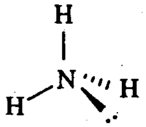
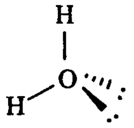
The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs. The order of repulsive force between different possibilities is as under.

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair

The shapes of the molecules given in Table 5.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair – bond pair and lone pair – bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 5.2.

Table 5.2 : Molecular geometries of molecules with 4 electron pairs with different combinations of Ione pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107
H_2O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron –

dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! Have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

Intext Questions 5.2

1. What are the basic postulates of VSEPR theory?

   ....

2. Predict the shape of methane (CH_4) on the basis of VSEPR theory?

   ....

3. What is the effect of Hydrogen bond on boiling points?

   ....

5.5 Modern Theories of Chemical Bonding

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

5.5.1 Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1s orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy, Fig.5.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

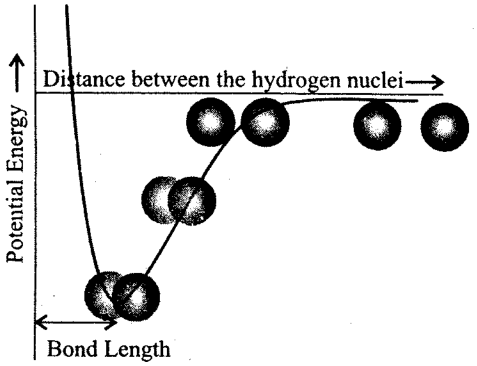
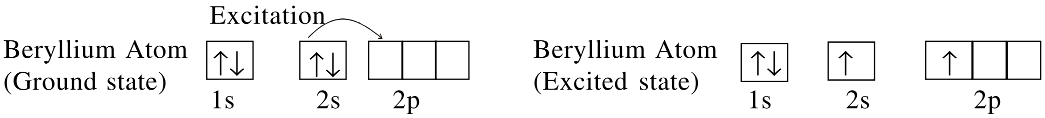


Fig. 5.1: *Formation of hydrogen molecule from overlapping of two hydrogen atoms*

This simple approach can be used to explain the bonding in simple diatomic molecules like HF, F_2 etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridization need to be used.

5.5.1.1 Hybridisation

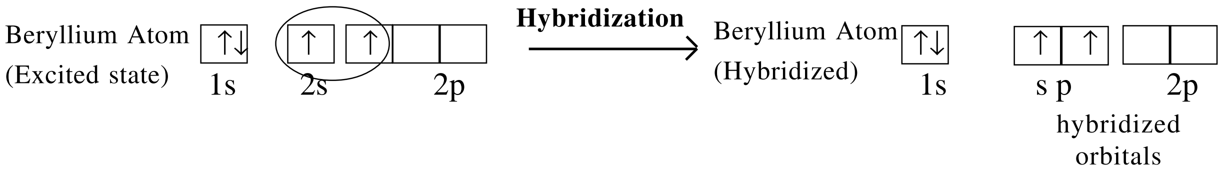
Let us take up the example of bonding in a diatomic molecule; say beryllium hydride (BeH_2) to understand the concept of hybridization of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2\ 2s^2$. In order to form bonds with the 1s electrons of the two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e.,2s) it cannot overlap with the 1s orbital of hydrogen atoms containing one electron.[You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the 2s orbital of beryllium atom gets momentarily excited to the empty 2p orbital as shown below.



Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2s orbital of beryllium with 1s orbital of hydrogen while the other would involve overlapping of 2p orbital of beryllium with 1s orbital of hydrogen. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of $BeCl_2$ the two singly occupied orbitals (2s and 2p) hybridize to give two sp- hybrid orbitals. This is called **sp-hybridisation**. These hybrid orbitals lie along the z-direction and point in opposite directions.



These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of $BeCl_2$ as shown below, Fig.5.2.

The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridization of suitable orbitals. Let us take up some more cases involving hybridization of s and p orbitals.

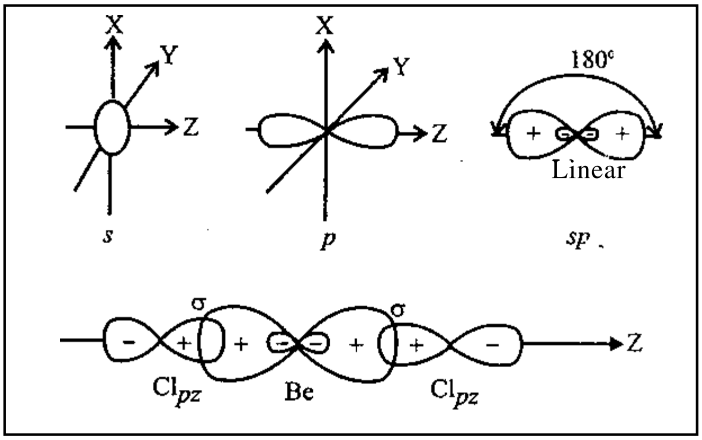
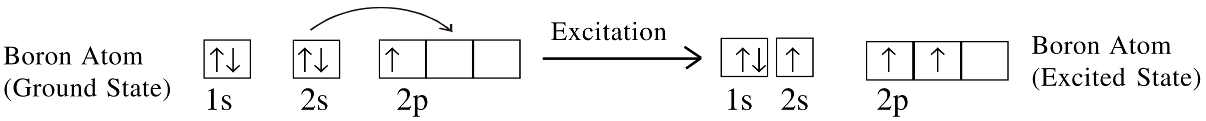
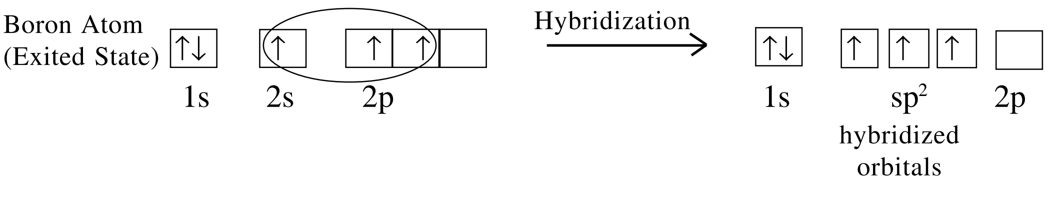


Fig. 5.2 : *Formation of $BeCl_2$; sp hybridisation*

Boron trichloride (*Sp^2* hybridisation) : In boron there are five electrons and the electronic configuration is $1s^2$, $2s^2$, $2p^1$. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.



One 2s orbital and two 2p orbitals hybridise to give three sp_2 hybridized orbitals. This is called **sp^2 - hybridisation**.



The three hyrbidized orbitals are coplanar and directed towards the corners of an equilateral triangle. These **hybrid** orbitals then form bonds with the p-orbitals of chlorine atoms as shown below. fig. 5.3

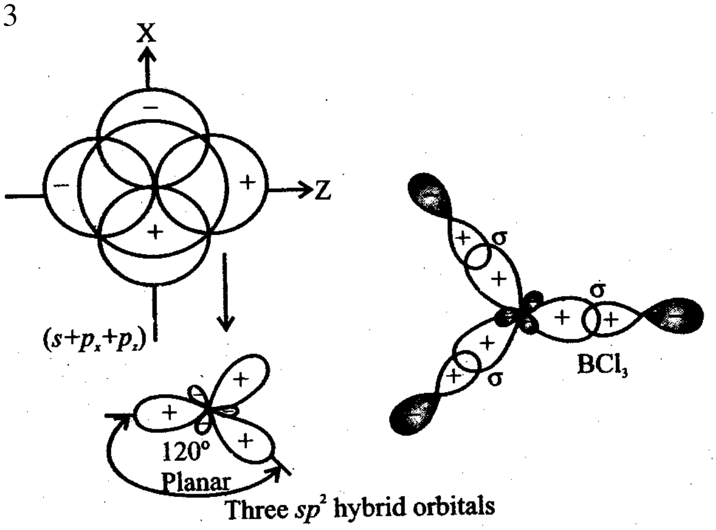
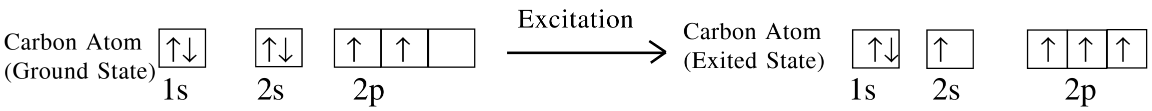
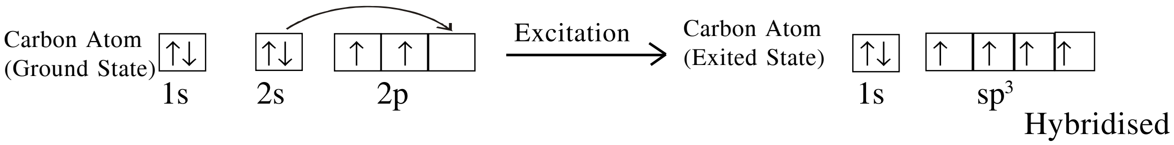


Fig. 5.3 : *Formation of* $BeCl_3$; sp^2 *hybridisation*

Bonding in Methane (*Sp*^{3} hybridisation) : In case of methane the central atom, carbon, has an electronic configuration of $1s^2$, $2s^2$, $2p^2$. In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital



One 2s orbital and three 2p orbitals of the carbon atom then hybridize to give four sp^3 hybridised orbitals. This is called **sp^3-hybridisation**.



These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These **hybrid** orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 5.4.

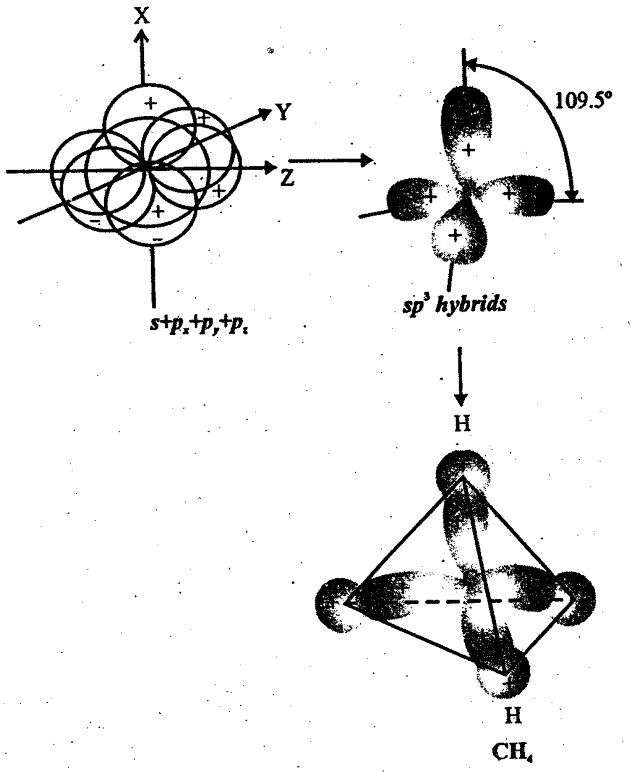


Fig. 5.4 : *Formation of CH_4; sp^3 hybridisation*

Phosphorus pentachloride (sp^{3}d hybridisation):

P (ground state)	↑↓	↑	↑	↑					
P (excited state)	↑↓	↑	↑	↑	↑				

sp^{3}d **hybridisation**

Five sp^{3}d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal (Fig. 5.5a). These orbitals overlap with singly filled p-orbitals of five chlorine atoms and five σ bons are formed. Thus PCl$_5$ molecule has a trigonal bipyramidal geometry. Three P-Cl bonds (equatorial) make an angle of 120^0 with each other and lie in one plane. The other two P-Cl bonds (axial) are at 90^0 to the equatorial plane, one lying above and the other lying below the plane.

SF$_6$ (sp^{3}d^2 hybridisation) :

P (ground state)	↑↓	↑↓	↑	↑					
P (excited state)	↑	↑	↑	↑	↑	↑			

sp^{3}d^2 **hybridisation**

Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form σ bonds giving a regular octahedral geometry (Fig. 5.5b).

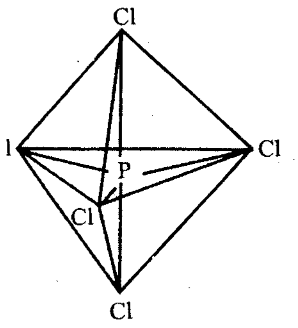


Fig. 5.5(a) : *Trigonal bipyramidal geometry of PCl_5 molecule*

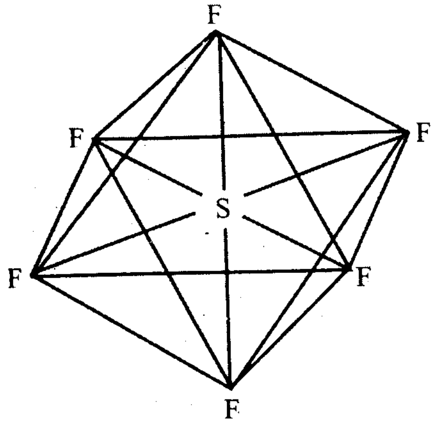


Fig. 5.5(b) : *Octahedral geometry of SF_6 molecule*

5.5.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon - carbon bond by sp^3 - sp^3 overlapping. The remaining six sp^3 hybridized orbitals overlap with 1s orbitals of hydrogen atoms to give a molecule of ethane, C_2H_6 as shown in fig. 5.6 The C-C bond so formed is along the internuclear axis. Such a bond is called a **6 bond**.

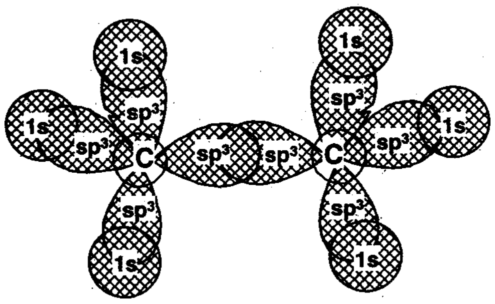


Fig. 5.6 : *Formation of ethane molecule*

Bonding in ethane : In case of ethene, the relevant orbitals of the carbon atoms undergo sp^2 hybridisation. Here, only two of the three p orbitals of the carbon atoms hybridize with the 2s orbital of from three sp^2 hybrid orbitals each. The remaining p-orbitals (one on each carbon atom) do not take part in hybridization. A carbon - carbon bond is formed by overlapping of sp^2 orbital on the two carbona atoms (Fig. 5.7(a)]. The remaining four sp^2 hybridized orbitals overlap with the 1s orbitals of hydrogen atoms to give the basic skeleton of the molecule. This leaves an un-hybridized p orbital each on both the carbon atoms (Fig. 5.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plance above and below the molecule [Fig. 5.7 (b and c)]. This is called a **π-bond**. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

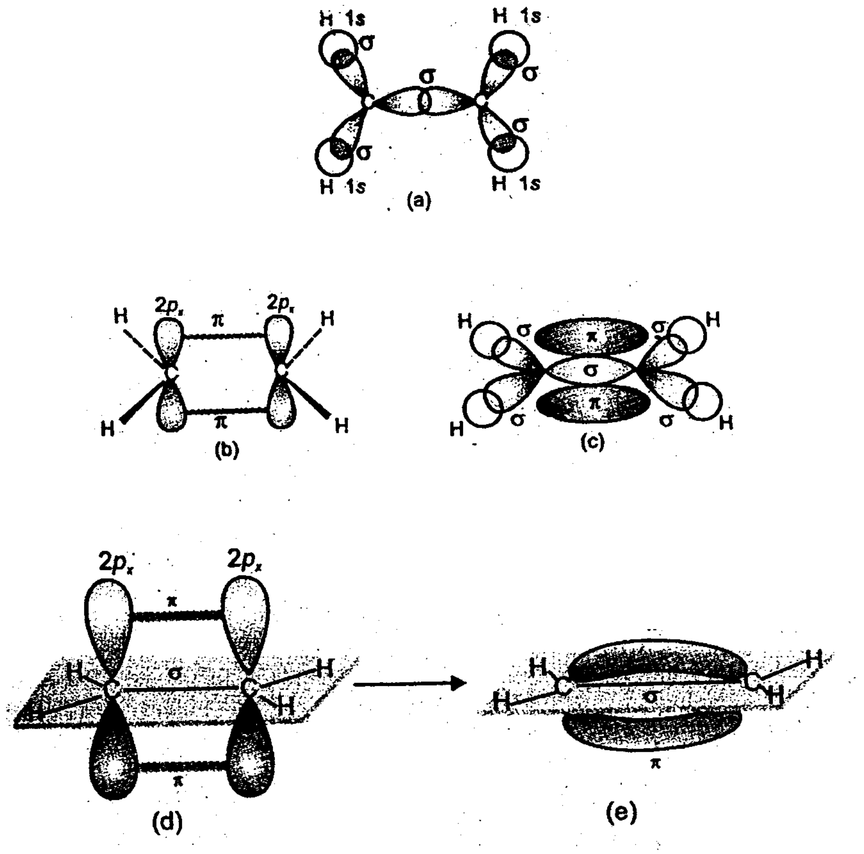


Fig. 5.7 : *Formation of ethylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) a π–bond d) and (e) complete picture of ethylene molecule.*

Bonding in ethyne (acetylene) : In case of acetylene the bonding can be explained in terms of sp-hybridisation in carbon atoms. One 2s and one 2p orbitals hybridize to give two sp-hybridized orbitals. This leaves two mutually perpendicular unhybridized p orbitals each on both the carbon atoms. The carbon - carbon bond is formed by sp - sp overlapping with each other. The remaining sp orbital on each carbon overlaps with the 1s orbital of hydrogen to give C-H bonds (Fig. 5.8). The unhybridised p orbitals each on both the carbon atoms overlap sideway to give two π-bonds.

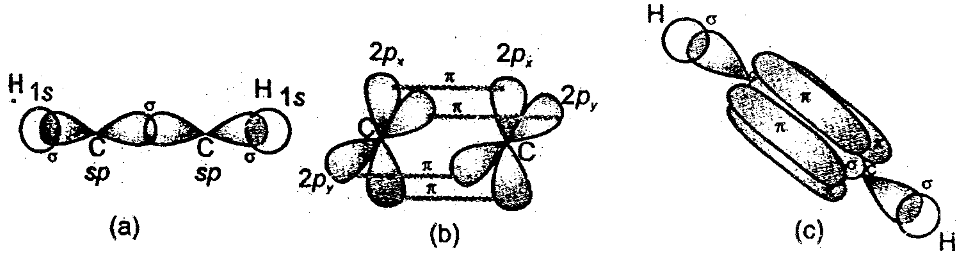


Fig. 5.8 : *Formation of acetylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) two mutually perpendicular π–bond*

Intext Questions 5.3

1. What do you understand by the term. “hybridisation”?

   ....

2. How would you explain the shape of ammonia molecule on the basis of hybridisation ?

   ....

5.5.2 Molecular Orbitals Theory

You have just learnt about valence bond theory. It describes bond formation as result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory (MOT) developed by F. Hund and R.S. Mulliken in 1932, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals)**. These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not “belong” to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals (LCAO) approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**
- The available **electrons then fill lthese orbitals in the order of increasing energy as in the Aufbau princile** used in the electron configurations of atoms.

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have an electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other MO is obtained by substration of the atomic orbitals. The combination of the 1s orbitals on the two hydrogen atoms are shown in fig. 5.9

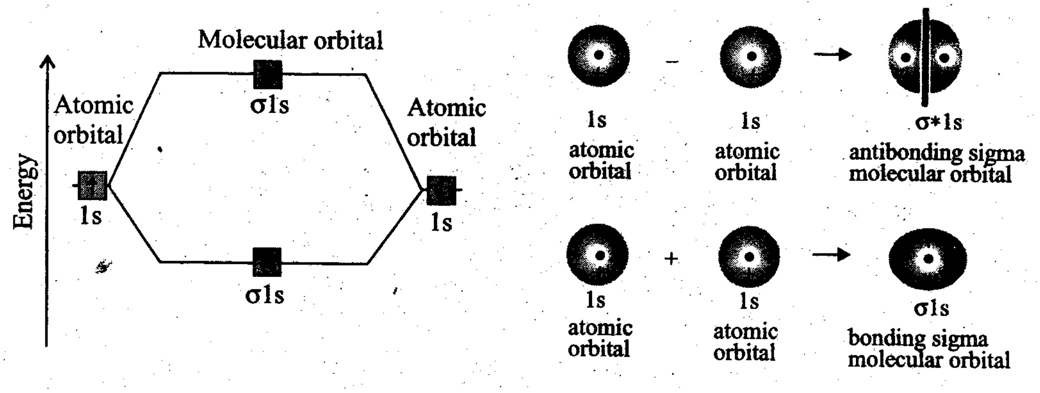
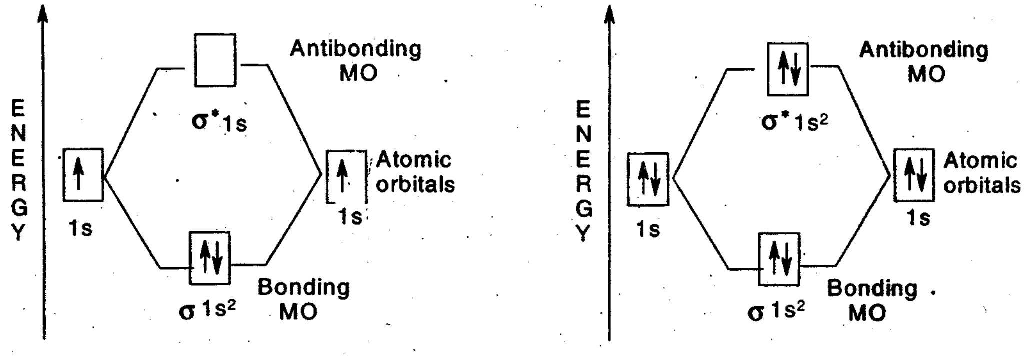


Fig. 5.9 : *Formation of bonding (σ) and anti bonding (σ*) molecular orbitals*

The molecular orbital obained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital**. On the other hand, the orbital obtained by substraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital**. You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma** (σ) molecular orbitals. The bonding orbital obtained above is denoted as σ 1s while the anti-bonding orbital is denoted as σ* 1s. Here σ indicates the type of molecular orbital; 1s tell about the atomic orbital involved and * is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule, according to Aufbau principle these are filled into σ^{1s} orbital. Since the σ^{1s} orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as $(\sigma\ 1s)^2$. The molecular orbital energy level diagram are given in Fig. 5.10 (a and b).



(a) (b)

Fig. 5.10 : *Molecular orbital energy level diagram for a)H_2 and b)He_2 molecules*

Bond Order : we may define a new parameter called bond order as

Bond order = (b.o.) = 1/2 (n_b - n_a)

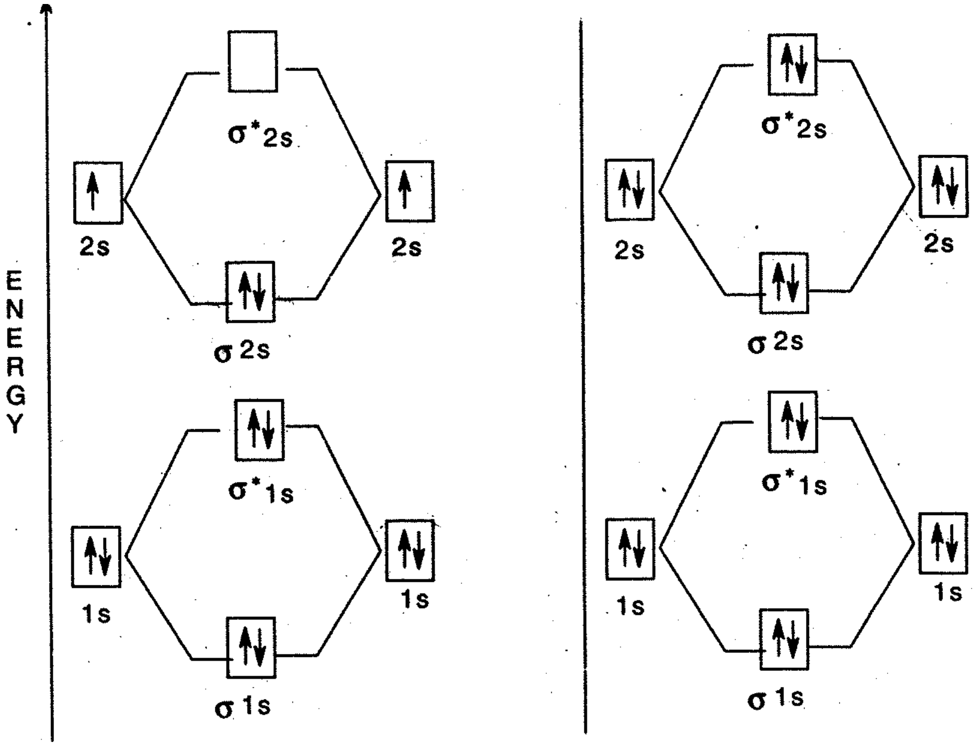
Where, n_b and n_a refer to the number of electrons present in bonding and antibonding molecular orbitals respectively. For hydrogen molecule the bond order will be $^1/_2$(2-0) = 1, i.e., there is a single bond between two hydrgen atoms.

Helium (He_2) molecule

In case of He_2, also there will be linear combination of 1s orbitals leading to the formation of σ 1s and σ* 1s orbitals. The four electrons would be distributed as per the MO electronic configuration : $(\sigma\ 1s)^2\ (\sigma^*\ 1s)^2$. The molecular orbital energy level diagram is given in fig. 3.10 (b). This is gives a bond order of $^1/_2$ (2-2) = 0, that is there is no bond between two helium atoms. In other words He_2 molecule does not exist.

Li_2 and Be_2 molecules

The bonding in Li_2 and Be_2 can be explained by combining the 1s and 2s orbitals to give appropriate MO's. the molecular orbital diagrams for Li_2 and Be_2 are given in Fig. 5.11



(a) (b)

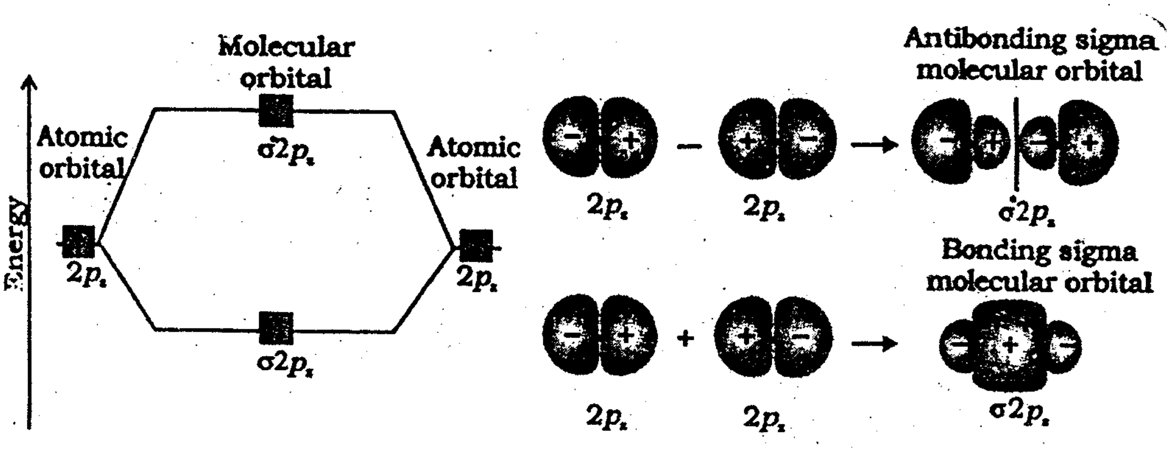
Fig. 5.11 : *Molecular orbital energy level diagram for a) Li_2 and b) Be_2 molecules*

5.5.2.1 Moelcular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of s orbitals. Incase of the atoms of second period (beyond Be) elements both s and p orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in the process. Let us try to understand the nature of MO's obtained in this case.

Here also the 1s and 2s orbitals of the two would combine to give corresponding bonding and anti-bonding molecular orbitals as shown in Fig. 5.11 (b). Let us learn about the formation of MO's from the combination of p orbitals.

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is normally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three p orbitals are directed towards three mutually perpendicular direction namely the x, y and z directions. Therefore the Pz orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below fig. 5.12 Since these molecular orbitals are symmetric around the molecular axis these are called σ orbitals. The designation of the orbitals would be σ_{2pz} and σ^*_{2pz}.



(a) (b)

Fig. 5.12 : *Overlapping of two 2Pz orbitals to give molecular orbitals*

Combination of a Pz - orbital with either a Px or Py orbital would not lead to any bonding. On ther other hand a Px orbital will combine with a P_x and the P_y with a P_y as shown in Fig. 5.13

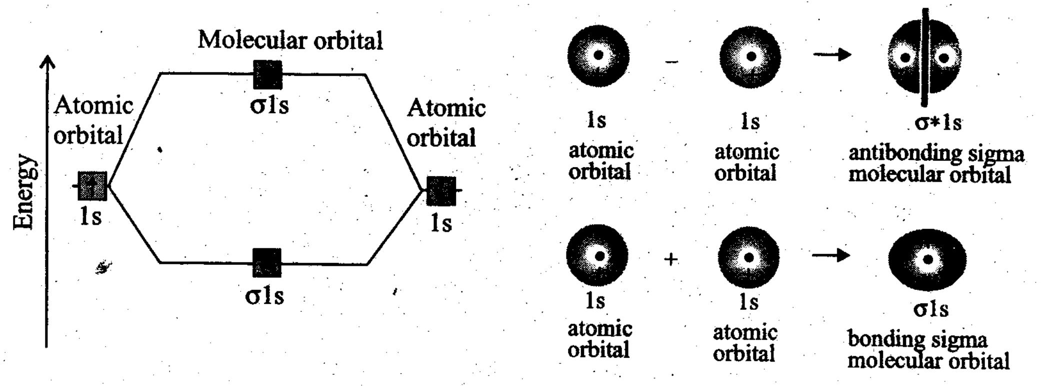


Fig. 5.13 : *Formation of molecular orbitals from two $2P_x$ atomic orbitals*

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called π-molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding π orbital, π* 2Px (or π* 2Py) have a node (a region of zero electron density) between the nuclei.

The molecular orbitlas obtained as a result of combination of respectie AO's of two atoms can be represented in the form of following energy level diagram, Fig 5.14 (a). The MO's obtained from the combination of 1s orbitals are not shown. (these beong to the inner core and are completely filled). The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

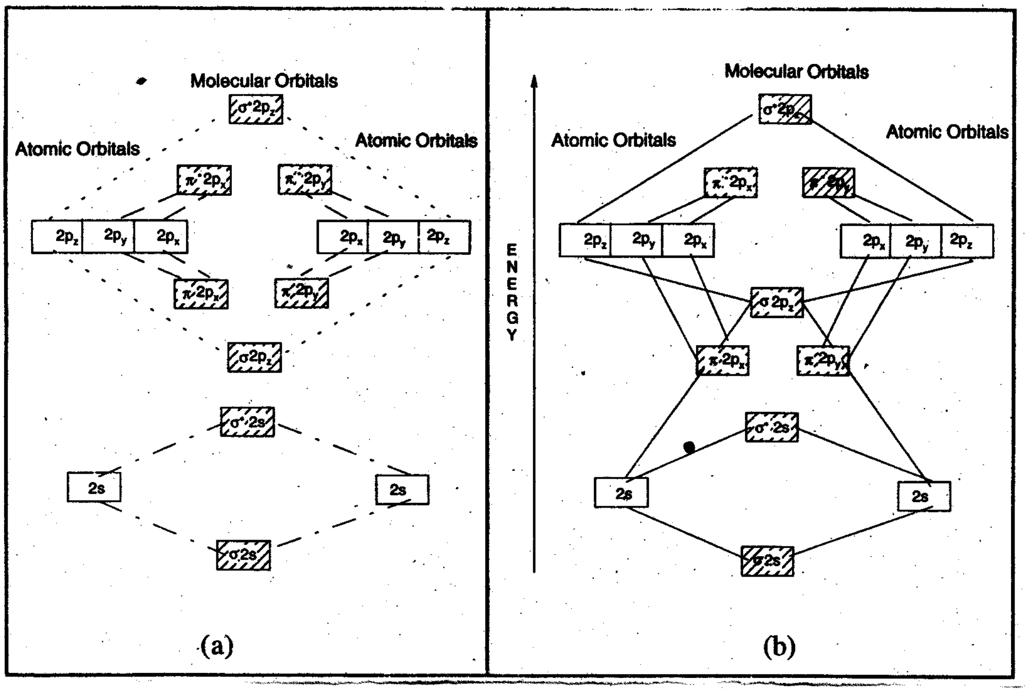


Fig. 5.14 : *Molecular orbital energy level diagams (a) for O_2 and F_2 and (b) for diatomic orbitals of lighter elements Li, Be, B, Cand N*

However, this energy level diagram is valied for the diatomic molecules O_2 and F_2 only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of 2s and 2p orbitals is very low and s and p orbitals on the two atoms get mixed up. In place of normal pure 2s-2s or 2p-2p combinations we may have s-p combinations; for example 2s orbital of first atom can have a reasonable overlapping with $2P_z$, orbital of the second atom and vice versa. The modified level diagram is given in Fi.g 5.14 (b).

5.5.2.2 Electronic Configuration and Properties of the Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of the molecule. This in turn provides the information about some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's Using Fig. 5.14, the MO electronic configuration can be writeen as $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2p_x{}^2$, $\pi 2p_y{}^2$, $\sigma 2s_z{}^2$,

Bond order : $^1/_2\,[n_b\text{-}n_a] = {}^1/_2\,[8\text{-}2] = {}^1/_2\,[6] = 3$; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Megnetic nature : molecules show magnetic behaviour depending on their MO electronic configuration. If all the MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied,** the substance shows **paramagnetic** behaviour. The MO electronic configuration of O_2 (with 12 valence electrons) is $\sigma 2s^2$, $\sigma^* 2s^2$, $\pi 2s_z{}^2$, $\pi 2p^2$, $\pi 2p_y{}^2$, $\pi 2p_y{}^2$, $\pi^* 2p_x{}^1$, $\pi^* 2p_y{}^1$; Since it contains unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example $O_2{}^2$ -(oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2) while oxygen molecule cation $O_2{}^+$ would have 12-1 = 11 valence electrons.

Intext Questions 5.4

1. What is the basic difference between the valence bond and molecular orbital theories ?

   ....

2. Calculate the bond orders for Li_2 and Be_2 molecules using the molecular orbital diagrams given in Fig. 5.12

   ....

3. Predict the magnetic behaviour of O_2.

   ....

What You Have Learnt

- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.
- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character inthe molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based onthe interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based onthe wave mechanical model of atom.
- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence shell of the central atom 'hybridise' or merge and given never orbitals with proper orientations, which explain the shape of the molecule.
- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e. these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.

- The number of bonds between the two atoms is called bond order and is defined as Bond order = b.o. = $1/2\ (n_b = n_a)$.
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO's are doubly occupied the substance shows diamagnetic behaviour and if one or more MO's are singly occupied the substance shows paramagnetic behaviour.
- The favourable conditions for the formation of ionic bond and properties of ionic compounds
- Valence bond theory is discussed.
- The consequences of hydrogen bond.

Terminal Exercise

1. What do you understand by a chemical bond ?
2. Explain the process of bond formation as a decrease in energy.
3. What do you understand by the term, 'bond length' ?
4. Describe the two possible ways in which the noble gas electronic configuration is achieved inthe process of bond formation.
5. What are Lewis electron-dot symbols ? Show the formation of $MgCl_2$ in terms of Lewis symbols.
6. Define a coordinate bond and give some examples.
7. What is VSEPR theory ? predict the shape of SF_6 molecule using this theory.
8. Why do we need the concept of hybridisation ? How does it help in explaining the shape of methane ?
9. Give the salient features of molecular orbital theory.
10. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.
11. Write down the molecular orbital electronic configuration of the following species and compute their bond orders.

    O_2 ; O_2^+ ; O_2^- ; O_2^{2-}

Answers to Intext Questions

5.1

1. An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.

2.

$$:\overset{\cdot}{\underset{\cdot}{N}}\cdot + \cdot\overset{\cdot}{\underset{\cdot}{N}}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\cdot\cdot N: \rightarrow :N \equiv N:$$

3. In a covalnet bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar

4. A bond in which both the bonding electrons are contributed by one atom only

5. i) Low iozation energy ii) Low charge on the ion

   iii) Large atomic size

6. As ionic bond is non directional hence ionic compounds does not show isomerison.

5.2

1. The two postulates of VSEPR theory are

   i) The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion.

   ii) The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger than that between two bond pairs. The order of repulsive force between different possibilities is as under.

   lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

2. In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

3. Boiling point increase due to H-bonding.

5.3

1. Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals. The hybrid ortbitals have identical energies and shapes.

2. In ammonia the 2s and three 2p orbitals hybridize to give four sp^3 hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The sp^3 hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the pair the ammonia molecule has a distorted tetrahedras shape which is some what like a trigonal pyramid.

1. Valance bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.

2. Bond order = b.o. = $^1/_2$ $(n_b - n_a)$

   for Li_2 ; Bond order = $^1/_2$ [4-2] = $^1/_2$ [2] = 1

   for be_2 : Bond order = $^1/_2$ [4-4] = $^1/_2$ [0] = 0

3. MO configuration of O_2 is $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_z^2$, $\pi 2p_x^2 = \pi 2p_y^2$.

   $\pi^* 2p^1_x = \pi^* 2p^1_y$

   Due to 2 unpaired electrons O_2 molecule is paramagnetic.

6

THE GASEOUS STATE

We know that matter exist in three *different states namely solid, liquid and gas. The most familiar example to show these different states of matter is water. Water exists as a solid (ice), a liquid (water) and a gas (steam) under different conditions of temperature and pressure. The difference between these three states of matter is due to the difference in their intermolecular distance and intermolecular forces. In addition to these, temperature and pressure also play an important role in deciding the states of matter.

In this lesson we shall first discuss the differences in properties of the solid, liquid and gaseous state and the factors due to which these differences arise. We shall also study the effect of pressure and temperature on the volume of the given amount of gas. These are governed by the gas laws namely Boyles' law, Charles' law and Avogadros' law.

Objectives

After reading this lesson you will be able to:

- differentiate between the three states of matter - solid, liquid and gas;
- list the characteristic properties of gases;
- state the gas laws (Boyle's law, Charle's law and Avogadro's law) and express them mathematically.
- draw the *p-V, p-1/V, p-pV* and *V-T* graphs.
- Interpret the effect of temperatue and pressure on the volume of a gas from the graph;
- derive the ideal gas equation from the gas laws;
- State the Dalton's law of partial pressure and explain its significance;
- state Graham's law of diffusion;
- state the postulates of Kinetic Molecular Theory of gases;
- explain the Maxwell's distribution of velocities.

- differentiate between u_{rms}, u_{mp} and u_{av},
- explain the deviation of real gases from ideal behaviour in term of compressibility factor;
- state the van der Waals equation and explain the significance of van der Waals constants and
- explain the liquifaction of gases with the help of Andrews curves

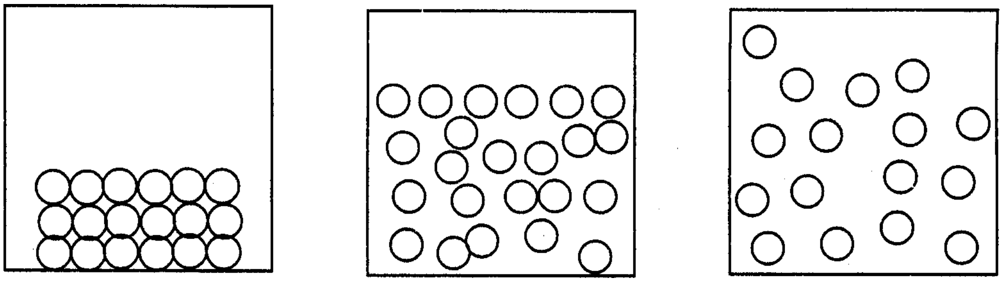
6.1 The Three States of Matter

At any given conditions of temperature and pressure matter exists in one of the three states namely solid, liquid and gas. The characteristic properties of solid, liquid and gaseous state are listed in Table 6.1.

Table 6.1 : Properties of different states of matter

Property	Solid	Liquid	Gas
Shape	Definte	Indefinite; takes up the upthe shape of the vessel.	Indefinite
Volume	Definite	Definite	Indefinite (fills the container completely)
Density	High	Less than solids but much higher than gases.	Low
Compressibility	Incompressible	Largely incompressible	Highly compressible

The different characteristics of the three states of matter as listed above depend upon the relative closeness of particles that make up the substance. In solid state, the particles are held close together in a regular pattern by strong intermolecular forces. In liquid state, intermolecular forces are weak as compared to solid state hence the particles are less tightly held and allow them to move away from each other. In the gaseous state, the molecules are farthest apart as compared to solid and liquid states and the intermolecular forces are negligible so the particles move randomly. A simplified picture of particles in solid, liquid and gaseous state is represented in Fig. 6.1.



Solid (a) Liquid (b) Gas (c)

Fig. 6.1 : A simplified picture of particles in solid, liquid and gaseous state

6.2 General behaviour of Gases : The Gas Laws

The volume of a given mass of gas depends upon the temperature and pressure under which the gas exists. It is, therefore, possible to describe the behaviour of gases in terms of the four variables : temperature, T; pressure p; volume V and amount (number of moles, *n*). For a given amount of gas the volume of gas changes with change in variables such as temperature and pressure. The relationship between any two of the variables is studied, keeping the other variable constant by various laws which are described below.

6.2.1 Effect of Pressure on the Volume of the Gas (Boyle's law)

The effects of pressure on the volume of gas for a given amount of gas at constant temperatue was studied by Robert Boyle in 1662 for different gases. He observed that if the volume of gas is doubled the pressure is halved and vice versa. Boyle's law states that at constant temperature, the volume of a given amount of a gas is inversely proportional to its pressure.

Mathematically Boyle's law is expressed as shown below :

$$V \propto {}^{1}/_{p} \qquad \text{(at constant T and } n\text{)}$$

or

$$p_1 V_1 = p_2 V_2$$

when the pressure of the gas, *p* is plotted against volume of the gas, V the exponential curve is obtained (Fig. 6.2). However when the pressure, *p* of the gas is plotted against $\frac{1}{V}$ a straight line is obtained (Fig. 6.2). If the product of pressure and volume (*pV*) is plotted against pressure (*p*) a straight line parellel to x-axis (pressure is axis) is obtained (Fig. 6.4)

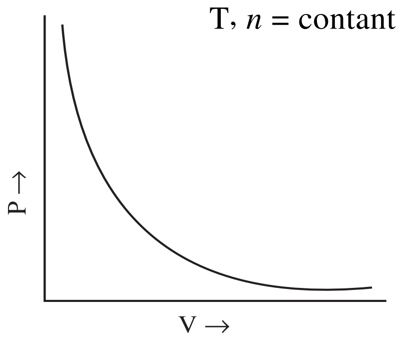


Fig. 6.2 : *A graph of p versues V*

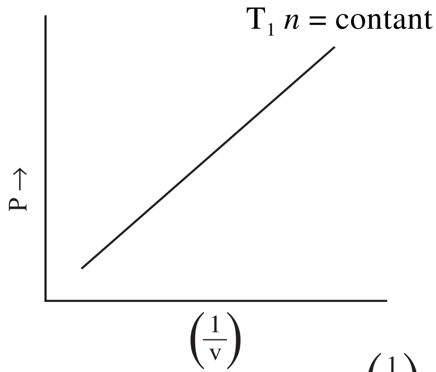


Fig. 6.3 : *A graph of p versues* $\left(\frac{1}{V}\right)$

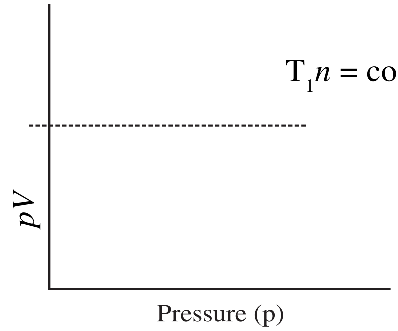


Fig. 6.4 : *A graph of p V versues p*

Example 6.1 : The volume occupied by a given mass of a gas at 298K is 24 mL at 1 atmospheric pressure. Calculate the volume of the gas if the pressure is increased to 1.25 atmosphere keeping temperature constant.

Solution : Given that

$V = 25$ mL $\qquad p_1 = 1\ atm$

$V_2 = ?$ $\qquad p_2 = 1.25\ atm$

According to Boyle's Law, $p_1 V_1 = p_2 V_2$

substituting the value of p_1, V_1 and p_2 in the above expression we get

$$V_2 = \frac{p_1 V1}{p_2} = \frac{(1\ \text{atm})\ (25\text{mL})}{(1.25\ \text{atm})} = 20\ \text{mL}$$

The volume occupied by the gas is 20 mL at 298 K and 1.25 atm pressure.

Example 6.2 : The volume of a certain amount of a gas is decreased to one fifth of its initial volume at a constant temperature. What is the final pressure ?

Solution : Let

Initial volume $= V_1$ $\qquad$ Initial pressure $= p_1$

Final volume $V_2 = V_1/5$ $\qquad$ Final pressure $= p_2$

By Boyle's law, we know that at constant temperature

$$p_1 V_1 = p_2 V_2$$

$$p_2 = \frac{p_1 V_1}{p_2} = \frac{p_1 V_1}{\frac{V_1}{5}} = 5p_1$$

Thus when volume is decreased to 1/5th of the initial volume, the pressure in increased bv 5 times of the initial volume.

6.2.2 Effect of Temperature on the Volume of Gas (Charle's Law)

The effects of temperature on the volume of the gas was studied by Jacques Carles in 1787 and Gay Lussac in 1802 at constant pressure for different gases. Their conclusion can be given as Charles' law which states that at a constant pressure, the volume of a given amount of gas is directly proportional to the absolute temperature.

So, according to Charles' Law, the volume of a gas increases as its absolute temperature is being raised, if its absolute temperature is lowered, its volume will consequently decrease. Mathematically, Charle's Law is expressed as shown below:

$$V \propto t \qquad \text{(at constant } p \text{ and } n\text{)}$$

or $$V = k.1 \qquad (k \text{ is a constant})$$

Therefore $$V_1/t_1 = V_2/t_2$$

Graphical representation of Charle's Law is a straight line pointing away from the origin of the graph as shown in Fig. 6.5

Here graph of the volume of a gas (V) plotted against its temperature at constant pressure and amount (in moles). Notice that the graph is a straight line with a positive gradient (slope).

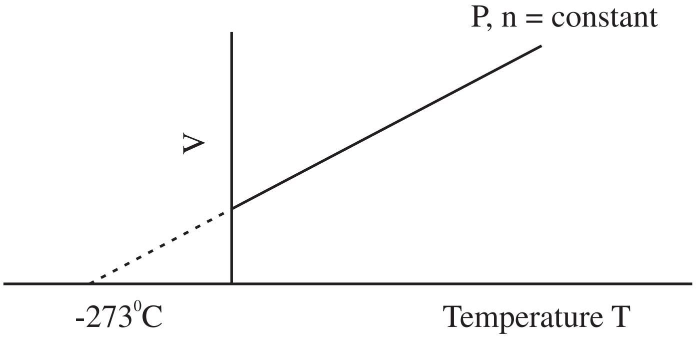


Fig. 6.5 : *A graph of V versues T*

Mathematically volume of a gas at temperature t is given as

$$v_t = v_o + \frac{v_0}{273} xt = v_0\left(1+\frac{t}{273}\right) = v_0\left(\frac{273+t}{273}\right)$$

Thus at $$t = -273^0C$$

$$v_t = v_o\left(\frac{273-273}{273}\right) = 0$$

This means that at -273⁰C, the volume of the gas is reduced to zero i.e., the gas ceases to exist. Thus this temperatue (-273⁰C) at which the gas hypothetically ceases to exist is called **Aboslute zero**. It is represented by zero K.

This is the theoretically lowest possible temperature. In actual practice, we cannot reduce the temperature of the gas to zero kelvin.

Kelvin Scale of Temperature

The scale of temperature which has -273⁰C as zero is called Kelvin Scale. Degree celcius is converterd to Kelvin by adding 273. Thus

$$t\,/^{0}C + 273 = T/K$$

where T = temperature in Kelvin

t = temperature in celcius

For example $15^{0}C$ can be converted in K by adding 273 to 15.

6.2.3 Effect of Temperature on Pressure (Pressure-Temperature Law)

This law states that.

Pressure of given amount of gas at constant volume is directly proportional to its absolute temperature.

$$p \propto T$$

$$p = kT$$

Example 6.3 : A given amount of a gas is maintained at constant pressure and occupies a volume of 2 liters at $1000^{0}C$. What would be volume if gas is cooled to $0^{0}C$ keeping pressure constant.

Solution : Given that,

Initial volume $V_1 = 2L$	$T_1 = 1000 + 273 = 1273$ K
Final volume $V_2 = ?$	$T_2 = 0 + 273 = 273$ K

Now using Charle's Law $V_1 / T_1 = V_2 / T_2$ or $V_2 = (V_1 / T/_1) \text{ x } T_2$

On substituting the values we get

$V_2 = (V_1 / T_1) \text{ x } T_2 = (2L / 1273 \text{ K}) \text{ x } 273 = 0.4291$ L

6.2.4 Avogadros' Law

The Italian physicist Amadeo Avogadro was the first to propose, in 1811, a relationship between the volume of a gas and the number of molecules present in it. This, relationship is known as Avogadros' Law. It states that :

Equal volumes of all gases at the same temperatue and pressure contain equal number of molecules.

Mathematically, Avogadros' law is expressed as :

$V \propto N$ (at constant temperature and pressure)

Where V and N are volume and number of molecules respectively.

At a given temperature and pressure, the number of molecules present in the gas is directly proportional to the number of moles.

therefore, $N \propto n$

Where n is the number of moles

$\therefore$ $V \propto n$

or

$$\frac{V}{n} = \text{constant}$$

Also

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} =$$

He also found that the number of molecules present in 1 mole of any substance (22.4 litre of any gas at 273K temperature and 1 atmosphere pressure) is 6.022×10^{23} molecules. This number is known as **Avogadros' number**.

It is the number of molecules (6.022×10^{23}) of any gas present in a volume of 22.4 L(at 273 K and 1 atm) and it is the same for the lightest gas (hydrogen) as for a heavy gas such as carbon dioxide or bromine.

Example 6.4 : 0.965 mol of a gas occupies a volume of 5.0L at 298 K / temperature and 1 atm pressure. What would be the volume of 1.80 mol of the gas at the same temperature and pressure ?

Solution :

$$V_1 \; n_2 = V_2 \; n_1$$

$$\frac{V_2 \, n_2}{n_1} = \frac{(5.0L)(1.8mol)}{(0.965mol)}$$

$$V_2 = 9.33 \text{ L}$$

Example 6.5 : Compare the volumes of 16g of oxygen and 14g nitrogen at the same temperature and pressure.

Solution : Number of moles of O_2 = 16 g/32 g mol^{-1} = 0.5 mol

Number of moles of N_2 = 14 g/28 g mol^{-1} = 0.5 mol

Since the two gases are at the same temperature and pressure, and contain equal number of mole, hence according to the Avogadro's Law they should also occupy the same volume.

Intext Questions 6.1

1. The density of a gas is usually less than that of the liquid. Explain.

   ....

2. Calculate the pressure (atm) required to compress 500 mL of gas at 0.20 atm into a volume of 10mL.

   ....

3. Equal volumes of oxygen gas and an unknown gas weigh 2.00 and 1.75 g respectively under the same experimental conditions. What is the molar mass of the unknown gas ?

   ....

6.3 The Ideal Gas Equation

Boyle's Law, Charle's Law and Avogadro's Law can be combined to give a single equation which represents the relation between the pressure, volume and kelvin temperature of a given amount of gas under different conditions. Thus

$V \propto 1/p$ at constant temperature (Boyle's Law)

$V \propto T$ at constant pressure (Charle's Law)

$V \propto n$ at constant temperature and pressure (Avogadros' Law)

All the three expressions can be combined into a single expression.

$$V \propto nT/P \quad or \quad pV \propto nT$$

$$or\ pV = constant \text{ x } nT$$

The constant in this equation is called "**universal gas constant**' or '**molar gas constant**', represented by R. Thus we can write for 1 mole of a gas.

$$pV = RT$$

Correspondigly, for *n* moles of a gas we have

$$pV = n\ RT$$

This is known as the ideal gas equation because it holds only when gases are behaving as 'ideal' gases.

Since for a given mass of gas we can write

pV/T = a constat, we have

$p_1 V_1/T_1 = p_2 V_2/T_2$

Where p_1, V_1 and T_1 refer to one set of conditions and p_2, V_2 and T_2 refer to a different set of conditions.

The numerical value of R can be found by substituting experimental quantities in the equation. At STP, T = 273.15 K, p = 1 atm and for 1 mol of gas (n = 1), v = 22.414 L. Consequently,

$R = pV/nT$ = (1 atm) (22.414L) / (1 mol) (273.15K)

= 0.082057 L atm mol^{-1} K^{-1}

The value of R depednds on the units adopted for the quantities in the equation $pV = nRT$. The various values are :

R = 0.082057 L atm K^{-1} mol^{-1}	(for caluculation purpose the value is taken as 0.0821 L atm K^{-1} mol^{-1})
R = 8.314 x 10^7 erg K^{-1} mol^{-1}	
R = 8.314 J K^{-1} mol^{-1}	
R = 1.987 cal K^{-1} mol^{-1}	

Example 6.6 : At 273 K, 10 mol of gas is confined in container of volume 224 L. Calculate the pressure of the gas. R = 0.821 L atm mol^{-1} K^{-1}.

Solution : The ideal gas equation $pV = nRT$ will be used here

n = 10 mol, R = 0.0821 atm L K^{-1} mol^{-1}

V = 224 L T = 273 K p = ?

On substituting these values in the above equation we get

$p = nRT/V$ = (10 mol x 0.0821 atm L mol^{-1} K^{-1} x273 K) / 224L = 0.99998 atm = 1 atm.

6.4 Dalton's Law of Partial Pressure

The behaviour observed when two or more non-reacting gases are placed in the same container is given by Dalton's Law of partial pressures. Dalton's Law states that.

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the various gases present in the mixture.

The partial pressure is defined as the pressure the gas would exert if it was alone in the container. Suppose a sample of hydrogen is pumped into a one litre box and its pressure is found to be 0.065 atm. Suppose, further a sample or argon is pumped into a second one litre box and its pressure is found to be 0.027 atm. If both samples are now tranferred to a third one litre box, the pressure is observed to be 0.092 atm. For the general case, Dalton's Law can be written as

$$P_{total} = P_A + P_B + P_C + \ldots\ldots$$

Where P_A , P_B , P_C .... are the partial pressure of gases A, B, C..... respectively. This gas laws provide a simple way of calculating the partial pressure of each component, given the composition of the mixture and the total pressure. First we introduce the mole fractions X_a and X_B. These are defined as

$$X_A = \frac{n_A}{n} \text{ and } X_B = \frac{n_B}{n}$$

Where n_A and n_B are the number of moles of gas A and B respectively and $n = n_A + n_B$.

Since $P_A = n_A RT/V,\ P_B = n_B RT/V,$ and $p = n\ RT/V,$

it follows that $P_A = X_A p$ and $p_B = X_B p$

This is an exceptionally useful (and simple) way of calculating at partial pressures when the composition and total (measured) pressure of a mixture of gas is known.

Example 6.7 : Atomosphere is oten considered mainly as a mixture of nitrogen and oxygen: 76.8% by mass of nitrogen and 23.2% by mass of oxygen. Calculate the partial pressure of each gas when the total pressure is 1 atm.

Solution : The number of moles of each component is

$$P_{N_2} = 76.8 \text{ g} / 28 \text{ g mol}^{-1} = 2.74 \text{ mol}$$

$$P_{O_2} = 23.2 \text{ g} / 32 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

The mole fractions of the components are therefore

$$X_{N_2} = \frac{2.74}{2.74 + 0.725} = 0.791\ ; \qquad X_{O_2} = \frac{0.725}{2.74 + 0.725} = 0.209$$

The partial pressures are therefore given by

$$P_{N_2} = 0.791 \text{ x } 1 \text{ atm} = 0.791 \text{ atm}$$

$$P_{O_2} = 0.209 \text{ x } 1 \text{ atm} = 0.209 \text{ atm}$$

6.5 Graham's Law of Diffusion

If we open a bottle of perfume in one corner of a room or burn an incense stick we can feel the smell of the perfume or the incense stick all over the room also. The smell of perfume or incense stick spreads from one point of the room to the other by mixing with air. This free intermingling of gases when placed in contact with each other is known as **diffusion**.

Diffusion occurs in liquids as well as in gases. **Effusion** is the escape of a gas through a small hole, as in case of a puncture in a tyre.

The experimental observation of the rate of effusion of gases through a small hole in the side of the led Graham (1829) to formulate the following law;

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Graham's law is applicable to both diffusion and effusion.

If the time for a given volume of gas A to escape is t_A, while the time of the same volume of gas B to escape is t_B, it follows, that,

t_A/t_B = (rate)$_B$ / (rate)$_A$ = $\sqrt{\rho_A/\rho_B}$ where ρ_A and ρ_B are the densities of gases A and B respectively.

The ratio of the densities of the molecules is the same as the ratio of the molecular masses of the gases at the same temperature and pressure.

hence, t_A/t_B = (rate)$_B$ / (rate)$_A$ = ρ_A / ρ_B = $\sqrt{M_A/M_B}$ where M_A and M_B are the molecular masses of gases A and B respectively.

Intext Questions 6.2

1. What is the difference between diffusion and effusion.

   ....

2. Explain why Dalton's law is not applicable to a system of ammonia and hydrogen chloride gas.

   ....

3. The rates of diffusion of CO_2 and O_3 were found to be 0.29 and 0.271. What is the molecular mass of O_3 if the molecular mass of CO_2 is 44.

   ....

4. Calculate the pressure exerted by 5.0 mol of carbon dioxide in a 1 litre flask at 47^{0}C using ideal gas equation.

   ....

6.6 Kinetic Molecular Theory of Gases (Accounting for the Gas Laws)

To explain the behaviour of the gases theoretically, Claussius, Maxwell and Boltzmann made the following assumptions :

1) Gases consist of large number of tiny particles called molecules.

2) The gas molecules are so small and so far apart that the total volume of the molecules is a negligible fraction of the total volume occupied by the gas.

3) The molecules are in state of constant, rapid and random motion colliding with one another and with the walls of the container.

4) There are no attractive or repulsive forced between the molecules of the gas.

5) The collisions of the molecules among themselves and with the walls of the containing vessel are perfectly elastic, so that there is no loss of energy during collisions.

6) The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel.

7) The kinetic energy of a gas is directly proportional to the absolute temperature of the gas.

On the basis of this model, it is possible to derive the following expression for a gas:

$$pV = \frac{1}{3} mN\overline{C^2}$$

Where p is pressure, V denotes volume, m is the mass of a gas molecule. N is the total number of molecules. and C is the root mean square velocity of the gas molecules.

6.6.1 Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically.

$$\text{RMS Velocity} = \sqrt{(C_1^2 + C_2^2 + ... + C_N^2)/N}$$

where C_1, C_2 ..... C_N the molecular velocities.

Kinetic gas equation - Deduction of gas law's from the kinetic gas equation

All the gas laws can be deduced from the kinetic gas equation.

$$\text{Pv} = \frac{1}{3}\text{mnc}^2$$

a) Boyle's law : According to kinetic gas equation Pv = 1/3 mnc^2

Here, P is pressure of the gas molecules we can write

$$\text{Pv} = \frac{2}{3}(\frac{1}{2}\text{mnc}^2)$$

The kinetic energy of 'm' mole's of the gas is 1/2 mnc^2. Change the line to next row according to kinetic molecular theory, kinetic energy is directly proportional to the temperature in Kelvin, or 1/2 mnc^2 = KT.

Where 'K' is constant on substituting this result in the above equation expression we have

Pv = 2/3 KT .... (1)

At constant temperature (T) = Pv = constant.

This is Boyle's law equation.

b) **Charles law :** From the equation (1) Pv = 2/3 KT

$$\text{Or } v = \frac{2}{3}\ \frac{KT}{p} \ldots\ldots\ldots\ldots\ldots\ (2)$$

At constant pressure (P), we have v = constant x T (or) v α T (p, n are constants)

This is Charles law.

c) **Avogadro's law :** consider equal volumes of the two different gases at same temperature and pressure. As per the kinetic gas equation.

$Pv = 1/3\ m_1\ n_1\ c_1^2$ .... Kinetic gas equation for the first gas

$Pv = 1/3\ m_2\ n_2\ c_2^2$ .... Kinetic gas equation for the second gas

Since $1/3\ m_1\ n_1\ c_1^2$ .... $1/3\ m_2\ n_2\ c_2^2$ .... (3)

(Since on left side both equation have same Pv)

Since temperature (T) is the same for the two gases their average Kinetic energy per molecule will also be the same

$$\text{i.e. } \frac{1}{2}\ m_1\ c_1^2 = \frac{1}{2}\ m_2\ c_2^2 \ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

Dividing equation (3) by equation (4)

$$\therefore \frac{\frac{1}{3}m_1n_1c_1^2}{\frac{1}{2}m_1c_1^2} = \frac{\frac{1}{3}m_2n_2c_2^2}{\frac{1}{2}m_2c_2^2} (or) n_1 = n_2$$

It means that equal volumes of any two gases at the same temperatures and pressures will have equal number of molecules. This is Avogadro's law.

d) **Dalton's law of partial pressures :** Consider a gas in a vessel of volume V. If 'n_1' is the number of molecules 'm_1' is the mass of a molecule and 'c_1'is the RMS velocity. According to Kinetic gas equation, pressure of the gas.

$$P_1 = \frac{\frac{1}{3}m_1n_1c_1^2}{V}$$

If the gas is replaced by another gas in the same vessel we will have

$P_2 = \frac{\frac{1}{3}m_2n_2c_2^{\,2}}{V}$ Where P_2 is the pressure of the 2nd gas, m_2, the mass of its molecules.

n_2 the number of its molecule and C_2 the R.M.S. velocity of its molecule.

Suppose that the two gases are taken in the same vessel. Let the total pressure's of the mixture be 'P'.

$$PV = 1/3\ m_1\ n_1\ c_1^{\,2} \ \ + \ \ 1/3\ m_2\ n_2\ c_2^{\,2}$$

$$P = \frac{\frac{1}{3}m_1n_1c_1^{\,2}}{V} + \frac{\frac{1}{3}m_2n_2c_2^{\,2}}{V} \text{ or}$$

$P + P_1 + P_2$. This is Dalton's law of particle pressures

e) **Graham's law of diffusion** : According to Kinetic gas equation

$$Pv = 1/3\ mnc^2$$

'mn' is the expression that represents mass of the gas. If the gas contains Avogadro's number of molecules, then 'mn' becomes equal to gram molecular mass 'M' of the gas

$$Pv = 1/3\ mnc^2 \ \text{ or } C = \sqrt{\frac{3pv}{M}}$$

$$\text{Since } \frac{V}{M} = \frac{\text{Gram molar volume}}{\text{Gram molecular mass}} = d \text{ (density)}$$

$$\therefore\ C = \sqrt{\frac{3p}{d}}$$

At Constant pressure, $C = \frac{\text{Constant}}{\sqrt{d}} = C\alpha\ \frac{1}{\sqrt{d}}$ or

This shows that the RMS velocity or the rate of diffusion of gas is inversely proportional to the square of its density. This is Graham law of diffusion.

6.6.2 Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + ... + u_N}{N}$$

and is given by the expression

$$u_{av} = \sqrt{\frac{8RT}{\pi M}}$$

6.7 Distribution of Molecular Speeds

According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the redistribution of the energy takes place. As a result their speed and the kinetic energy changes. Therefore at any instant different molecules have different speed and hence different kinetic energy. At the given temperature even though the speed of the individual molecule continuously changes, the fraciton of the molecules having the same speed remains constant and this is known as **Maxwell-Bolttzmann Distribution Law**.

At the given temperature this fraction is denoted by $\frac{dN}{N}$ where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown in figure 6.6.

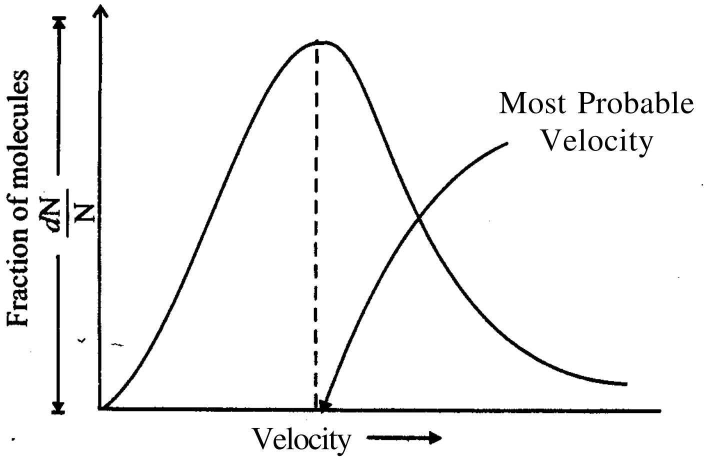


Fig. 6.6 : *Maxwells' distribution of velocities at constant temperature*

In above Fig. 6.6 the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as **most probable speed**. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increase thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown in Fig. 6.7.

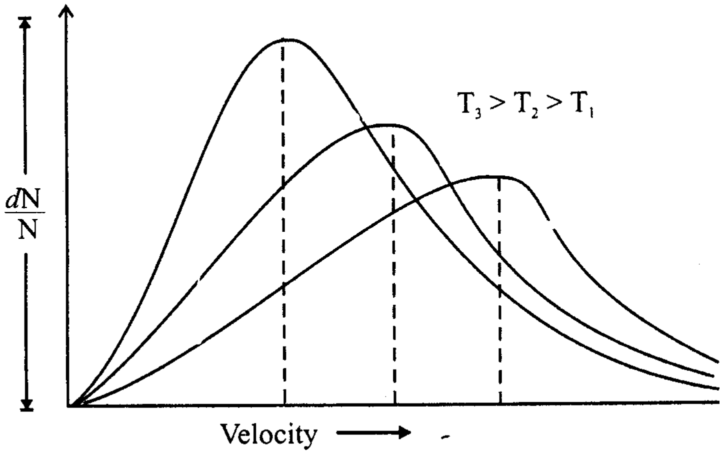


Fig. 6.7 : *Effect of temperature on distribution of velocities.*

At the given temperature the most probable speed is given by the following expression.

$$U_{mp} = \sqrt{\frac{2RT}{M}}$$

the three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{rms} > u_{av} > u_{mp}$$

The most probable velocity u_{mp} increases with the use in temperature of gas.

6.8 Deviation from Ideal Gas Behaviour

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real gases show deviation from these laws at low temperature and high pressure. These deviations can be shown clearly by plotting $\frac{pV}{nRT}$ as a function of pressure at constant temperature,

$$\frac{pV}{nRT} = \frac{V_{observed}}{V_{ideal}} = Z \text{ (compressibility factor)}$$

Gases deviate from ideal behaviour due to the following faulty assumption of kinetic theory:

1. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
2. There is no force of attraction between the molecules of a gas.

Contrary to assumption (1), the volume occupied by the molecules of a gas becomes significant at high pressures. If *nb* is the volume occupied by the molecules, the actual volume of the gas is (*V-nb)*. Assumption (2) too doesn't hold good as at high pressures molecular interactions start operating. Molecules are dragged back by other molecules which affects the pressure exerted by them on the walls of the container.

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

(P_{real} is observed pressure and $\frac{an^2}{V^2}$ is correction term)

In view of the corrections for pressure and volume, ideal gas equation can be rewritten as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This is known as van der Waals equation

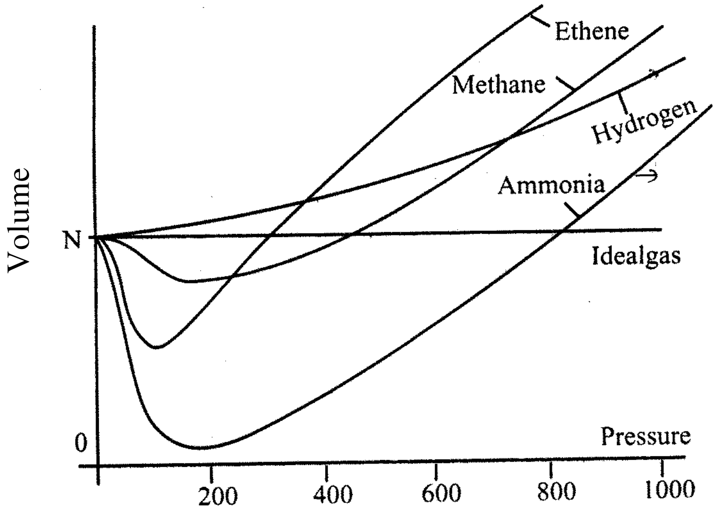


Fig. 6.8 : *The plot volume versus P for real gases*

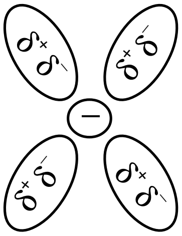
Behaviour of real gases, deviation from ideal behaviour, Compressibility factor Vs pressures diagram's of real gases.

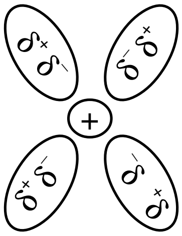
Intermolecular forces :

We know about molecular polarities. They give rise to some of the forces that occur between the molecules. Take H_2O for example. H_2O molecule consists of two hydrogen atoms and one oxygen atom joined together in a specific way by the intermolecular forces known as

"Covalent bonds". But water exists either as solid ice or liquid water or gaseous steam, depending on its temperature. For this, there must be some intermolecular forces between molecules that hold them together at certain temperatures. These intermolecular forces are usually called Vander Walls forces after J. Vander walls (1837-1923). These forces are of several different types like ion - dipole, dipole - dipole, dipole - induced dipole and induced dipole - induced dipole (London dispersion) forces - Hydrogen bond is specific intemolecular force limited to certain kinds of molecules. All these intermolecular forces are electrical. They result from the mutual attractions of unlike charges or repulsions of like charges. If the species are ions full charges are present and ion-ion interactions are very strong (500-1000 k J. mol-1). They give rise to the so called ionic bond's. If the molecules are neutral, then partial charges are possible to give substantial attractive forces.

Ion - Dipole force :

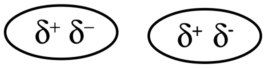




Water molecule's are polar and in them hydrogen atoms possess partial positive charges and oxygen atoms posses partial negative charges due to electronegativity different between hydrogen and oxygen atoms. When ionic compounds like NaCl dissolve in water, they dissociate into its components. Negative and positve charges are possible to give substantial attractive forces, they disccociate into component ions like. Na^+ and Cl^-. Now the water molecules orient in the presence of ion's in such away that the positive end of the dipole is near an anion and the negative end of the dipole is near a cation. The magnitude of interaction energy depends on its charge 'z', molecule's dipole moment 'm' and on the inverse square of the distance 'r' between the ion and the dipole $E = z\mu/r^2$. Ion dipole forces are mainly important in aqueous solutions of ionic substance. Such as NaCl in which dipolar water molecules surround the ion's.

Dipole - Dipole forces :

Neutral but polar molecules experience dipole - dipole forces. These are due to the electrical interaction's among dipoles on neighbouring molecules. These forces are again attractive between unlike poles and repulsive between like poles and depend on the orientation of the molecules. The net forces in a large collection of molecules results from many individual interactions of both types. The forces are generally weak (energies of the order of 3-4 kJ mol^{-1}) and are significant only when the molecules are in close contact. The strength of a given dipole - dipole interaction depends on the sizes of the dipole moments involved. The more polar the molecules or the higher the dipole moment the greater is the strength of interactions and higher is the boiling points of those substances. Dipole-Dipole interaction energy between stationary polar molecules as in solid's is proportional to $1/r^3$ and that between rotating molecules is proportional to $1/r^6$ 'r' is the distance between the polar molecules.



Dipole - induced Dipole forces :

These forces are between polar molecules with permanent dipole moments and the molecules with no permanent dipole - moment. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming into electronic cloud. Here also the interaction range is proportional to $1/r^2$ where 'r' is the distance between the molecules. The magnitude of induced of dipole moment also depends on the magnitude of dipole moment of permanent - dipole and polarisability of neutral molecule. Large molecules are easily polarized. Here also commulative effect of dispersion forces and dipole-induced dipole interactions exist.

There are repulsive forces between the particles (atoms, molecules or ion's) due to electron-electron repulsions or (Nucleus-Nucleus) repulsion's.

Thermal energy :

It is due to the motion of the atoms or molecules of the substance. This energy is directly proportional to the absolute temperature of the substances. It is a measure of average kinetic energy of the molecule's of the substance. The movement of particles is called thermal motion.

Intermolecular forces Vs thermal energy :

Intermolecular forces tend to keep the molecules together but thermal energy tends to keep them apart. If thermal energy predominates over inter molecular forces the substances would change from.

$$\text{Solid} \longrightarrow \text{liquid} \longrightarrow \text{gas}$$

And if intermolecular forces predominate, then the substances change from

$$\text{Gas} \longrightarrow \text{liquid} \longrightarrow \text{Solid.}$$

6.9 Liquifaction of Gas

Any gas can be liquified at atmospheric pressure if it is cooled sufficiently. Many gases (but not all) can be liquified at ordinary temperature by compressing them.

The conditions of temeperature and pressure under which gases liquify were first investigated by Andrews in 1869.

Andrews subjected CO_2 to various pressures at different temperatures and plotted the effect of pressure on volume (Fig. 6.9). The curve obtained at a given temperature is called an *isotherm*. As can be seen in the figure, at 321K the volume of the gas decreased with the increased pressure approximately in accordance with the Boyle's Law. At 294 K, however, the volume first decreases in accordance with Boyle's Law until the pressure was increased

Boyle's Law until the pressure was increased to about 60 atm. At this pressure there was a sudden break in the curve and liquid carbon dioxide appeared. The pressure been converted into liquid. Subsequent increase of pressure caused practically no change in volume. In accordance with the general rule that extremely high pressures are required to compress liquids appreciably.

Similar changes took place when the isotherms were constructed for temperatures below 294 K, except that the pressure required to liquify the gas became smaller as the temperature decreased. Andrews found that liquifaction could be brought about at all temperatures below 304.1 K. But above this temperature no liquifaction occured no matter how much pressure was increased. This temperature was therefore called the **critical temperature** for CO_2. The pressure required to liquify the gas at the critical temperature was called **critical pressure**, and the volume of 1 mole of the substance at the critical temperature and pressure, the **critical volume**.

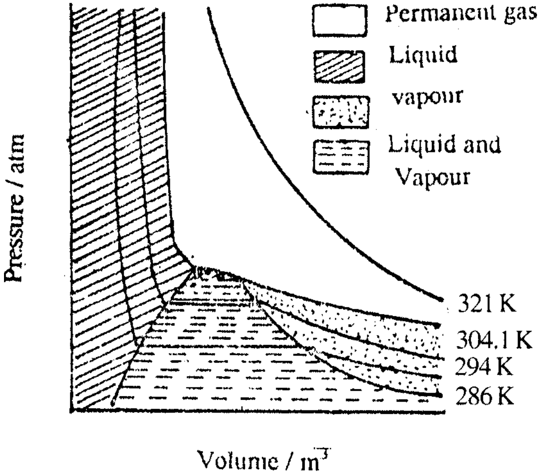


Fig. 6.9 : *Isotherms of carbon dioxide*

The temperature above which a gas cannot be liquified, however large the pressure may be is known as critical temperature.

Table 6.2 list values of the critical temperature and pressure critical volume for some common substances.

Table : 6.2 Critical temperatures and critical pressures

Substance	Critical Temperature (K)	Critical Pressure (atm)
Water, H_2O	647	217.7
Sulphur dioxide, SO_2	430	77.7
Ammonia, NH_3	406	112.5
Hydrogen Chloride, HCl	324	81.6
Carbon dioxide, CO_2	304	73.0
Oxygen, O_2	154	49.7
Nitrogen, N_2	126	33.5
Hydrogen, H_2	33	12.8

Intext Questions 6.3

1. What are the conditions under which real gases behave as ideal gas.

   ....

2. Which term in van der waals equation accounts for the molecular volume.

   ....

3. Calculate the root mean square velocity of ozone kept in a closed vessel at 20^0 C and 1 atm pressure.

   ....

4. What is compressibility factor.

   ....

What You Have Learnt

- Matter exists in three states, namely, solid, liquid and gas.
- The three states of matter differ in the relative closeness of the molecules constituting them.
- There exists a definite relationship between the pressure, volume, temperature and number of moles of a gas and they are given by Boyle's law, Charle's law and Avogadro's law.
- The gases obeying gas laws are known as ideal gases.
- Dalton's law give the relationship between partial pressures exerted by the non-reacting gases to the total pressure.
- Most of the gases deviate from the ideal behaviour. The deviations of gases from ideal behaviour is due to the wrong assumptions of kinetic molecular theory.
- Real gases can be liquified under appropriate conditions.

Terminal Exercise

1. Draw the graphs of the following :

   a) p vs V at constant T and n.

   b) $1/T$ vs p at constant T and n.

   c) T vs V at constant p.

2. What is the volume occupied by one mole of a gas at STP ?

3. The volume of a sample of gas is 500mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at

   i) 1 atm ii) 5.0 atm.

4. List the wrong assumptions of kinetic theory of gases which led to van der Waals equation.

5. What is the standard temperature and pressure ?

6. What is the lowest possible temperature ?

7. CO_2 can not be liquefied at 35^0C, however large the pressure may be, why ?

8. A sample of nitrogen gas weighing 9.3 g at pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What will be its volume when the temperature is 220 K? Assume pressure is kept constant.

9. Calculate the volume of one mole of oxygen at 27^0C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.

10. What is the Maxwell-Boltzmann Law?

Answers to Intext Questions

6.1

1. Due to more intermolecular distances in gaseous molecule compared to liquid.

2. Boyle Law equation is

$$p_1 V_1 = p_2 V_2$$

$$(.20 \text{ atm}) (500 \text{ mL0} = p_2 (10 \text{ mL})$$

$$p_2 = \frac{(0.20\text{atm})(500\text{ml})}{10\text{ml}}$$

$$p_2 = 10 \text{ atm.}$$

3. By Avogadro's Law

$$\text{moles of } O_2 = \text{moles of unknown gas}$$

$$\frac{2.00\text{g}}{32\text{gmol}^{-1}} = \frac{1.75 \text{ g}}{\text{Molecular weight of unknown gas}}$$

$$\text{Molar mass of unknown gas} = \frac{1.75\text{x}32}{2.00} = 28 \text{ g mol-1}$$

6.2

1. Movement of gas molecules through another gas is called diffusion.

   When gas escapes from a container through a very small opening it is called effusion.

2. Ammonia and hydrogen chloride gases are reacting gases and Dalton's Law is applicable to mixture of non-reacting gases.

3. $$\frac{rO_3}{rco_2} = \left(\frac{M_{co_2}}{M_{o_3}}\right)^{1/2}$$

   $$\frac{0.271}{0.290} = \left(\frac{44}{M_{o_3}}\right)^{1/2}$$

   Squaring both sides

   $$\frac{(0.271)^2}{(0.290)^2} = \frac{44}{Mo_3}$$

   $$Mo_3 = \frac{44x0.29x0.29}{0.271x0.271} = 50.4$$

   Molecular mass of $O_3 = 50.4$

4. By ideal gas equation

   $$pV = nRT$$

   $$p \text{ x } 1.0 = (5.0 \text{ mol})\ (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\ 320 \text{ K}$$

   $$p = \frac{(5.0 \text{ mol})\ (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})\ 320 \text{ K}}{1.0 \text{ L}}$$

   $$p = 131.3 \text{ atm.}$$

6.3

1. Low pressure and high temperature.

2. b

3. $$U_{rms} = \sqrt{\frac{3RT}{M}}$$

   $$= \sqrt{\frac{3.(8.314Jk^{-1}mol^{-1})(293K)}{(0.048kgmol^{-1})}} = \sqrt{\frac{(8.314Kgm^2s^{-2}K^{-1}mol^{-1})(293K)}{0.048kgmol^{-1}}}$$

   $$= 390.3 \text{ ms}^{-1}$$

7

THE LIQUID STATE

You are familiar with gases, liquids and solids in your daily life. You are aware that water can exist as a liquid, a solid (ice) or as a gas (vapour). These are called three *states of matter*. In lesson 6, you have learnt about the differences in properties of these three states of matter. The properties of gaseous state can be explained in terms of large separation of molecules and very weak intermolecular forces. In this lesson we shall study about the intermolecular forces in liquids and see how their properties can be explained in terms of these forces.

Objectives

After reading this lesson you will be able to:

- explain the properties of liquids in terms of their structure (molecular arrangement and intermolecular forces);
- differentiate between evaporation and boiling;
- define vapour pressure of a liquid and correlate it with its boiling point;
- define surface tension and explain the effect of various factors on it;
- explain the consequences of surface tension and
- define viscosity of a liquid and correlate it with intermolecular forces.

7.1 Nature of Liquids

Look at Figure 7.1 in which the molecular arrangement has been shown in the three states of matter. What do you notice ?

In figure 7.1a, you would find that the molecules are far apart, A gaseous state can be represented by this arrangement. In liquid state (figure 7.1b), molecules are closer as compared to gaseous state. You would notice that they have very little spaces between them. However, there is no order in arrangement of molecules. Further we say that, these molecules can move about, but with lesser speeds than those in gases. They can still collide with one another as in the gaseous state. You would recall that the molecules in gases have very little attraction berween them. But in liquid state the attraction between the molecules is comparatively much stronger as compared to that in the gaseous state. The attractions are strong enough to keep the molecules in aggregation. Contrary to this, in solids (Fi.g 7.1a) you notice that the molecules are arranged at the closest possible distance.

Solid state is a well ordered state and has very strong intermolecular forces. You would learn more about solids in lesson 8.

We would say, in a gas there is complete choose due to very weak termolecular forces, whereas in solids there is a complete order due to strong forces. Liquids falls between gases and solid state. Liquid molecules have some freedom of gases state and some order of solid state. Intermolecular forces in liqudis are strong enough to keep the molecules close to one another but not strong enough to keep them in perfect order.

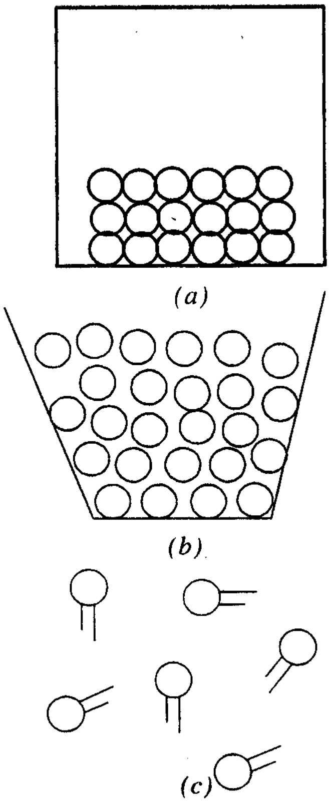


Fig. 7.1 : *Arrangement of molecuels in (a) solids; (b) liquids and (c) gases*

7.2 Nature of Liquids

In this section you would learn how the properties of liquids can be explained in terms of molecular arrangement and intermolecular forces. Let us consider a few properties of liquids as examples.

7.2.1 Volume and Shape

You would recall that the liquids (for example water) take the shape of the container in which they are kept. However, they have a definite volume. How can you explain the properties of definite volume and variable shape? In liquids, the attractive forces are strong enough to keep the molecules moving within a definite boundary. Thus, they maintain a definite volume. These intermolecular forces are not strong enough to keep them in definite positions. The molecules can, therefore, move around and take the shape of the container in which they are kept.

7.2.2 Compressibility

Compressibility of a substance is its ability to be squeezed when a force is applied on it. Let us study the compressibility of liquids with the help of the following activity.

Activity 7.1

Aim : To study the compressibility of water.

What is required ?

A 5 mL syringe and water.

What to do ?

i) Take the syringe and fill it with water by pulling out the plunger.

ii) Note the volume of water.

iii) Press the plunger while blocking the nozzle of the syringe with a finger.

What to observe ?

Observe the volume of water in the syringe while pressing the plunger. Does the volume of water change by pressing the plunger? You would observe that it does not change.

The above activity clearly shows that liquids arr largely incompressible. It is because there is very little empty space between the molecules. In contrast, the gases are highly compressible because of large empty spaces between their molecules.

The large difference in the free space in gaseous and liquid states becomes evident from the fact that the volume occupied by a given amount of a substance in liquid state is 100-1000 times less than that in the gaseous state.

7.2.3 Diffusion

Diffusion is the process of spreading of a substance from a region of higher concentration to a region of lower concentration. Let us study the phenomenon of diffusion in liquids with the help of the following activity.

Activity 7.2

Aim : To study the phenomenon of diffusion through water.

What is required ?

A glass, water, blue ink and a dropper.

What to do ?

i) Take some water in the glass.

ii) Add a few drops of blue ink into water with the help of a dropper.

What to observe ?

Observe the water and ink in the beaker.

Initially the ink does not mix with water. After some time it starts spreading slowly. After a few hours the whole of water in the glass becomes coloured due to diffusion of ink through water.

The above activity demonstrates that diffusion occurs in liquids. Why does it happen? Because the molecules of both the liquids are moving and help in the diffusion process.

7.2.4 Evaporation

You know that water left in an open pan evaporates slowly until the pan becomes dry. Evaporation is the process by which a liquid changes into vapour. It occurs at all temperatures from freezing point to boiling point of the liquid.

In a liquid, at any temperature, a small fraction of the molecules is moving with relatively high velocity. Such molecules have high kinetic energy. These can overcome the intermolecular attractive forces and escape through the surface of the liquid.

Rate of evaporation of aliquid depends on a number of factors. For example, more is the surface area, faster will be the evaporation. For faster dying, we increase the surface area by spreading the wet clothes. If we supply heat to the liquid, evaporation is faster. The wet clothes dry faster in the sun. The increase in temperature increases the kinetic energy of the molecules of the liquid and the liquid evaporates at a faster rate. We feel cool after the bath. Why do we feel so ? It is because during evaporation water takes the heat from our body and we feel cold.

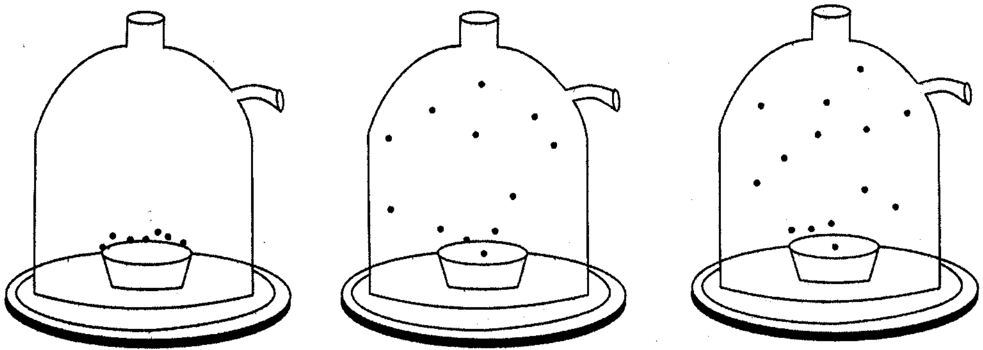
Now let us compare the rate of evaporation of two liquids, for example, water and alcohol. Which of these two liquids evaporates faster ? You mut have experience that alcohol evaporates faster. Why does this happen? The number of molecules escaping from a liquid depends upon the attractive forces. When these forces are stronger, fewer molecule escape. In alcohol, these attractive forces are weaker than those in the water. Hence, alcohol evaporates faster than water.

7.3 Vapour Pressure and Boiling Point

In the previous section you have learnt that liquids evaporate when kept in an open vessel. Different liquids evaporate to different extent under similar conditions. The extent of evaporation of a liquid is measured with the help of **vapour pressure** of a liquid. In this section, you will study about it and also about the boiling point of a liquid.

7.3.1 Vapour Pressure of a liquid

You know that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed vessel say in stoppered bottle or a bell jar, evaporation occurs, but after sometime the level of the liquid does not change any further and become constant. Let us understand how does it happen. In the closed vessel, the molecules evaporating from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air and some of them may start moving towards the surface of the liquid and enter into it. This is known as condensation. In the beginning, rate of evaporation is greater than the rate of condensation. But as more and more molecules accumulate in the space above the liquid, rate of condensation gradually increases. After some time, rate of evaporation becomes equal to the rate of condensation and an equilibrium state is reached (Fig. 7.2).



Initially molecules evaporate

After some time condensation begins

At equilibrium the rates of evaporation and condensation become equal

Fig. 7.2 : *Establishing (vapour liquid) equilibirum under a evacuated jar*

The number of molecules in the vapour above the liquid becomes constant. These molecules exert certain pressure over the surface of the liquid. This pressure in known as (equilibrium vapour pressure, saturated vapour pressure) or simply as (vapour pressure). The vapour pressure of a liquid has a characteristic value at a given temperature. For example, vapour pressure of water is 17.5 torr and that of benzene is 75.00 torr at 20^{0}C. The vapour pressure of a liquid increases with increase in temperature. It is so because at a higher temperature more molecules have sufficiently high energy to overcome the forces of attraction and escape to form vapour. A plot of vapour pressure as a function of temperature is called **vapour pressure curve**. Figure 7.3 depicts the vapour pressure curves of some liquids.

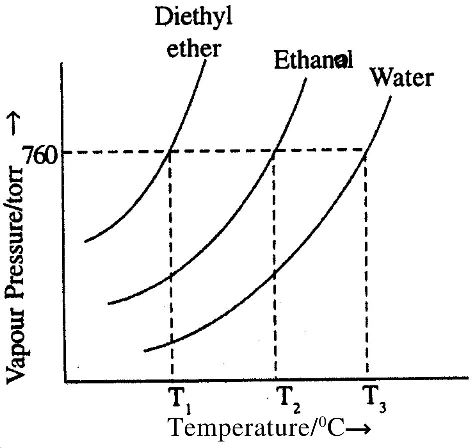


Fig. 7.3 : *Vapour pressure curves of some liquids*

What would happen if we remove some of the vapour from the closed vessel. Would the vapour pressure of the liquid increase, decrease or remain constant? Vapour pressure of the liquid would remain constant at that temperature. In the beginning, the vapour pressure would decrease after the removal of the vapour, but soon more liquid would evaporate to maintain the equilibrium and the original vapour pressure would be restored. So the vapour pressure of a liquid has a definite value at a particular temperature.

7.3.2 Boiling

You must have seen the formation of bubbles at the base of a vessel, in which a liquid is heated. The rate of formation of bubbles increases with increase in heat supplied. What are the bubbles made up of? The first bubbles that you see are of the air, which is driven out of the liquid by increase in temperature. After some time, bubbles of the liquid are formed throughout it. These bubbles rise to the surface and break. When this happens, we say that the liquid is boiling. The bubbles of the liquid would form only if its vapour pressure is equal to the atmospheric pressure.

The temperature at which boiling occurs is called the boilling point of the liquid. At this temperature the vapour pressure of the liquid is equal to the atmospheric pressure. The boiling point, therefore, depends upon the atmospheric pressure. For example, water boils at 100^0C at 760 torr and at 97.7^0C at 700 torr.

The normal boiling point of a liquid is defined as the temperature at which the vapour pressure of a liquid is equal to one atmosphere or 760 torr.

The boiling point of a liquid depends upon its nature. A more valatile liquid would boil at a lower temperature than a less volatile liquid. You can refer to figure 7.3 and note that diethyl ether boils at a much lower temperature than water, because it is highly volatile liquid. The boiling point of ethanol lies in between those of diethyl ether and water. Vapour pressures or boilin points of liquids give us an idea of the strength of attractive forces between molecules in liquids. Liquids having lower boiling points have weaker attractive forces in comparison tot hose havinng higher boiling points.

You can make a liquid boil at temperature other than normal boiling point. How? simply alter the pressure above the liquid. If you increase this pressure, you can increase the boiling point and if you can decrease this pressure you decrease the boiling point. On the mountains, the atmospheric pressured decrease and therefore boiling point of water also decreases. People living on hills face problem in cooking their meals. They, therefore, use pressure cooker. How food is cooked fater in it? The lid of pressure cooker does not allow water vapour to escape out. On heating the water vapour accumulate and the inside pressure increases. This makes the water boil at a higher temperature and the food is cooked faster.

7.3.3 Evaporation and Boiling

Evaporation and boiling, both involve conversaion of a liquid into vapour and appear to be similar. However, they differ from each other in some aspects. Evaporation occurs at all temperatures from freezing point of a liquid to its boiling point, while boiling occurs at a definite temperature only i.e., it is boiling point. Evaporation occurs slowly while boiling is a fast process. Evaporation of a liquid occurs at its surface alone while boiling occurs throughout the liquid. These differences between evaporation and boiling have been summarized in Table 7.1.

Table 7.1 : Differences between evaporation and boiling

S.No.	Evaporation	Boiling
1.	It takes place at all temperatures.	It takes place at a definite temperature.
2.	It is a slow process.	It is a fast process
3.	It occurs only at the surface of the liquid.	It occurs throughout the liquid.

Intext Questions 7.1

1. Match the following.

Column I		Column II
i) liquids have a definite volume.	a)	The molecules in a liquid can move about
ii) Liquids acquire the shape of their container.	b)	The molecules in liquids are close and have very little free space.
iii) Liquid are largely incompressible.	c)	The inter molecular forces liquid strong enough to keep the molecules moving with in a definite space.

2. When a liquid is heated till it starts boiling.

   i) What are the small bubbles that appears initially at the bottom and sides of the vessel made up of ?

   ....

   ii) What are the large bubbles that from in the boiling liquid made up of ?

   ....

3. Liquids A, B and C boil at 65^{0}C, 120^{0}C and 90^{0}C respectively. Arrange them in the decreasing order of the strength of intermolecular forces.

....

7.4 Surface Tension

Liquids show the effects of inter molecular forces most dramatically in another property, namely, **surface tension**. Any molecule in the interior of liquid is equally attracted by neighbour molecules from all sides and it does not experience any 'net' force. On the other hand, any molecule at the surface of a liquid is attracted by other molecules at the surface of the liquid or below it. Due to the imbalance of forces, any molecule at the surface experiences a net inward pull (Figure 7.4). As a result the surface is under tension as if the liquid were covered with a tight skin (or stretched membrane). The phenomenon is called *surface tension*, Quantatively, the **surface tension** *is defined as the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side* as shown in Figure 7.5 It is represented bythe Greek letter gamma, r. Its SI unit is newton per meter (N m^{-1}) and CGS unit is dyne per centimeter (dyne cm^{-1}). The two units are related as : 1 $Nm^{-1} = 10^3$ dyne cm^{-1}.

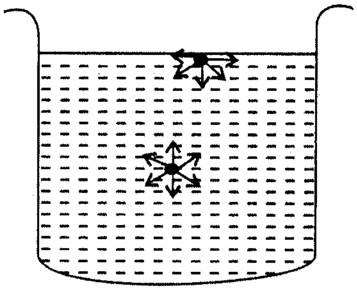


Fig. 7.4 : *Forces acting one molecules, at the surface and in bulk of liquids*

Surface molecules of a liquid experience a constant inward force. Therefore they have a higher energy than the molecules in the bulk of the liquid. Due to this reason liquids tend to have minimum number of molecules at their surface. This is achieved by *minimising the surface area*. In order to increase the *surface area* more molecules must come to the surface. This can happen only if some energy is supplied or work is done. *The energy supplied (or work done) for increasing the surface area of a liquid by a unit amount is known as its* **surface energy**. Its units are joule per square meter J m^{-2} or N m^{-1} (since 1J = 1Nm). Thus dimensionally, the surface tension and surface energy are similar quantities and they have the same numerical value.

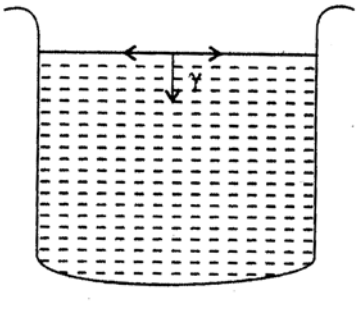


Fig. 7.5 : *Surface tension force acting on the surface of a liquid.*

Effect of Temperature

One raising the temperature surface tension of a liquid decreases. It completely vanishes at the critical temperature. This happens due to the following two factors :

i) On heating, the liquids expand. This increases the intermolecular distances.

ii) On heating, the average kinetic energy of molecules and hence their chaotic motion increases.

Due to both of these factors, the intemolcular forces become weak and the surface tension decreases.

Effect of adding Surface Active Solutes

The solutes which get more concentrated on the surface of the liquid than in the bulk called **surface active solutes** or **surfactants.** Alcohols are examples of such substances. Their addition to a liquid lowers its surface tension. The cleaning action of soaps and detergents is based on this fact.

Some Effects Surface Tension

Surface tension results in many interesting and important properties of liquids. Let us now study some of them.

i) Spherical Shape of liquid drops

You have already learnt that liquids tend to have a minimum surface area. For a given volume, the geometrical shape having minimum surface area is a sphere. Hence, liquids have a natural tendency to form spherical drops, when no external force acts on them. Rain drops are distroted and the distortion is due to the friction of air.

ii) Wetting and Non- wetting propeties

When a drop of liquid is placed on solid surface, the force of gravity should cause it to spread out and form a thin layer (Fig. 76). Such a liquid is called a **wetting liquid**. This happens in case of most of the liquids. For example, drops of water or alcohol spreadout on the surface of glass. Some liquids behave differently. When a drop of mercury is placed on the surface of glass, it does not spread out (Fig. 7.6). Solid liquids are called **non-wetting liquids**.

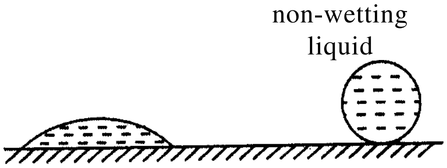


Fig. 7.6 : *Establishing (vapour liquid) equilibirum under a evacuated jar*

Wetting or non-wetting nature of a liquid depands upon two types of forces. The intermolecular attractive forces between molecules of a liquid are called **cohesive force** while those between the molecules of the liquid and the solid (whose surface is in contact with the liquid) are called **adhesive forces**. If adhesive forces are stronger than cohesive forces, the liquid would be wetting in nature and when cohesive forces are stronger than adhesive forces it would be non-wetting in nature on the surface of a particular soild

iii) Capillary Action

Let us carry out the following activity.

Activity 7.3

Aim : To study the capillary action.

What is required ?

Glass capillary tubes, water, mercury and two petri dishes.

What to do ?

i) Take some water in a petri dish.

ii) Dip one end of a 3-4 cm long capillary in it.

iii) Take some mercury in another petri dish.

iv) Dip one end of another 3-4 cm long capillary in it.

What to observe ?

Observe the levels of water and mercury in the capillaries. Is it below or above the levels of the liquid in petri dishes.

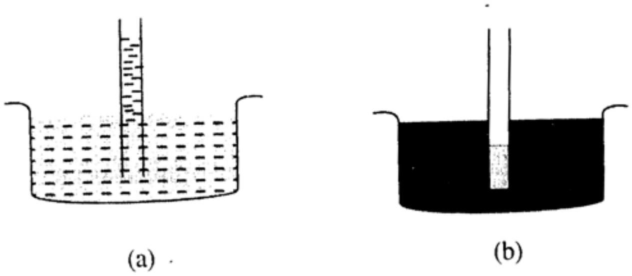


Fig. 7.7 : *Capillary Action*

You would observe that when end of a capillary tube is dipped in water, it rises in the capillary as shown in Fig. 7.7(a). On the other hand when one end of a capillary tube is dipped in mercury, its level falls in the capicllary as in Fig .7.7 (b).

The phenomenon of rise or fall of a liquid in a capillary is known as **capillary action**. The rise of water in the glass capillary is due to its wetting nature as the adhesive forces are stronger then cohesive forces. Water tends to increase the area of contact with glass wall of the capillary by rising in it. Mercury being non-wetting with respect of glass (its cohesive forces are stronger than adhesive forces) tends to minimise the area of contact by depressing inside the capillary.

iv) Curved menisus

When a wetting liquid such as water is taken in a glass tube, the liquid tends to rise lightly along the walls of the tube for increasing its area of contact with glass. The surface of the liquid (meniscus) becomes curved. It is concave in shape (Fig. 7.8 (a)]. When a non-wetting liquid like mercury is taken a glass tube, it tends to decrease its area of contact and depresses along the walls of the glass tube. The meniscus is convex in shape in this case (Fig. 7.8)(b)].

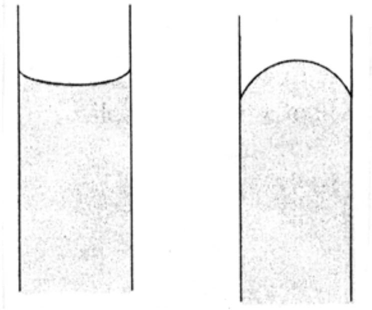
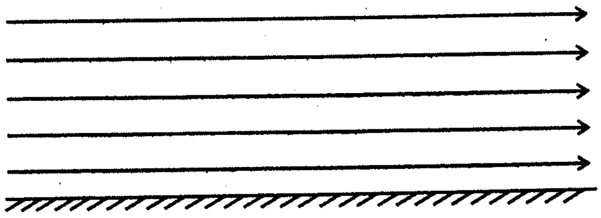


Fig. 7.8 : *Curved meniscus of liquids*

(a) Concavemeniscus (b) Convex meniscus

7.5 Viscosity

Every liquid has the ability to flow. It is due to the fact that molecules in a liquid move freely, although within a limited space. Water flows down a hill *under gravitational force* or through pipes when forced by a pump. Some external force is always required for a liquid to flow. Some liquids like glycerol or honey flow slowly while others like water and alcohol flow rapidly. This difference is due to the internal *resistance to flow* which is called **viscosity**. The liquids with higher viscosity flow slowly and are more viscous in nature like glycerol or - honey. Water and alcohol have lower viscosity and are less viscous in nature. They flow more rapidly.



Surface of a solid

Fig. 7.9 : *Flow of different layers of a liquid*

The viscosity is related to the intermolecular forces. Stronger the intermolecular forces more viscous are the liquids. Let us understand this with the help of Figure 7.9. When a liquid flows steadily, it flows in different layers with one layer sliding over the other. Such a flow is known as **laminar flow**. Consider a liquid flowing steadily on a plane surface. The layer closest to it is almost stationary due to adhesive forces. As the distance of the layer from the surface increases, is velocity increases. Thus different layers move with different velocities. Due to intermolecular forces (cohesive forces) each layer experiences a force of friction from its adjacent layers. This force of friction, f between two layers depends upon :

i) area of contact between them A.

ii) distance between the layers, dx.

iii) difference in velocity between the layers, du.

These quantities are related as

$$f = \eta A \frac{du}{dx}$$

Hence η (Greek letter 'eeta') is called the coefficient of viscosity and $\frac{du}{dx}$ is the *velocity gradient* between the layers.

If $A = 1\ \text{cm}^2$, $du = 1\ \text{cm s}^{-1}$ and $dx = 1$ cm, then

$$f = \eta$$

Thus, coefficient of viscosity is the force of friction between two parallel layer of the liquid which have 1 cm^2 area of contact, are separated by 1 cm and have a velocity difference of 1cm s^{-1}. It may be noted that f is also equal to the **external force** which is required to overcome the force of friction and maintain the steady flow between two parellel layers having A area of contact, and which are dx distance apart and moving with a velocity difference of du.

Units

CGS unit of viscosity is dyne cm^{-2} s. This unit is also known as **poise(P)**. The SI unit of viscosity is N m^{-2}s or Pas. The two units are related as:

1 pas = 10 P

The unit paise is found to be too large and its submultiples **centipoise** (1 cP = 10^{-2} P) and **milli poise** (1 mP = 10^{-3} P) are used for liquids and micropoise (μP = 10^{-6} P) is used for gases.

Effect of Temperature

Viscosity of a liquid decreases on raising the temperature. It is due to decrease in intermolecular forces on heating as discussed in previous section (Section 7.4).

Intext Questions 7.2

i) A molecule at the surface of a liquid has .... energy than the one within the liquid.

ii) Surface tension of liquid .... on cooling.

iii) Meniscus of a non-wetting liquid is .... in shape while that of a wetting liquid is .... in shape.

iv) When one end of a glass capillary tube was dipped in a liquid, the level of liquid inside the capillary was observed to fall. The adhesive forces in this liquid are .... than the cohesive forces between the liquid and glass.

v) Liquid X is more viscous than liquid Y. The intermolecular forces in Y are .... than in X.

2. What are the SI units of

i) Surface tension.

....

ii) Coefficient of viscosity

....

3. Why do liquids have a tendency to acquire minimum surface area ?

....

What You Have Learnt

- In liquids the intermolecular force are quite strong as compared to gases but weak enough to allow the molecules to move within a limited space and athe intermolecular distance is short.
- Liquids have definite volume but no definite shape, are almost incompressible and can diffuse.
- Liquids eveporate and exert a definite vapour pressure at speficied temperature.
- Boiling point is the temperature at which the vapour pressure of the liquid becomes eqaul to the external pressure.
- Surface tension is the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side.
- Due to surface tension, liquids tend to have minimum surface area and show the phenomena of capillary rise or fall and curved meniscus.

- Viscosity is the internal force of friction to the flow of liquid.

Terminal Exercise

1. Explain the following properties of liquids on in basis of their structure.

   i) Volume ii) Shape iii) Compressibility iv) Ability to flow

2. Why diffusion can occur in liquids. Explain.
3. Define i) vapour pressure and ii) boiling point.
4. Differentiate between evaporation and boiling.
5. Explain the effect of temperature on vapour pressure of a liquid.
6. Define surface tension and give its CGS and SI units.
7. What is surface energy ?
8. Why is energy required to increase the surface area of a liquid ?
9. What is the effect of addition of a surface active substance on the surface tension of a liquid.
10. Why are liquid drops spherical in shape ?
11. What are wetting and non-wetting liquids ?
12. The cohesive forces acting in liquids A and B are C_1 and C_2 respectively $C_1 > C_2$ which of them would have higher surface tension.
13. Liquid A rises in glass capillary tube. If one drop of its is put on a plane glass surface, would it spread out or not. Explain.
14. A liquid forms a convex meniscus in glass tube. Commnet on its nature.
15. Define viscosity.
16. What is coefficient of viscosity ?
17. Give CGS and SI units of coefficient of viscosity.
18. What is the effect of temperature on (i) vapour pressure (ii) surface tension and (iii) viscosity of a liquid ?

Answers to Intext Questions

7.1

1. i) C; ii) A; iii) B
2. i) Air ii) Liquid

3. B > C > A

7.2

1. i) more ii) increases iii) convex; concave
   iv) Stronger v) weaker

2. i) N m^{-1}; ii) $Nm^{-2}s$

3. Molecules in the surface of a liquid have higher energy due to an inward force on them. Therefore liquids tend to have minimum number of molecules in the surface or have minimum surface area.

8

SOLID STATE

You are aware that the matter exists in three different states viz., solid liquid and gas. In these, the constituent particles (atoms, molecules or ions) are held together by different forces of attraction between them. However, the nature and magnitude of the forces varies. In the first two lessons of this module you have learnt about the gaseous and the liquid states of matter. In this lesson you would learn about solid state- a compact state of matter. The solids are distinguished from a liquid or gas in terms of their rigidity which makes them occupy definite volume and have a well defined shape. In solid state, the constituent particles are in close contact and have strong forces of attraction between them. Here, you would learn about structure, classification and properties of solids.

Objectives

After reading this lesson, you should be able to:

- explain the nature of solid state;
- explain the properties of solids in terms of packing of particles and intermolecular attractions;
- explain the melting point of a solid;
- differentiate between crystalline and amorphous solids;
- classify the crystalline solids according to the forces operating between the constituent particles;
- explain different types of packing in the solids;
- define coordination number;
- explain different types of unit cells;
- calculate the number of particles in simple cubic, face-central cubic and body centered cubic unit cells;

- define radius ratio;
- correlate the radius ratio with the structure of solids;
- explain the structure of simple ionic compounds and
- explain Frenkel and Schottky defects.

8.1 Nature of Solid State

You have learnt in lesson 6 that according to *Kinetic Molecular Theory*, the gases consist of a large number of molecules, which are in constant random motion in all directions in the available space. These molecules have very weak or negligible forces of attraction between them. A sample of gas can be compressed, as there is a lot of free space between the molecules Fig.8.1(a). In liquids Fig.8.1(b) on the other hand the molecules are also in constant motion but this motion is relatively restricted. Since there is very little free space available between the molecules the liquids are relatively incompressible.

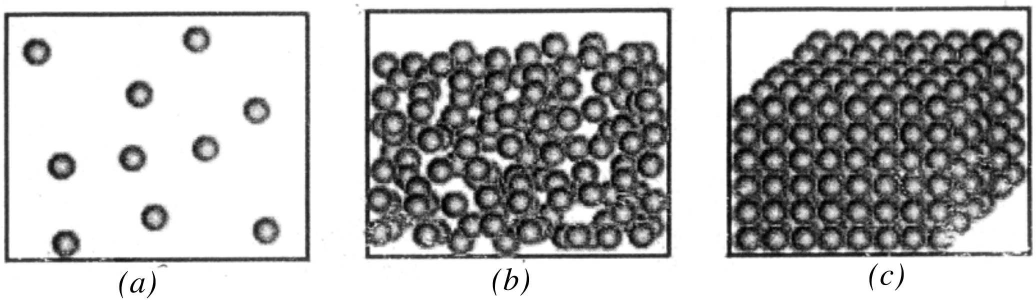


Fig. 8.1 : *A pictorial representation of the three states of matter : (a) gas (b) liquid and (c) solid state.*

In solid state the constituent particles are arranged in a closely packed ordered arrangement Fig.8.1(c) with almost no free space. They can just vibrate about their fixed positions. These are in close contact and cannot move around like the molecules of a gas or a liquid. As a consequence, the solids are incompressible, rigid and have a definite shape. Like liquids, the volume of a solid is independent of the size or the shape of the container in which it is kept.

8.2 Classification of Solids

On the basis of nature of arrangements of the constituent particles the solids are classified into amorphous and crystalline solids.

8.2.1 Amorphous and Crystalline Solids

In **crystalline solids** the constituent particles are arranged in a regular and periodic pattern and give a well defined shape to it. The term 'crystal' comes from the Greek word, *krustallos* meaning ice. The regular pattern extends throughout the solid and such solids are said to have **long range order**. On the other hand, some solids have only a short range of order. This means that the particles are arranged regularly in only some regions of the solid and are relatively disordered in other regions. Such solids are called **amorphous solids**. In Greek, a means without and *morph* means form. Thus the word *amorphous* means without form. Sodium chloride and sucrose are common examples of crystalline solids while glass, fused silica, rubber and high molecular mass polymers are some examples of amorphous solids.

An important difference between the amorphous and crystalline solids is that while amorphous solids are isotropic in nature (i.e., these exhibit same value of some physical properties in all directions) the crystalline solids are **anisotropic** (i.e., the values of some physical properties are different in different directions). Refractive index and coefficient of thermal expansion are typical physical properties, Which have different values between amorphous and crystalline solids is that while crystalline solids have a sharp or definite melting point, whereas the amorphous solids do not have definite melting point, these melt over a range of temperature.

The crystalline solids can be further classified on the basis of nature of interaction between the constituent particles as discussed below.

8.2.2 Classification of Crystalline Solids

In crystalline solids the constituent particles are arranged in an ordered arrangement and are held together by different types of attractive forces. These forces could be coulombic or electrostatic, covalent, metallic bonding or weak intermolecular in nature. The differences in the observed properties of the solids are due to the differences in the type of forces between the constituting particles. The types of forces binding the constituent particles can be used as a basis for classification of crystalline solids. On this basis, the crystalline solids can be classified into four different types- ionic- molecular, covalent and metallic solids. The characteristics and the properties of different types of solids are compiled in Table 8.1.

Table 8.1 : Characteristics and properties of different types of solids.

Type of Solid	Constituent Particles	Nature of interaction between the particles	Appearance	Melting Point	Examples
Ionic	Ions	Coulombic	Hard and brittle	High	Sodium chloride zinc sulphide, etc
Molecular	Molecules				Water, carbon
Non polar		van der Walls	Soft and	low	dioxide, iodine etc
Polar		Dipole-dipole	brittle		
Covalent	Atoms	Covalent bonding	Hard	Very high	Diamond, graphite silica, etc.
Metallic	Atoms	Metallic bonding	Hard and malleable	Variable	Copper, silver, etc.

Sodium chloride is an example of an ionic solid because in this case the sodium ions and chloride ions are attracted to each other by electrostatic interactions. Iodine on the other hand is an example of a molecular solid because in this the molecules are held together by weak vander Waals forces. Diamond, with strong covalent between the constituent carbon atoms is an example of covalent solids while in metals a large number of positive cores of the atoms are held together by a sea of electrons.

8.3 Properties of Crystalline Solids

You are familiar with the following properties of solids on the basis of handling solids in day to day work.

- Solids are rigid in nature and have well defined shapes
- Solids have a definite volume irrespective of the size and shape of the container in which they are placed.
- Solids are almost incompressible.

You are familiar with a number of crystalline solids like sugar, rock salt, alum, gem stones, etc. You must have noticed that such solids have smooth surfaces. These are called 'faces' of the crystal. These faces are developed in the process of crystal formation by ordered arrangement of the constituent particles. It is generally observed that the faces of crystals are developed unequally. The internal angle between a pair of faces is called **interfacial** angle and is defined as the angle between the normals to the intersecting faces. An important characteristic of crystalline solids is that irrespective of the size and shape of the crystal of a given substance, the interfacial angle between a pair of faces is always the same. This fact was stated by Steno as *the law of constancy of interfacial angles* (Fig. 8.2).

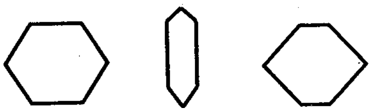


Fig. 8.2 : *The constancy of interfacial angles*

8.3.1 Melting Point of a Solid

What is the effect of heat on a solid? You would have observed that when a solid is heated it becomes hot and eventually gets converted into a liquid. This process of conversion of a solid to a liquid on heating is called **melting**. You would also have observed that different solids need to be heated to different extents to convert them to liquids. The temperature at which a solid melts to give a liquid is called its **melting point**. Every solid is characterized by a definite melting point. This in fact is a test of the purity of the solid. The melting point of a solid gives us an idea about the nature of binding forces between constituent particles of the solid. Solids like sodium chloride (m.p = 1077 K) have very high melting points due to strong coulombic forces between the ions constituting it. On the other hand molecular solids like naphthalene (m.P. 353 K) have low metling points.

The effect of heat on a solid can be understood in terms of energy and motion of the constituent particles. You are aware that in a solid the constituent particles just vibrate about their mean position. As the heat is supplied to the solid, the constituent particles gain energy and start vibrating more vigorously about their equilibrium positions. As more and more heat is supplied, the energy keeps on increasing and eventually it becomes greater than the binding forces between them. As a consequence the solid is converted into a liquid.

Intext Questions 8.1

1) Differentiate between solid, liquid and gaseous state.

....

2) How are solids classified on the basis of the intermolecular forces.

....

3) What is Steno's law of constancy of interfacial angels ?

....

8.4 Close Packed Structures of Solids

In the process of the formation of crystal the constituent particles get packed quite closely. The crystal structures of the solids can be described in terms of a close packing of identical spheres as shown in Fig. 8.3 These are held together by forces of attraction. Let us learn about the possible close packed structures of solids and their significance.

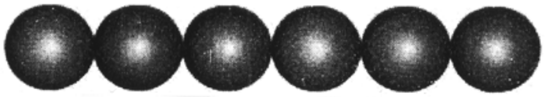
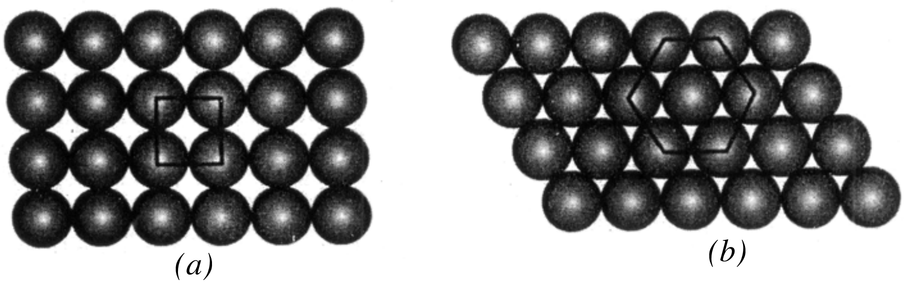


Fig. 8.3 : *Arrangement of identical spheres in one dimension*

A linear horizontal arrangement of identical spheres in one dimension forms a row (Fig. 8.3). A two dimensional close packed structure can be obtained by arranging a number of such rows to form a layer. This can be done in two possible ways. In one of these, we can place these rows in such a way that these are aligned as shown in (Fig. 8.4 (a)). In such an arrangement each sphere is in contact with four other spheres. This arrangement in two dimensions is called **square close packing**.



(a) *(b)*

Fig. 8.4 : *(a) Square close packing and (b) hexagonal close packing of identical spheres in two dimensions*

In the other way we can place the spheres of the second row in the depressions of the first row and so on so forth (Fig. 8.4 (b)). You may notice that in such an arrangement each sphere is in contact with six other spheres. Such an arrangement in two dimensions is called hexagonal **close packing**. In such a packing, the spheres of the third row are aligned with the first row. You may also have noticed that in the hexagonal close packed the spheres are more effectively packed. In Fig. 8.4 an equal number of identical spheres are arranged in two different types of packing.

A three dimensional structure can be generated by placing such two dimensional layers on top of each other. Before we move on to the three dimensional packing let us look at the hexagonal close packed layer some what more closely (Fig. 8.5).

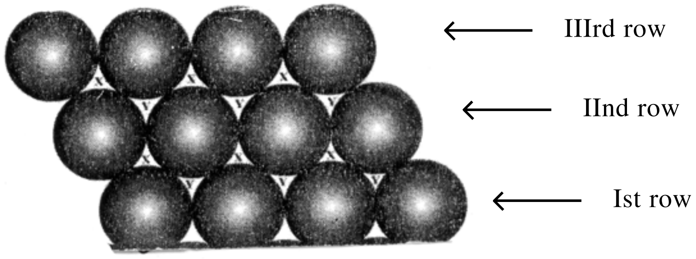


Fig. 8.5 : *A hexagonal close packed layer showing two types of triangular voids.*

You may note from Fig. 8.5 that in a hexagonal close packed layer there are some unoccupied spaces or voids. These are triangular in shape and are called **trigonal voids**. You can further note that there are two types of triangular voids, one with the apex pointing upwards and the other with the apex pointing downwards. Let us call these as X type and Y type voids respectivly as makred in the Fig. 8.5

Close Packed Structures in three dimensions

Let us take a hexagonal close packed layer and call it A layer and place another hexagonal close-packed layer (called the B layer) on it. There are two possibilities.

1. In one, we can place the second layer in such a way that the spheres of the second layer come exactly on top of the first layer.
2. In other, the spheres of the second layer are in such a way that these are on the depressions of the first layer. The first possibility is similar to square close packing discussed above and is accompanied by wastage of space. In the second possibility when we place the second layer into the voids of the first layer, the spheres of the second layer can occupy either the X or Y types trigonal voids but not both. You may verify this by using coins of same denomination. You would observe that when you place a coin on the trigonal void of a given type, the other type of void becomes unavailable for placing the next coin (Fig. 8.6).

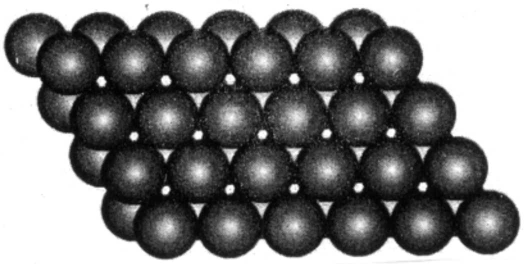


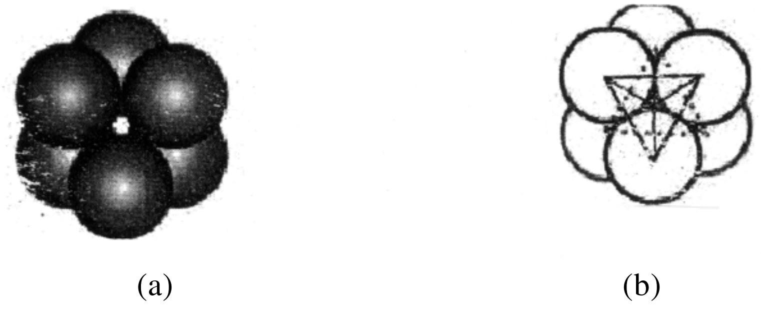
Fig. 8.6 : *Two layers of close packed spheres, the second layer occupies only one type (either X or Y) of triangular voids in the first layer.*

In this process, the sphere of second layer covers the trigonal voids of the first layer. It results into voids with four spheres around it, as shown in Fig. 8.7 (a). Such a void is called a **tetrahedral void** since the four spheres surrounding it are arranged on the corners of a regular tetrahedron, Fig. 8.7 (b). Similarly, the trigonal voids of the second layers will be placed over the spheres of the first layer and give rise to tetrahedral voids.

(a) (b)

Fig. 8.7 : *A tetrahedral void*

In a yet another possibility, the trigonal voids of the first layer have another trigonal void of the opposite type (B type over C and C type over B type) from the second layer over it. This generates a void which is surrounded by six spheres, Fig. 8.9 (a). Such a void is called an **octahedral void** because the six spheres surrounding the void lie at the corners of regular octahedron, Fig. 8.8 (b).



(a) (b)

Fig. 8.8 : *An octahedral void*

A closer look at the second layer reveals that it has a series of regularly placed tetrahedral and octahedral voids marked as ‘t’ and ‘o’ respectively in Fig. 8.9

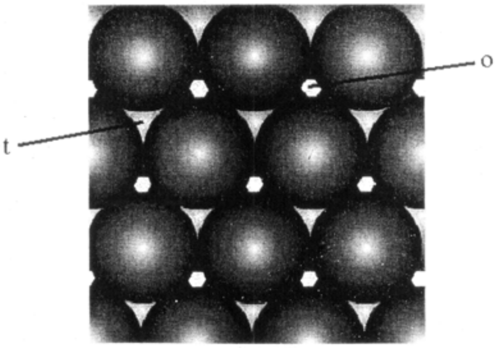
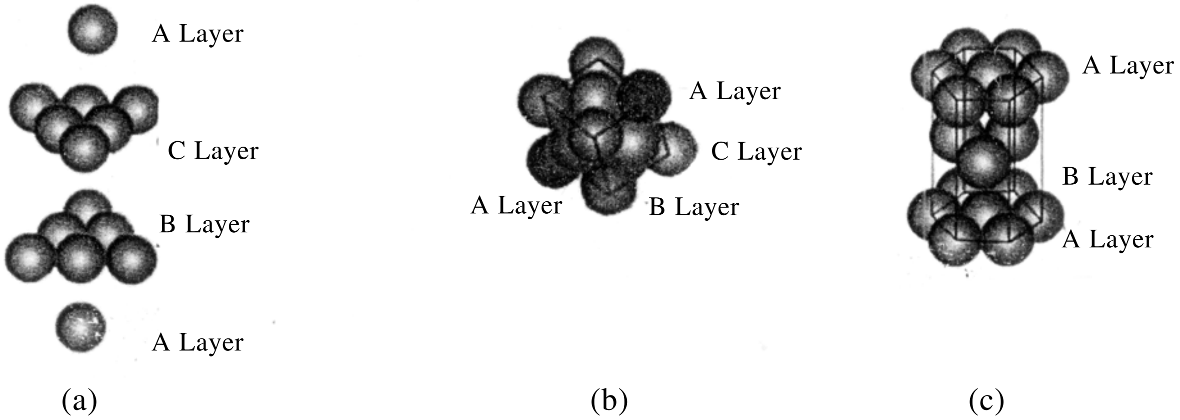


Fig. 8.9 : *The top view of the second layer showing the tetrahedral and octahedral voids*

Now when we place the third layer over the second layer, again there are two possibilities i.e., either the tetrahedral or the octahedral voids of the second layer are occupied. Let us take these two possibilities. If the tetrahedral voids of the second layer are occupied then the spheres in the third layer would be exactly on top (i.e., vetically aligned) of the first or A layer the next layer (4th layer) which is then placed would align with the B layer. In other words, every alternate layer will be vertically aligned. This is called AB AB..... pattern or AB AB ... repeat. On the other hand if the octahedral voids of the second layer are occupied, the third layer is different from both the first as well as the second layer. It is called the C layer. In this case the next layer, i.e., the fourth layer, howsoever it is placed will be aligned with the first layer. This is called ABC ABC ... pattern or ABC ABC... repeat. In three dimensional set up the AB AB ... pattern or repeat is called **hexagonal closed packing** (hcp) (Fig. 8.10 (c) while the ABC ABC .... pattern or repeat is called **cubic closed packing** (ccp) (Fig. 8.10 (a)).



(a) (b) (c)

Fig. 8.10 : *a) Cubic closed packing (ccp) as a result of ABC pattern of close packed spheres: b) the layers in a) tilted and brought closer to shows fcc arrangement c) hexagonal closed packing (hcp) as a result of ABAB pattern of close packed spheres.*

This process continues to generate the overall three dimensional packed structure. These three dimensional structures contain a large number of tetrahedral and octahedral voids. In general there is one octahedral and two tetrahedral voids per atom in the close packed structure. These voids are also called as **interstices**. As mentioned earlier, the identical spheres represent the positions of only one kind of atoms or ions in a crystal structure. Other atoms or ions occupy these interstices or voids.

In the close packed structures (hcp and ccp) discussed above each sphere is in contact with six spheres in its own layer (as shown in Fig. 8.5) and is in contact with three spheres each of the layer immediately above and immediately below it. That is each sphere is in contact with a total of twelve spheres. This number of nearest neighbor is called its **coordination number**. The particles occupying the interstices or the voids will have a coordination number depending on the nature of the void. For example an ion in a tetrahedral void wil be in contact with four neighbours i.e., would have a coordination number of four. Similarly the atom or ion in an octahedral void would have a coordination number of six.

Intext Questions 8.2

1) What is the difference between the square close packed and hexagonal close packed structures ?

....

2) Which of the above two, is more efficient way of packing ?

....

3) Clearly differentiate between, triogonal, tetrahedral and octahedral voids.

....

8.5 Crystal Lattices and Unit Cells

You know, the crystalline solids have long-range order and the closely packed constituent particles are arranged in an ordered three dimensional pattern. The structure of the crystalline solids can be represented as an ordered three dimensional arrangement of points. Here each point represented the location of a constituent particle and is known as **lattice point** and such an arrangement is called a **crystal lattice** or **space lattice** or simply a **lattice**.

To understand the meaning or the term lattice let us first take a repetitive pattern in two dimension. In the crystal structure of sodium chloride in two dimensions the Na^+ and Cl^- ions are arranged in an ordered fashion as shown in Fig. 8.11 (a). If the position of each ion is represented as a point then the same crystal can be represented as an array of such points in two dimensions (Fig. 8.11 (b)). It is called a two dimensional lattice.

Na^+ Cl^- Na^+ Cl^- Na^+
Cl^- Na^+ Cl^- Na^+ $^-$
Na^+ Cl^- Na^+ Cl^- Na^+
Cl^- Na^+ Cl^- Na^+ Cl^-

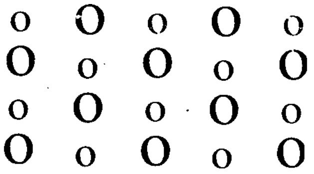


Fig. 8.11 : *a) A two dimensional arrangement of ions in sodium chloride*

(b) the lattice corresponding to the arrangement of ions in (a)

Similarly, in three dimensions, the crystal structure of a solid is represented as a three dimensional array of lattice points. Remember that the lattice points represent the positions of the constituent particles of the solid (Fig. 8.12).

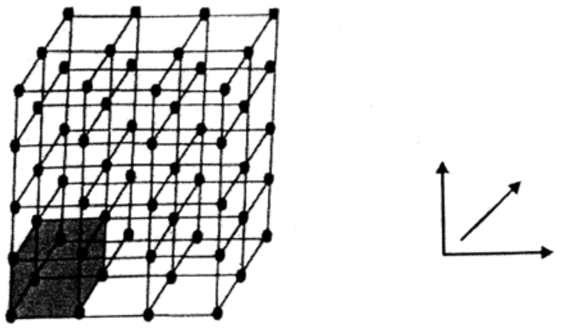


Fig. 8.12 : *Schematic representation of a three dimensional crystal lattice.*

In a crystal lattice we can select a group of points which can be use to generate the whole lattice. Such a group is called **repeat unit** or the **unit cell** of the crystal lattice. The shadded region in the Fig. 8.12 represent a unit cell of the crystal lattice. The unit cell is characterized by three distances along the three edges of the lattice and the angles between them as shown in the figure. We can generate the whole crystal lattice by repeating the unit cell in the three directions.

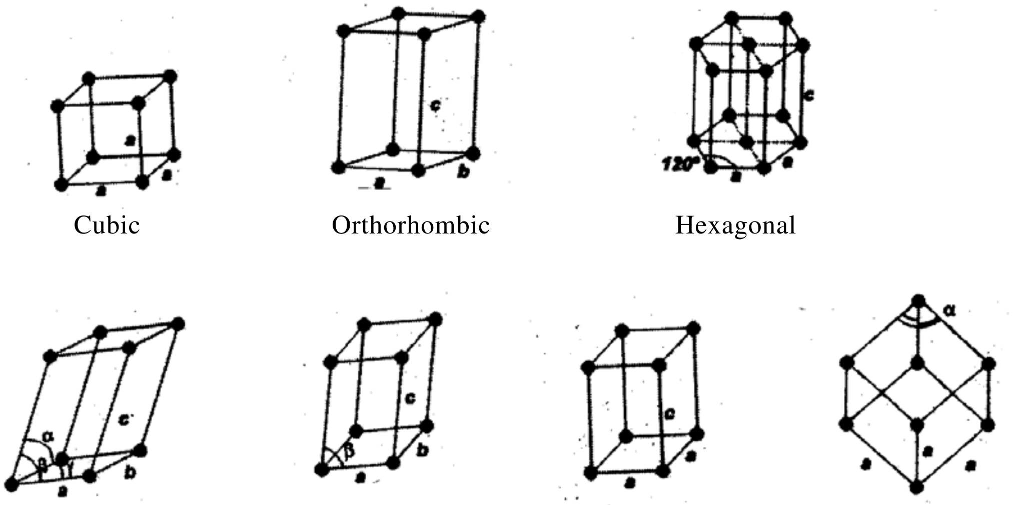
On the basis of the external appearance the known crystals can be classified into seven types. These are called **crystal systems**. In terms of the internal structure also the crystal lattices contain only seven types of unit cells. The seven crystal systems and the definition of their unit cells in terms of their unit distances and the angles are compiled in Table 8.2 The seven simple unit cells are given in Fig. 8.13

Table 8.2 : The seven crystal systems and their possible lattice types.

Systems	Axes	Angles	Possible lattice types
Cubic	$a = b = c$	$a = \beta = \gamma = 90^0$	P, F, I
Tetragonal	$a = b \neq c$	$a = \beta = \gamma = 90^0$	P, I
Orthorhombic	$a \neq b = c$	$a = \beta = \gamma = 90^0$	P, F, I, C
Rhombohedral	$a = b = c$	$a = \beta = \gamma \neq 90^0$	P
Hexagonal	$a = b \neq c$	$a = \beta = 90^0$; $\gamma = 120^0$	P
Monoclinic	$a \neq b = c$	$a = \gamma = 90^0$; $\beta \neq 90^0$	P, I
Triclinic	$a \neq b \neq c$	$a \neq \beta \neq \gamma \neq 90^0$	P

*** P = primitive, I = body centered, F = face centered and C = side centered**

The unit cell shown in Fig. 8.12 and the ones given in Fig. 8.13 have the lattice points at the corners only.



Cubic Orthorhombic Hexagonal

Triclinic Monoclinic Tetragonal Rhombohedral

Fig. 8.12.a : *The primitive unit cells; the relative dimensions of the three repeat distances (a, b and c) and the angles between them (a, β and γ) are given in Table 8.2*

Such unit cells are called primitive (P) unit cells. Sometimes, the unit cell of crystal contains lattice point(s) in addition to the ones at the corners. A unit cell containing a lattice point each at the centers of its faces in addition to the lattice points at the corners is called a **face centered** (F) unit cell. On the other hand a unit cell with lattice points at the center of the unit cell and at the corners is called a body centered unit cell (I). In some cases, in addition to the lattice points at the corners there are two lattice points located at the centers of any two opposite faces. These are called as **end centered** (C) unit cells. The possible lattice types in different crystal systems are also indicated in Table 8.2 The seven crystal systems when combined with these possibilities give rise to 14 lattice types. These are called **Bravais lattices**.

X-Ray diffraction of Crystals (X-rays and Crystal system)

The arrangement of particles in solid structures are determined by x-ray diffraction and to a lesser extent by electron diffraction. These processes are based on the fact that both x-rays and electrons have wave lengths which are of the same order as interatomic distances (10^{-10} m) and so crystals may be used as diffraction grating for them. The fundamentals of x-rays are discussed below.

X-ray diffraction :

Bragg Method : The Bragg's or reflection method gives results which are easier to interpret.

X-rays are produced when cathode rays fall on metlas. The effect of atomic sized particles on metal is similar to the effect in a pond, a series of ripples (or water waves) are produced when the handful of pebbles thrown into a pond. In a pond, a series of ripples (or water waves) are produced and the crests of some of them will meet and reinforce each other. While some crests will meet through and cancel each other and cause interference. In the same way, two x-ray waves that are in same phase reinforce each other and produce a wave that is stronger than either of the original waves. The resultant wave has a greater amplitude than either of the primary waves, but the wave length, λ, remains the same. Two x-rays waves that are completely out of phase cancel each other, the resultant has negligible intensity.

In crystals there are regular layers of atoms or ions and it is possible to calculate the conditions under which reinforcement will occur if a beam of x-ray strikes them. When x-rays are diffracted by the layers they behave as if they are being reflected.

Fig. 8.5a illustrates the determination of crystal spacing's by the use of x-rays of a single wave length. The rays inspinge upon parallel planes of the crystal at an agnle θ, an angle of reflection equals the angle of incidence. Some of the rays are reflected from the upper plane, some from the second plane, and some from the lower planes. A strong reflected beam will result only if the rays are in phase. In the illustration, the ray DFH travels further the ray ABC by an amount equal to EF + FG. These rays will be in phase at CH only if this difference equals a whole number of wave length. Thus EF + FG = nλ.

When 'n' is a single integer.

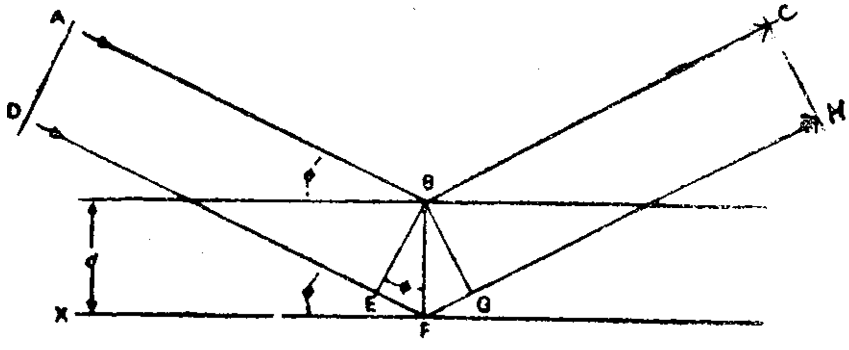


Fig. 8.13 : *Bragg's method*

The line BE is drawn perpendicular to DF. Angle BEF, therefore equals 90^0, since the sum of the angles of any triangle equals 180^0, the sum of other two angles (EBF and EFB) of the triangle BEF must also equal 90^0.

That is :

$\angle EBF + \angle EFB = 90^0$

Angle XFB is a right angle, and angle XFE is θ, therefore angle EFB is equal to 90^0, minus θ, consequently.

$\angle EBF + (90^0 - \theta) = 90^0$

and angle EBF equals θ.

The sine of this angle, θ, is equal EF/BF, and since BF is equal to d (the distance between the planes of the crystal).

$$\text{Sin } \theta = \frac{EF}{d}$$

or $EF = d \text{ Sin } \theta$

Likewise, $FG = d\text{Sin } \theta$

$EF + FG = 2d \text{ Sin } \theta$

or $n\lambda = 2d \text{ Sin } \theta$

This equation was derived by William Henry Bragg and his son William Lawrence Bragg.

The Bragg equation be rearranged as $\text{Sin } \theta = \frac{n\lambda}{2d}$

Thus with x-rays of a definite wave length, reflections of various angles will be observed for a given set of planes with a spacing equal to d. These reflections correspond to n = 1,2,3 and so as, and are spoken of as first, second, third order and so on. With each successive order, the angle increases, and the intensity of reflected beam weakens.

Sample Problem :

The diffraction of a crystal of barium with x-ray of wave length 2.29 A^0 gives first order reflection at $27^0 8^1$. What is the distance between the diffracted planes ?

Solution :

$n\lambda = 2d \text{ Sin } \theta$ Bragg's relation

$$d = \frac{n\lambda}{2d \text{ Sin } \theta}$$

$$= \frac{(1)\ (2.29 \text{ x } 10^{-8} \text{cm})}{2 \text{ x } 0.456} \quad (\text{Since sin } 27^0 8^1 = 0.456)$$

$$= 2.51 \text{ x } 10^{-8} \text{ cm}$$

$$= 2.51 \text{ A}^0$$

8.5.1 Cubic Unit Cells

Of the seven crystal systems, let us discuss unit cells belonging to the cubic crystal system in somewhat details. As you can see from Table 8.2 that in the cubic crystal system the three repeat distances are equal and all three angles are right angles. The unit cells of three possible lattice types viz., primitive or simple cubic, body centered cubic and the face centered cubic, belonging to cubic crystal system are shown in Figure 8.14.

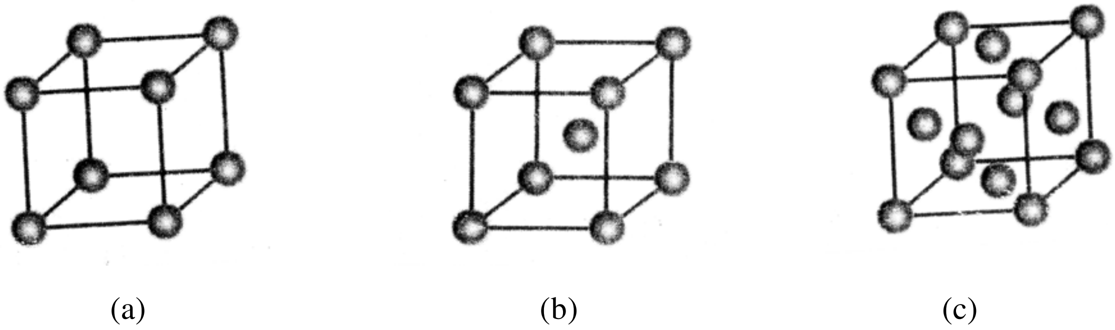

(a) (b) (c)

Fig. 8.14 : *Bragg's method*

Number of atoms per unit cell

As you know that in unit cells the atoms can be on the corners, in the body center and on face centers. All the atoms do not belong to a single unit cell. These are shared amongst diffrent unit cells. It is important to know the number of atoms per unit cell. Let us learn how to compute these for different cubic unit cells.

Simple Cubic Unit Cell

The simple or primitive unit cell has the atoms at the corners of the cube (Fig. 8.14 (a)). A lattice point at the corner of the unit cell is shared by eight unit cells as you can see from the encircled atom inthe Fig. 8.15. Therefore, the contribution of an atom at the corner to the unit cell will be 1/8. The number of atoms per unit cell can be calculated as follows :

Number of corner atoms = 8.

Number of unit cells sharing atoms of the corner = 8.

The number of atoms in a simple cubic unit cell = 8 x 1/8 = 1.

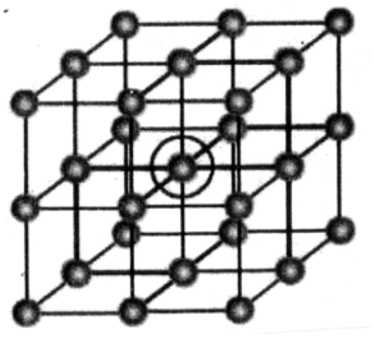


Fig. 8.15 : *A corner lattice point is shared by eight unit cells*

Body Centered Cubic Unit Cell

A body centered cubic (*bcc*) unit cell has lattice points not only at the corners but also at the center of the cube (Fig. 8.14 (b)). The atom in the center of the cube belongs entirely to the unit cell, i.e., it is not shared by other unit cells. The corner atoms, on the other hand, as in the case of simple cubic unit cell, are shared by eight unit cells. Thus the number of atoms per unit cell can be calculated as

Number of corner atoms = 8.

Number of unit cells sharing atoms of the corner = 8.

Contribution to the unit cell = 8 x 1/8 = 1

Number of atoms at the center of the cube = 1.

Contribution to the unit cell = 1 (as it is not shared)

The number of atoms in a body centered cubic unit cell = 1 + 1 = 2

Face Centered Cubic Unit Cell

A face centered cubic (*fcc*) unit cell has atoms not only at the corners but also at the center of each face. Thus it has eight lattice points at the corners and six at the face centers (Fig. 8.14 (c)). A face centered lattice point is shared by two unit cells, Fig. 8.16. As before,

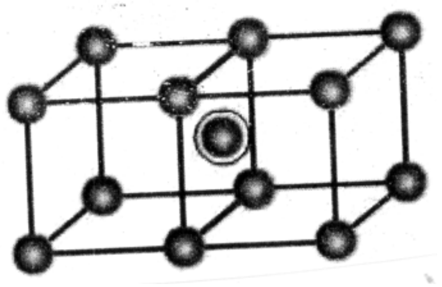


Fig. 8.16 : *A face centered lattice point is shared by two unit cells*

Number of corner atoms = 8.

Number of unit cells sharing these = 8.

Contribution to the unit cell = 8 x 1/8 = 1

Number of atoms at the center = 1.

Number of unit cells sharing a face centered lattice point = 2

Contribution of the face centered atoms to the unit cell = 6 x 1/2 = 3

The number of atoms points in a face centered cubic unit cell = 1 + 3 = 4.

The number of atoms per unit cell in different types of cubic unit cells is given in Table 8.3

Table 8.3 : Atoms per unit cell

Simple cubic	1
Body centered cubic	2
Face centered cubic	4

8.5.2 Structures of Ionic Solids

In case of ionic solids that consist of ions of different sizes, we need to specify the positions of both the cations as well as the anions in the crystal lattice. Therefore, structure adopted by an ionic solid depends on the relative sizes of the two ions. In fact it depends on the ratios of their ratios of their radii called **radius ratio**. Here r + is the radius of the cation and r - is that of the anion. The radius ratios and the corresponding structures are compiled in Table 8.4.

Table 8.4 : The radius ratios (r + / r-) and the corresponding structures

Radius ratio (r + /r-)	Coordination number	Structure adopted
0.225-0.414	4	Tetrahedral
0.414-0.732	6	Octahedral
0.732-0.91	8	Body centered cubic
> = 1.00	12	Close Packed structure

The common ionic compounds have the general formulae as MX, MX_2 and MX_3 where M represents the metal ion and X denotes the anion. We would discuss the structures of some ionic compounds of MX and MX_2 types.

8.5.2.1 Structures of the Ionic Compounds of MX Type

For the MX type of ionic compounds three types of structures are commonly observed. These are sodium chloride, zinc sulphide and caesium chloride structures. Let us discuss these in some details.

Caesium Chloride Structure

In CsC1 the cation and the anions are of comparable sizes (the radius ratio = 0.93) and has a bcc structure in which each ion is surrounded by 8 ions of opposite type. The Cs^+ ions is in the body center position and eight Cl-ions are located at the corners (fig. 8.17) of the cube. Thus it has a coordination number of 8.

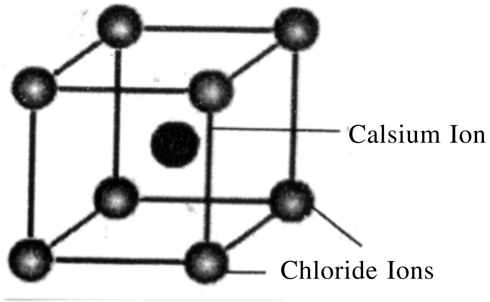


Fig. 8.17 : *Caesium chloride structure*

Sodium Chloride Sturcture

In case of NaCl the anion (Cl-) is much larger than the cation (Na^+). It has a radius ratio of 0.52. According to Table 3.3 it shoud have an octahedral arrangement. In sodium chloride the (Cl-) form a *ccp* (or *fcc*) structure and the sodium ion occupy the octahedral voids. You may visualise the structure having chloride ions at the corners and the face centers and the sodium ions at the edge centers and in the middle of the cube (Fig. 8.18).

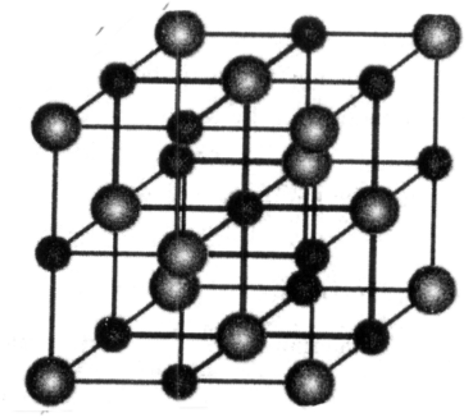


Fig. 8.18 : *Sodium Chloride structure*

Zinc Sulphide Structure

In case of zinc sulphide the radius ratio is just = 0.40. According to Table 3.3 it should have an tetrahedral arrangement. In Zinc sulphide structure, the sulphide ions are arranged in a ccp structure. The zinc ions are located at the corners of a tetrahedron, which lies inside the cube as shown in the Fi.g 8.19. These occupy alternate tetrahedral voids.

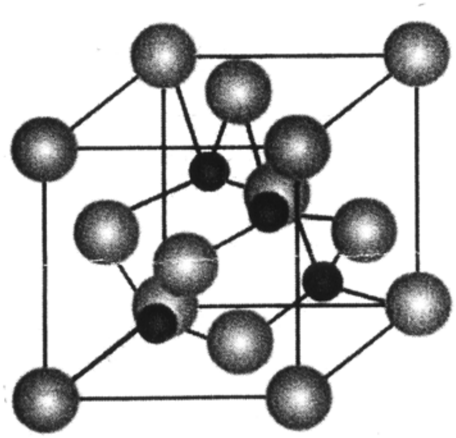


Fig. 8.19 : *Zinc Sulphide structure*

Calcium flouoride or fluorite structure

In this structure the Ca^{2+} ions form a fcc arrangement and the fluoride ions are located in the tetrahedral voids (Fig. 8.20).

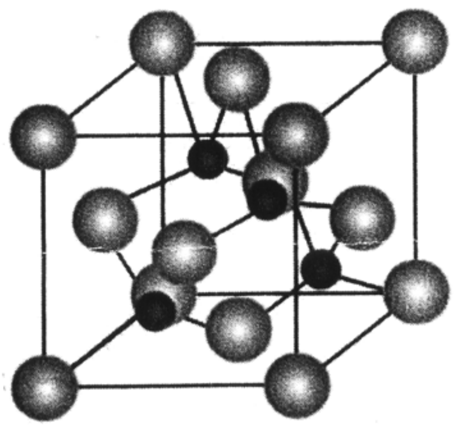


Fig. 8.20 : *Calcium fluoride or Fluorite structure; calcium ions occupy the corners of the cube and face centers the F^- ions are on the corners of the smaller cube.*

Antifluorite Sturcture

Some of the ionic compounds like Na_2O have antiflourite structure. In this structure the poisitions of cations and the anions in fluorite structures are interchanged. That is why it is called anti fluorite structure. In Na_2O the oxide ions form the ccp and the sodium ions occupy the tetrahedral voids (Fig. 8.21).

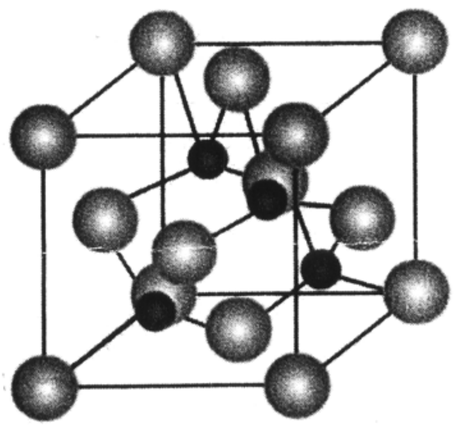


Fig. 8.21 : *Antifluorite structure adopted by Na_2O; The oxide ions occupy the corners of the cube and face centers and the Na^+ ions (shown in black) are on the corners of the smaller cube.*

8.6 Defects in Ionic Crystals

you have leartn that in a crystalline solid the constituent particles are arranged in a ordered three dimensional network. However, in actual crystals such a perfect order is not there. Every crystal has some deviations from the perfect order. These deviations are called imperfections or defects. These defects can be broadly grouped into two types. These are

stoichiometric and **non-stoichiometric** defects depending on whether or not these disturb the stiochiometry of the crystalline material. Here, we would deal only with stoichiometric defects. In such compounds the number of positive and negative ions are in stoichiometry proportions. There are two kinds of stoichiometric defects, these are

- Schottky defects
- Frenkel defects

Schottky defects : this type of defect are due to the absence of some positive and negative ions from their positions. These unoccupied lattice sites are called holes. Such defects are found in ionic compounds in which the positive and negative ions are of similar size e.g., NaCl and CsCl. the number of missing positive and negative ions is equal. The presence of Schottky defects decreases the density of the crystal (Fig. 8.22(a)).

Frenkel defects : this type of defect arise when some ions move from their lattice positions and occupy interstitial sites. The interstitial sites refer to the positions in between the ions. When the ions leaves its lattice site a hole is created there. ZnS and AgBr are examples of ionic compounds showing Frenkel defects. In these ionic compounds the positive and negative ions are of quite different sizes. Generally the positive ions leave their lattice positions, as these are smaller and can accommodate themselves in the interstitial sites. The Frenkel defects do not change the density of the soilds (Fig. 8.22(b)).

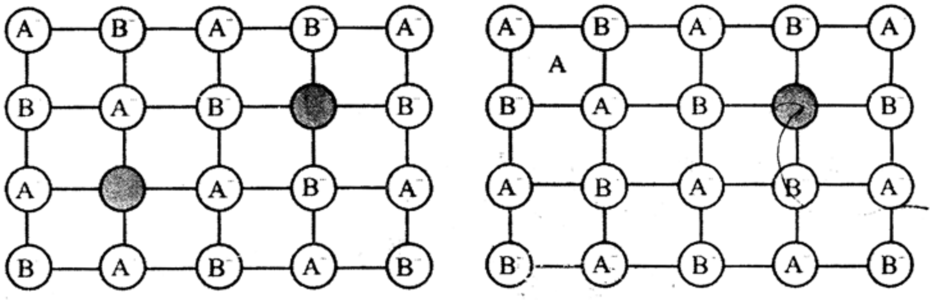


Fig. 8.22 : *Stoichiometric defects a) Schottky and b) Frenkel defects*

These defects cause the crystal to conduct electricity to some extent. The conduction is due to the movement of ions into the holes. When an ion moves into a hole it creates a new hole, which in turn is occupied by another ion, and the process continues.

Intext Questions 8.3

a) What do you understand by crystal lattice ?

....

b) What is a unit cell ?

....

c) How many atoms are there in a fcc unit cell ?

....

8.7 Treatment of metallic bond (elementary ideas)

The bonding in metals and their alloys is not completely understood. And therefore structures are also not fully, realized. Any theory that is proposed for the bonding in metals must be capable of explaning the following.

i) Bonding between atoms of the same element (identical atoms) and also between atoms of widely differing metlas as well as bonding in alloys.

ii) Should not involve directional bonding.

iii) The properties as metals in solutions and in liquid states etc.

iv) The mobility of electrons.

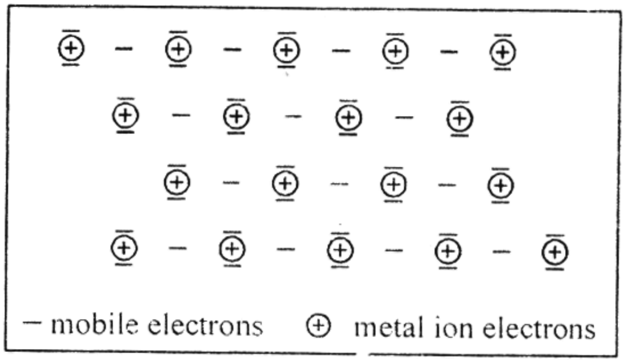
Various theories of bonding in metals have been suggested. The elementary ideas about these are given in the section that follows.

8.7.a Electron sea model :

This thoery was initially proposed by Drude in 1900. This was further refined by Lorentz in 1923. This theory is also known as. Drude - Lorentz theory.

According to this theory.

i) A metal lattice comprises of rigid spheres of metal ions.
ii) Each metal atom contributes its valence electrons to the sea.
iii) These electrons move freely in the lattice spaces i.e., interstices.
iv) Cohesive forces result from electrostatic attractions betwen the positive metal ions and the electron cloud.
v) "The force that binds a metal ion to the mobile electrons within its sphere of influence is known as metallic bond."



– mobile Electrons
⊕ metal ion Electrons

Fig. 8.23 : *Electron sea model of a metal*

Simply a metal was regarded as an asembly of positive ions immersed in a sea or pool of valence electrons. This theory explain qualitatively the model of a metal lattice but fails to explain quantitative calculations for lattice energies of ionic compounds.

8.7.b Valence bond theory of metals :

The theory was poposed by Linus Pauling 1937. This theory also referred as Resonance theory. According to this theory the metalic bond, is essentially a polar or a non-polar covalent bond. This is covalent bond involves resonance, between a number of structures, having one electron and electron pair bonds. As there is a possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal, it is assumed that resonance takes place throughout the solid metal. This resonance not only involves covalent bonds but also ionic linkages. The atoms undergo hybridization. For example, the resonance structure of sodium metal is represented taking four *Na* atoms only.

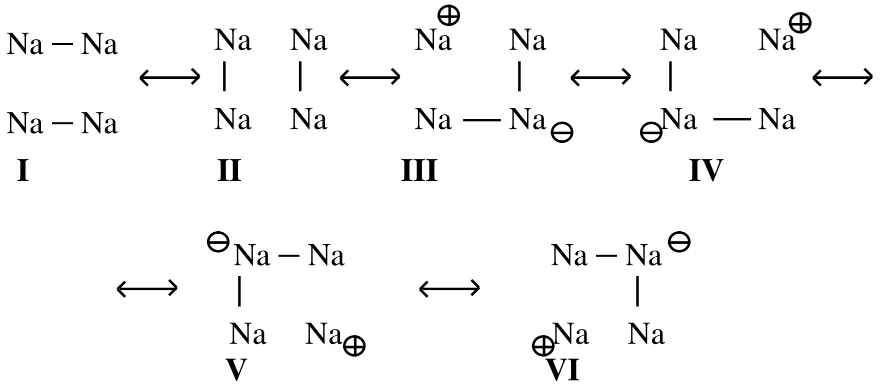


Fig. 8.7 b

This theory does not explain the conduction of the heat in solids or their luster or the reflection of the metallic, properties either in the liquid state or in the solution.

What You Have Learnt

- In solid state the constituent particles are arranged in a closely packed ordered arrangement with almost no free space. These are held together by strong forces of attraction and vibrate about their fixed positions. Solids are incompressible and rigid and have definite shapes.
- Solids are classified into amorphous and crystalline solids. The crystalline solids have long range order while amorphous solids have only short range order.
- The crystalline solids can be classified into four different types-ionic, molecular, covalent and metallic solids on the basis of nature of forces of attraction between the constituent particles.
- The temperature at which a solid melts to give a liquid is called its melting point.

- The crystal structure of the solids can be described in terms of a close-packing of identical spheres.
- In three dimensions there are two ways of packing identical spheres. These are hexagonal closed packing (hcp) and cubic closed packing (ccp). The hcp arrangement is obtained by ABAB repeat of the two dimensional layers whereas the ccp arrangement is obtained by ABCABC repreat.
- The three dimensional internal structure of a crystalline solid can be represented in terms of a crystal lattice in which the location of each constituent particle is indicated by a point.
- The whole crystal lattice can be generated by moving the unit cell in the three directions.
- On the basis of the external appearance the known crystals can be classified into seven types called crystal systems.
- The unit cells of cubic crystal system has three possible lattice types. These are simple cubic, body centered cubic and the face centered cubic.
- The atoms at the corner of a cubic unit cell is shared by eight unit cells while a face centered atom is shared by two unit cells. The atom at the body center, on the other hand is exclusive to the unit cell as it is not shared.
- The number of atoms per unit cell for the simple cubic, bcc and fcc unit cells are 1.2 and 4 respectively.
- The structure adopted by an ionic solid depends on the ratios of their radii (r+/r-) called radius ratio.
- The structures of some simple ionic solids can be described in terms of ccp of one type of ions and the other ions occupying the voids.
- Actual crystals have some kind of imperfections in their internal structure. These are called defects.
- There are two types of defects called stoichiometric and non-stoichiometric defects depending on whether or not these disturb the stoichiometry of the crystalline material.
- There are two kinds of stoichiometric defects, these are called Schottky defects and Frenkel defects.

Terminal Exercise

1. Outline the differences between a crystalline and an amorphous solid.
2. How can you classify solids on the basis of the nature of the forces between the constituent particles ?

3. What do you understand by the melting point of a solid ? What information does it provide about the nature of interaction between the constituent particles of the solids?

4. What do you understand by coordination number? What would be an ion occupying a/n octahedral void...?

5. Explain the following with the help of suitable examples.

   a) Schottky defect

   b) Frankel defect

Answers to Intext Questions

8.1

1. Solids have definite shape and definite volume.

   Liquids have indefinite shape but define volume.

   gases have indefinite shape and indefinite volume.

2. Coulombic forces, dipole-dipole attractions, covalent bonding and metallic bonding.

3. Irrespective of the size and shape of the crystal of a substance, the interfacial angle between a pair of faces is always the same.

8.2

1. Refer to section 8.4

2. Hexagonal close packed

3. Refer to sections 8.4

8.3

1. Ordered three dimensional arrangement of points representing the location of constituent particles.

2. A select group of points which can be used generate the whole lattice. Unit cell is characterised by three edges of the lattice and angles between them.

3. Four.

SENIOR SECONDARY COURSE
CHEMISTRY
Student's Assignment - 2

Maximum Marks : 50 Time : 1 1/2 Hrs.

INSTRUCTIONS :

- Answer all the questions on a separate sheet of paper.
- Give the following information on your answer sheet.
    - Name
    - Enrolment Number
    - Subject
    - Assignment Number
    - Address
- Get your assignment checked by the subject teacher at your study centre so that you get positive feedback about your performance.

Do not send your assignment to APOSS

1. a) Define Lattice energy.
   b) What an electrovalent bond.
   c) State charles' law and given mathematical expression for it.
   d) Why do molecular crystals have low melting point?
   e) Why do you feel cool after a both?
   f) State valence shell electron pair repulsion theory.
   g) State down van der Waal's equation.
   h) What is Kelvin scale of temperature?
   i) State Avogadro law.
   j) Liquids have a definite volume. Explain

2. a) Name the parameters of a chemical bond and define any one of them.
   b) List four characteristics of a covalent compound.
   c) Differenciate π- bond from σ - bond
   d) Define critical temperature and critical pressure of a gas
   e) List the four types of crystalling solids and give one example of each.
   f) Vapour pressure of a liquid at 25^0C is 35 mm Hg and its normal boiling points is 110^0C. What will be its vapour pressure at 110^0C?

g) Which assumptions of kinetic theory of gases are wrong?

h) Write two differences between amorphous and crystalline solids.

i) How will you calculate the enthalpy of formations of NaCl using Born-Haber Cycle.

j) At a certain altitude in the atmosphere, density is 10^{-9}th the density of earth's atmosphere at STP and the temperature is -100^0C. Assuming a uniform atmospheric composition, find the pressure at that attitude.

(2x10=20)

3. a) Assign the geometry to the following molecule using the VSEPR theory. State reasons for your decisions.

(i) Phosphorus (V) Chloride (PCl_5)

(ii) Sulphur (VI) Flouride (SF_6)

(iii) Boron (III) Flouride (BF_3)

b) Explain that HNH bond angle in ammonia is 107^0 while HOH bond angle in water is 104.5^0

c) The carbon-oxygen bond length in CO is shorter than in CO_2 molecule

d) Draw a diagram to show the arrangement of particles in gases, liquids and solids.

(3x4=12)

4. a) Calculate the volume of one mole of oxygen at 27^0C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.

b) An element has a *bcc* structure and a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?

(4x2=8)

9

SOLUTIONS

You know that when sugar or salt is added to water, if dissolves. The resulting mixture is called a solution. Solutions play an important role in our life. In industry, solutions of various substances are used to carry out a large number of chemical reactions.

Study of solutions of various substances is very interesting.

In this lesson, let us learn about the various components of a solution and the ways in which concentration of solutions is expressed. We shall also learn about some properties of solutions which are dependent only on the number of solute particles. (you will learn about solute in this lesson).

Objectives

After reading this lesson, you will be able to:

- identify the components of different types of solution;
- express the concentration of solutions in different ways;
- list different types of solutions;
- state Henry's law;
- define vapour pressure;
- state and explain Raoult's law for solutions;
- define ideal solutions;
- give reasons for non-ideal behavior of solutions;
- state reasons of positive and negative deviations from ideal behavior;
- explain the significance of colligative properties;
- state reasons for the elevation of boiling point and depression in freezing point of solutions;

- explain the abnormal colligative properties;
- define osmosis and osmotic pressure;
- define Van't Hoff factor;
- correlate the degree of dissociation of solute and
- solve numerical problems.

9.1 Components of a Solution

When we put sugar into water, it dissolves to form a solution. We do not see any more sugar in it. Like sugar, a large number of other substances such as common salt, urea, potassium chloride etc dissolve in water forming solution. In all such solutions, water is the solvent and substances which dissolve are the solutes.

Thus, solute and solvent are the components of a solution. Whenever a solute mixes homogeneously with a solvent, a solution is formed.

$$\text{solution} \quad + \quad \text{solvent} \quad \longrightarrow \quad \text{solution}$$

A solution is a homogeneous mixture of two more substances.

Solvent is that component of a solution that has the same physical state as the solution itself.

Solute is substance that is dissolved in a solvent to form a solution.

9.1.1 The Concentration of a Solution

Some of the properties of solutions, e.g... The sweetness of a sugar solution or the colour of a dye solution, depend on the amount of solute compared to that of the solvent in it. This is called the solution concentration. There are several ways for describing concentration of solution. They include molarity, molality, normality mole fraction and mass percentage.

Molarity: Molarity is defined as the number of moles of solute dissolved per litre of solution and is usually denoted by M. It is expressed as:

$$M = \frac{n}{v}$$

Where n is the number of moles of solute and V is the volume of the solution in litres. A 2.0 molar solution of sulphuric acid would be labeled as 2.0 M H_2SO_4. It is prepared by adding 2.0 mol of H_2SO_4 to water to make a litre of solution. Molarity of a solution changes with temperature because of expansion or contraction of the solution.

Molality: It is defined as the number of moles of solute dissolved per kilogram of solvent.

It is designated by the symbol m. The label 2.0m H_2SO_4 is read "2 mole l sulphuric acid" and is prepared by adding 2.0 mol of H_2SO_4 to 1 kg of solvent Molality is expressed as:

$$m = \frac{1000n_B}{W_A}$$

where n_B is the number of moles of the solute and W_A is the mass in grams of solvent. The molality of a solution does not change with temperature.

Example 9.1 : Find out the molarity of the solution whcih contains 32.0 g of methyl alcohol (CH_3OH) in 200 mL solution.

Solution : Molar mass of CH_3OH = 12 + 1 x 3 + 16 + 1 = 32 g mol^{-1}

Number of moles of $CH_3OH = \frac{32}{32 \text{ g mol}^{-1}} = 1$ mol

Volume of the solution = 200 mL = 0.2 litre

$$\therefore \text{Molarity} = \frac{\textit{No. of moles of solute}}{\textit{Volume of solution in litres}} = \frac{1}{0.2} = 5 \text{ M}$$

Example 9.2 : What is the molality of a sulphiric acid solution of density 1.20 g/cm^3 containing 50% sulphuric acid by mass.

Solution : Mass of 1cm^3 of H_2SO_4 solution = 1.20 g

Mass of 1 litre (1000 cm^3) of H_2SO_4 solution = 1.20 x 1000 = 1200 g

Mass of H_2SO_4 in 100 g solution of H_2SO_4 = 50 g

Mass of H_2SO_4 in 1200 g solution $H_2SO_4 = \frac{50}{100}$ x 1200 = 600 g

$\therefore$ Mass of water in the solution = 1200 - 600 = 600 g

Molar mass of H_2SO_4 = 98 g mol^{-1}

$$\text{No. of moles of } H_2SO_4 = \frac{\textit{Mass in grams}}{\textit{Molar mass}} = \frac{600 \text{ g}}{98 \text{ g mol}^{-1}}$$

$$\text{Molarity} = \frac{\textit{No. of moles of } H_2SO_4}{\textit{Mass of water in grams}} \times 1000$$

$$= \frac{600}{98} \times \frac{1}{600} \times 1000 = 6.8 \text{ m}$$

Normality: Normality is another concentration unit. It is defined as the number of gram equivalent weights of solute dissolved per litre of the solution.

The number of parts by weight of a substance (element of compound) that will combine with or displace, directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by

weight of oxygen and 35.5 parts by weight of chlorine is known as equivalent weight. Like atomic weight and molecular weight, equivalent weight is also a number and hence no units are used to express it. However, when equivalent weight is expressed in grams, it is known as gram equivalent weight of the substance.

Equivalent weight = $\frac{\text{Atomic or molecular weight}}{\text{Valency}}$

Equivalent weight of an acid = $\frac{\text{Molecular weight}}{\text{Basicity}}$

Equivalent weight of a base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Equivalent weight of salt = $\frac{\text{Molecular weight}}{\text{Total valency of the metal atom}}$

oxidising and reducing agents may have different equivalent weights if they react to give different products under different conditions. Thus, the equivalent weight of such substances can be calculated from the reactions in which they take part.

Normality is denoted by the symbol N.

$$\therefore \quad \text{Normality (N)} = \frac{\text{No. of gram equivalent weight of the solute}}{\text{volume of the solution in litres}}$$

$$= \frac{\text{Mass of the solute in grams}}{\text{Equivalent weight of the solute}} \times \frac{1}{\text{volume of the solution in litres}}$$

$$= \frac{\textit{Strength of solution in grams / litre}}{\textit{Equivalent weight of the solute}}$$

The lable 0.5 N $KMnO_4$ is read "0.5 normal" and represents a solution which contains 0.5 gram equivalent of $KMnO_4$ per litre of solution.

Mole Fraction : The mole fraction of a component in a solution is the ratio of its number of moles to the total number of moles of all the components in the solution. If a solution contains 2 mol of alcohol and 3 mol of water, the mole fraction of alcohol is $\frac{2}{5}$, an that of water $\frac{3}{5}$. The sum of mole fractions of all the components of a solution is equal to one. The mole fraction (X_A) of a component A in solution with B is :

$$\frac{n_A}{n_A + n_B}$$

Where n_A and n_B are the number of the moles of A and B respectively.

Mass Percentage : Mass percentage is the mass of solute present in 100 g of solution. Thus 5% solution of $KMnO_4$ in water means that 5 g of $KMnO_4$ is present in 100g of the aqueous solution of $KMnO_4$.

Example 9.3 : A solution contains 36.0 g water and 46.0 g ethyl alcohol (C_2H_5OH). Determine the mole fraction of each component in the solution.

Solution : Molar mass of water = 18 g mol^{-1}

$$\text{Number of moles of water} = \frac{36 \text{ g}}{18 \text{ g mol}^{-1}} = 2.0 \text{ mol}$$

$$\text{No. of moles of } C_2H_5OH = \frac{46 \text{ g}}{46 \text{ g mol}^{-1}} = 1.0 \text{ mol}$$

Total number of moles in the solution = 2.0 + 1.0 = 30

$$\text{Mole fraction of water} = \frac{\text{No. of moles of water}}{\text{Total no. of moles in the solution}} = \frac{2.0}{3.0} = 0.67$$

$$\text{Mole fraction of } C_2H_5OH = \frac{\text{No. of moles of } C_2H_5OH}{\text{Total no. of moles in the solution}} = \frac{1.0}{3.0} = 0.33$$

Example 9.4 : Calculate the normality of a solution of NaOH if 0.4 g of NaOH is dissolved in 100 ml of the solution.

Solution : Mass of NaOH present in 100 mL of the solution = 0.4 g

$$\therefore \text{Mass of NaOH present in 1000 mL of the solution} = \frac{0.4}{100} \text{ x } 1000 = 4.0\text{g}$$

Mol. wat. of NaOH = 23 + 16 + 1 = 40amu

$$\text{Eq. wt. of NaOH} = \frac{\text{Mol. Wt.}}{\text{Acidity}} = \frac{40}{1} = 40$$

$$\therefore \text{Normality} = \frac{\text{Strength in g/litre}}{\text{Eq. wt.}} = \frac{4}{100} = \frac{1}{10} \text{ N}$$

$$\text{Hence, the normality of the solution} = \frac{1}{10} \text{ N or } 0.1 \text{ N}$$

Intext Questions 9.1

1. List the various methods of expressing the concentration of a solution?

   ....

2. Define the following?

   i) Molarity ii) Molality ii) Normality

   ....

9.2 Types of Solution

Solutions can be solid, liquid or gaseous. Depending upon the physical state of the solute and the solvent, there are nine possible types of solutions consisting of two components (binary solutions). Different types of solutions are given in Table 9.1.

Table 9.1 Different types of Solutions

Solute	Solvent	Solution
Gas	Gas	Air
Gas	Liquid	Soda Water
Gas	Solid	Hydrogen in palladium
Liquid	Gas	Humidity in air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in gold
Solid	Gas	Camphor in air
Solid	Liquid	Sugar in water
Solid	Solid	Alloys such as brass (zinc in copper and bronze (tin in copper)

Generally, we come across only the following three types of solutions:

(a) Liquids in Liquids : In the solution of liquids in liquids such as alcohol in water, the constituent present in smaller amounts is designated as solute and the constituent present in larger amounts is called the solvent. When two liquids are mixed, three different situations may arise:

(i) Both the liquids are completely miscible, i.e., when, two liquids are mixed, they dissolve in each other in all proportions, e.g., alcohol and water, benzene and toluene.

(ii) The liquids are partially miscible, i.e., they dissolve in each other only to a certain extent, e.g., water and phenol.

(iii) The liquids are immiscible, i.e., they do not dissolve in each other, e.g., water and benzene, water and toluene.

The solubility of liquids in liquids generally increases with rise in temperature.

(b) Gases in Liquids : Gases are generally soluble in liquids. Oxygen is sufficiently soluble in water, which allows the survival of aquatic life in ponds, rivers and oceans. Gases like CO_2 and NH_3 are highly soluble in water. The solubility of a gas in a liquid depends on the pressure, temperature and the nature of the gas and the solvent. These factors are discussed below in detail:

(i) **Effect of Pressure :** The variation of solubility of a gas in a liquid with pressure is governed by *Henry's* law. *Henry's* law states that

The mass or mole fraction, of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.

Henry's law is represented by

$x = Kp$

where K is a constant, p is the partial pressure of the gas and x is the mole fraction of the gas in the solution. Let us now see what are the conditions for the validity of Henry's law.

(i) **Conditions for validity of Henry's law :** It is found that gases obey Henry's law under the following conditions.

i) the pressure is not too high.

ii) the temperature is not too low.

iii) the gas does not dissociate, associate or enter into any chemical reaction with the solvent.

(ii) **Effect of temperature :** The solubility of gas in a liquid at constant pressure decreases with rise in temperature. For example, the solubility of CO_2 in **water** at 20^0C is 0.88 cm^3 per cm^3 of water, where as it is 0.53 cm^3 per cm^3 of water at 40^0C. This happens because on heating a solution, containing a dissolved gas, some gas is usually expelled from the solution.

(iii) **Effect of the nature of the gas and the solvent :** Gases like CO_2, HCl and, NH_3 are highly soluble in water where as H_2, O_2 and N_2, are sparingly soluble.

(c) Solids in liquids : When a solid is dissolved in a liquid, the solid is referred as the solute and the liquid as the solvent. For example, in a solution of sodium chloride in water, the solute is sodium chloride and water is the solvent. Different substances dissolve to different extent in the same solvent.

9.3 Vapour Pressure

If we keep an inverted beaker over a small beaker containing a pure liquid, it is found that the molecules of the liquid start evaporating in the form of vapours and fill the empty space above the beaker containing the liquid. A time comes when the number of molecules evaporating per unit time is equal to the number of molecules condensing during that time (Fig 9.1). An equilibirum is thus established between the vapour and the liquid phase. The pressure exerted by the vapour of the liquid in such a case is called the vapour pressure of the liquid.

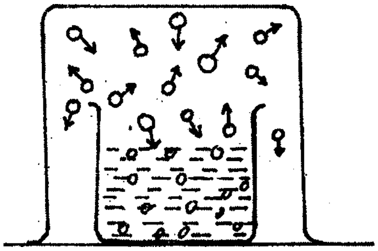


Fig. 9.1 : *Vapour pressure of a liquid*

9.4 Raoult's Law for Solutions

Did you ever think that if you mix two miscible volatile liquids A and B, what would be the vapour pressure of the resulting solution ? The relationship between vapour pressure of liquid and its mole fraction is given by Raoult's law.

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each liquid in the solution is directly proportional to its mole fraction.

Raoult's law is applicable only if the liquids are miscible. The vapour phase now consists of vapour of both the liquids A and B. The partial vapour pressure of each liquid will depend upon its mole fraction in the solution. Let the mole fractions of the liquids A and B be X_A and X_B respectively. Aslo, if P_A and P_B are the partial vapour pressures of A and B respectively, then

$$P_A \propto X_A \text{ or } P_A = P^o_A X_A$$

Similar ly, $$P_B = P^o_B X_B$$

where P^o_A and P^o_B represent the vapour pressures of pure liquids A and B respectively.

If the values of P_A and P_B are plotted against the values of X_A and X_B for a solution, two straight lines are obtained as shown in Fig. 9.2 the total vapour pressure P of the solution is given by the sum of partial vapour pressures P_A and P_B.

Thus,

$$P = P_A + P_B$$

or

$$P = P^O_A X_A + P^O_B X_B$$

The total vapour pressure (P) of a solution is represented by the line joining P^O_A and P^O_B. The solutions which obey Raoult's law are known as **ideal solutions**.

A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.

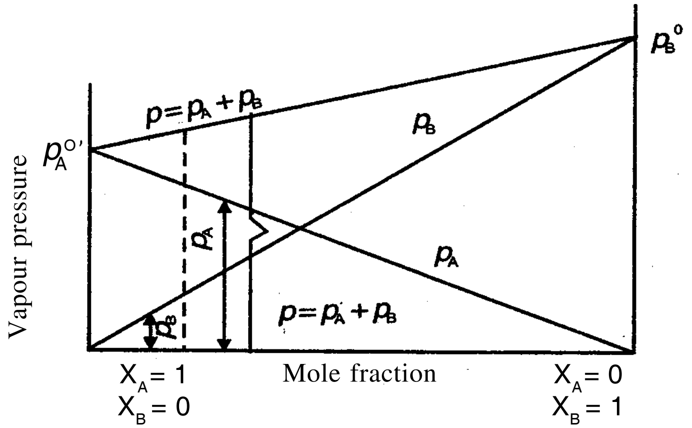


Fig. 9.2 : *Relationship between vapour pressure and mole fraction in a solution*

Intext Questions 9.2

1. State Raoult's law.

   ....

2. State Henry's law and list the conditions necessary for the validity of Henry's law.

   ....

9.5 Raoult's Law for Solution Containing Non-Volatile Solute

If we have an aqueous solution containing a non-volatile solute, such as sugar or salt, what do you think about the vapour pressure exerted by such a solution? The vapour phase of such a solution consists of vapours of solvent (A) only because the solute is non-volatile. Since the mole fraction of the solvent in solution is less than one, therefore according to Raoult's law, the vapour pressure of the solution will be less than the vapour pressure of the pure solvent. If the total vapour pressure of the solution is p, then

$$P_A = P_A^O X_A \quad \text{......... (9.1)}$$

for a binary mixture

therefore, $X_A + X_B = 1$

$$X_A = 1 - X_B$$

Substituting the value of X_A in equation (9.1) we get

$$P_A = P_A^O (1 - X_B)$$

$$\frac{P_A}{P^O_A} = 1 - X_B$$

therefore, $$\frac{P^O_A - P_A}{P^O_A} = X_B$$

In the above equation, $(P_A^O - P_A)$ reperesents the lowering of the vapour pressure and $\frac{P^O_A - P_A}{P^O_A}$ is called the relative lowering of the vapour pressure of the solution.

An alternative statement of Raoult's law for solutions of non-volatile solute is :

The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.

9.6 Ideal and Non-Ideal Solutions

Ideal solutions obey Raoult's Law and during their formation there is no change in heat and volume.

Non-ideal solutions are those solutions which do not obey Raoult's law and whose formation is accompanied by changes of heat and volume.

Most of the real solutions are non-ideal. They show considerable deviation from the ideal behaviour. Generally deviations are of two types :

i) Positive deviation : Positive deviations are shown by liquid pairs for which the A-B molecular interactions are weaker than the A-A and or B-B molecular interactions. The total vapour pressure for such solutions is greater than predicted by Raoults law. The total vapour pressure for such a solution will be maximum for a particular intermediate composition (Fig. 9.3).

Examples of non-ideal solutions showing positive deviation from the ideal behaviour are mixtures of liquids such as water-propanol, ethanol-chloroform, acetone-carbon disulfide, ethanol-cyclohexane etc.

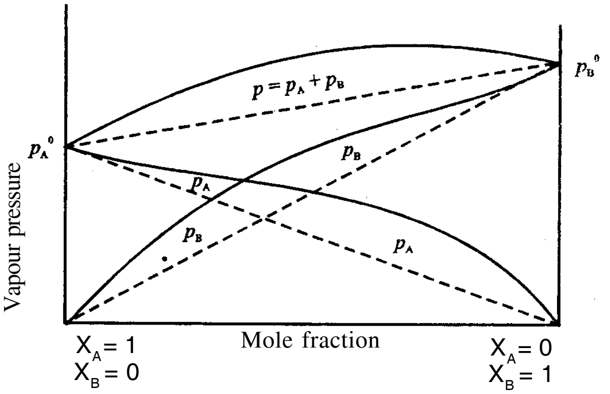


Fig. 9.3 : *Positive deviation for a liquid pair*

ii) Negative Deviation : Negative deviations are shown by liquid pairs for which the A-B molecular interactions - are stronger than A-A or B-B molecular interactions. The total vapour pressure for such solutions is less than that predicted by Raoult's law. For a particular intermediate composition, the total vapour pressure of such a solution will be minimum (Fig. 9.4). Examples of such liquid pairs are chloroform acetone, water-sulphuric acid, phenol-aniline, water-HCI etc.

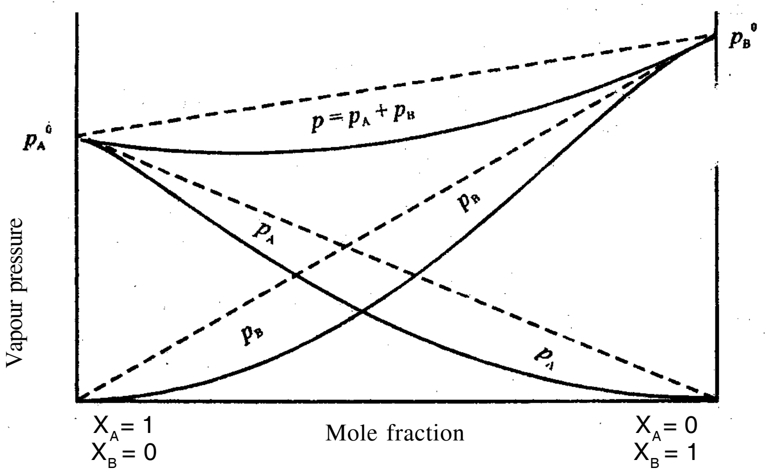


Fig. 9.4 : *Negative deviation for a liquid pair*

9.7 Colligative Properties

Do you know that there are certain properties of dilute solutions which depend only on the number of particles of solute and not on the nature of the solvent and the solute? Such properties are called **colligative properties**. There are four colligative properties : relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure.

Weh shall discuss these colligative properties in detail in the following sections.

9.7.1 Relative Lowering of Vapour Pressue

According to Raoult's law for solutions containing non-volatile solute

$$\frac{P^O_A - P_A}{P^O_A} = X_B \text{ (see section 9.5)} \quad \text{.........................(i)}$$

Also $$X_B = \frac{n_B}{n_A + n_B}$$

In a dilute solution $n_B << n_A$ Therefore the term n_B can be neglected in the denominator.

Hence, $$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B.M_A}{W_A.W_B}$$

Therefore equation (i) can be written as

$$\frac{P^0_A - P_A}{P^0_A} = X_B = \frac{W_B \cdot M_A}{W_A \cdot M_B}$$

The above expression can be used to determine the molecular mass of the solute B, provided the relative lowering of vapour pressure of a solution of known concentration and molecular mass of the solvent are known. However, the determination of molecular mass by this method is often difficult because the accurate determination of lowering of vapour pressure is difficult.

Example 9.5 : The relative lowering of vapour pressure produced by dissolving 7.2 g of a substance in 100g water is 0.00715. What is the molecular mass of the substance ?

Solution : We know that

$$\frac{P^O_A - P_A}{P^O_A} = \frac{W_B}{M_B} \text{ x } \frac{M_A}{W_A}$$

Substituting the values we get

$$0.00715 = \frac{7.2 \text{ x } 18}{M_B \text{ x } 100} \quad \text{or } M_B = \frac{7.2 \text{ x } 18}{0.00715 \text{ x } 100}$$

$\therefore$ Molecular mass of the substance = 181.26 amu

9.7.2 Elevation of Boiling Point

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

As you know, the vapour pressure of a pure solvent is always higher than that of its solution. So, the boiling point of the solution is always higher than that of the pure solvent. If you see the vapour pressure curves for the solvent and the solution (Fig. 9.5), you will find that there is an elevation in the boiling point of the solution.

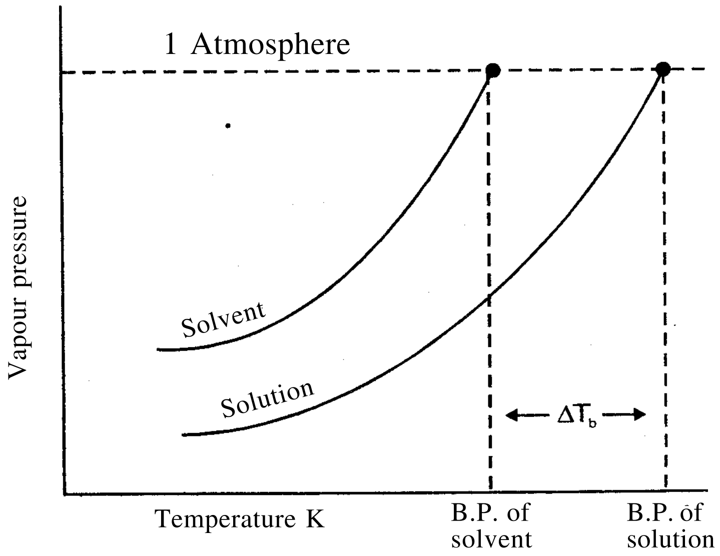


Fig. 9.5 : *Vapour pressure curves for solvent and solution*

Now let ΔT_b be the elevation in boiling point and Δp be the lowering in vapour pressure.

Then,

$\Delta T_b \ \alpha \ \Delta p \ \alpha \ X_B$ or $\Delta T_b = K \ X_B$

K is the proportionality constant

As you know $X_B = \dfrac{n_B}{n_A + n_B}$

In a dilute solution, $n_B << n_A$ and thus the term n_B is neglected in the denominator.

$$\text{Thus, } X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B}{M_3} \text{x} \frac{M_A}{W_A} = n_B \ \text{x} \ \frac{M_A}{W_A}$$

Substituting the value of X_B in the equation (i) we get

$$\Delta T_b = K \ \text{x} \ n_B \ \text{x} \ \frac{M_A}{W_A}$$

If we take the mass of the solvent W_A in kilograms the term $\dfrac{n_B}{W_A}$ is molality *m*. Thus

$$\Delta T_b = K \, M_A \, . \, m = K_B \, m$$

The constant K_b is called the **molal elevation constant** for the solvent. K_b may be defined as

the elevation in boiling point when one mole of a solute is dissolved in one kilogram of the solvent. K_b is expressed in degree per molality.

9.7.3 Depression in Freezing Point

Freezing point is the temperature at which the solid and the liquid forms have the same vapour pressure

The freezing point of the solution is always less than that of the pure solvent. Thus, there is a depression in the freezing point of the solution. This is because the vapour pressure of the solution is always less than that of the pure solvent.

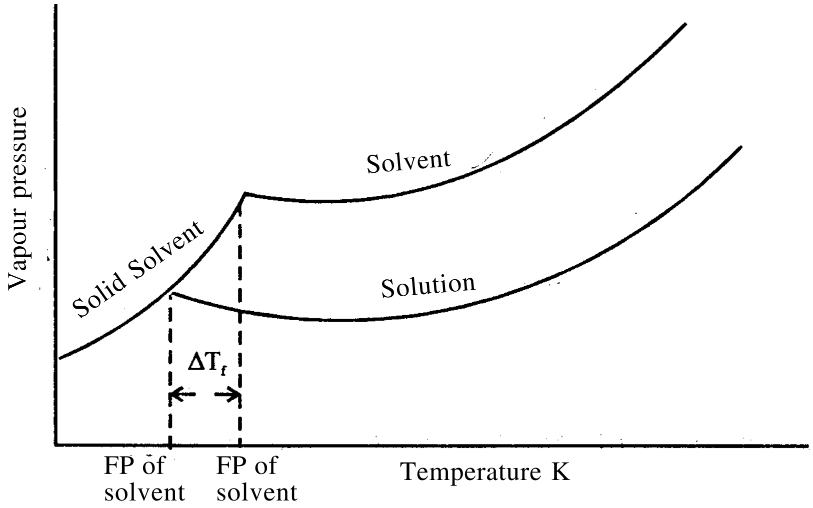


Fig. 9.6 : *Vapour pressure curves for solid, solvent and solution*

Let ΔT_f be the depression in freezing point. Then :

$$\Delta T_f \ \alpha \ \Delta X_B$$

or
$$\Delta T_f = KX_B \quad \text{..(ii)}$$

Where K the proportionality constant

You know that $X_B = \frac{n_B}{n_A + n_B}$

In dilute solution $n_B << n_A$

Therefore, the term n_B can be neglected from the denominator. Thus,

$$X_B = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{M_B} \text{x} \frac{M_A}{W_A} = n_B \text{ x } \frac{M_A}{W_A}$$

$$\left(\text{since } n_B = \frac{W_B}{M_B} \right)$$

Substituting the valoue of X_B in equation (ii) we get

$$\Delta T_f \;\; K \text{ x } n_B \text{ x } \frac{M}{W_A}$$

If the mass of the solvent W_A is taken in kg, then the term $\frac{n_B}{W_A}$ becomes molality *m*.

Thus, $\Delta T_f = K\,M_A.\, m = K_f .\, m$

The constant (K_f) for a solution is known as **molal depression constant or molal cryoscopic constant** for the solvent. K_f may be **defined as the depression in freezing point of a solution when one mole of a solute is dissolved in 1 kilogram of the solvent.**

Example 9.6 : Find the (i) boiling point and (ii) freezing point of a solution containing 0.520 g glocse ($C_6H_{12}O_6$) dissolved in 80.2g of water. (K_f = 1.86 K/m, K_b = 0.52 k/m).

Solution : Molality of glocose $= \frac{\text{Wt. of glucose}}{\text{mol. wt.}} \text{ x } \frac{1000}{\text{Wt. of solvent}}$

$$= \frac{0.52}{180} = \frac{1000}{80.2} = 0.036$$

$\Delta T_b = K_b m = 0.52 \text{ x } 0.036 = 0.018 \text{ K}$

$\therefore$ Boiling point = 373 + 0.018 = 373.018 = 373.02 K

(ii) K_f = 1.86 K/m

$$m = \frac{0.52}{180} = \frac{1000}{80.2} = 0.036$$

$\therefore$ ΔT_f = 1.86 x 0.036 = 0.66 K

$\therefore$ Freezing point = 273 - 0.66 = 272.34 K

9.7.4 Osmosis and Osmotic Pressure

You must have observed that if rasins are soaked in water for some time, they swell. This is due to the flow of water into the rasins through its skin which acts as a semipermeable membrane (permeable only to the solvent molecules). This phenomenon is also observed when two solutions of different concentrations in the same solvent are separated by a semipermeable membrane. In this case the solvent flows from a solution of lower concentration to a solution of higher concentration. The process continues till the concentrations of the solutions on both sides of the membrane become equal.

The spontaneous flow of the solvent from a solution of lower concentration (or pure solvent) to a solution of higher concentration when the two are separated by a semipermeable membrane is known as **osmosis.**

The flow of solvent into the solutionof higher concentration from a solution of lower concentration (on pure solvent) can be stopped if some extra pressure is applied to that side of the solution which has a higher concentration. The pressure that just stops the flow of the solvent is called **osmotic pressure**.

Thus, *ostmic pressure may be defined as the excess pressure that must be applied to the solution side to just prevent the passage of pure solvent into it when the two are separated by a perfect semipermeable membrane.* This is illustrated in Fig. 9.7

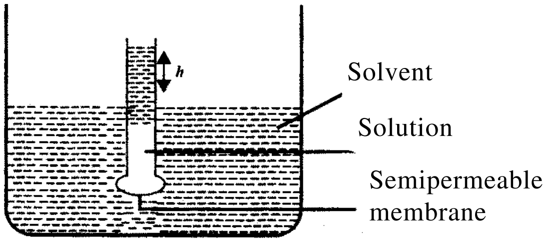


Fig. 9.7 : *Osmosis*

The pressure that must be applied to the solution side to prevent it from rising in the tube is the osmotic pressure. It is also equal to the hydrostatic pressure of the liquid column of heighth.

If the two solutions have the same osmotic pressure, they are known as **isotonic** solutions. The osmotic pressure is a colligative property. It depends on the number of particles of solute present in the solution and not on their nature. At a given temperature T, the osmotic pressure (π) of a dilute solution is experimentally found to be proportional to the concentration of the solution in moles per litre.

Mathematically, $\pi = CRT$

where π is the osmotic pressure and R is the gas constant

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

where n_B is the number of moles of solute present in V litres of the solution

or $$\pi V = \frac{w}{M_{solute}} RT$$

where w in the mass of solute dissolved in V litres of the solution and M_{solute} is the molar mass of the solute. Thus, knowing, π, v and w, the molar mass of the solute can be calculated.

Thus, the molar masses of the solutes can be determined by measuring the osmotic pressure of their solutions. This method has been widely used to determine the molar masses of macromolecules, protiens, etc., which have large molar masses and limited solubility. Therefore their solutions have very low concentrations and the magnitudes of their other colligative properties are too small to measure. Yet their osmotic pressures are large enough for measurements. As the osmotic pressure measurements are done at around room temperature, this method is particularly useful for determining the molar masses of biomolecules as they are generally not stable at higher temperature.

Example 9.7 : The osmotic presure of an aqueous solution of a protein containing 0.63 g of a protein in 100 g of water at 300 K was found to be 2.60 x 10^{-3} atm. Calculate the molar mass of the protein. R = 0.082 L atm K^{-1} mol^{-1}.

we know that osmotic pressure of a solution is given by the expression

$$\pi \; V = \frac{w}{M_{solute}} RT$$

or

$$M_{solute} = \frac{w}{\pi V} RT$$

Substituting the values, we get

$$\text{Msolute} = \frac{(0.63\,g) \times (0.082\,L - atm\,K^{-1}\,mol^{-1}) \times (300\,K)}{(2.60 \times 10^{-3}\ atm) \times (0.100\,L)}$$

$$= 61022 \text{ g mol}^{-1}$$

Thus, molar mass of the protein is 61022 g mol^{-1}

Reverse Osmosis and Water Purification

If a pressure higher than the osmotic pressure is applied to the solution side, the direction of flow of the solvent can be reversed. As a result, the pure solvent flows out of the solution through the semipermeable membrane. This process is called **reverse osmosis.** It is of great practical application as it is used for desalination of sea water to obtain pure water.

9.7.4.a Determination of Relative Lowering of Vapour pressure by Walker and Ostwald's dynamic method.

This method is very simple in which a slow current of dry air is drawn in succession through,

i) A series of two bulbs (A) containing the aqueous soltion (vapour pressue P).

ii) A similar series of two bulbs (B) containing the solvent (vapour pressure P_O).

iii) A 'U' tube containing anhydrous $CaCl_2$ solid.

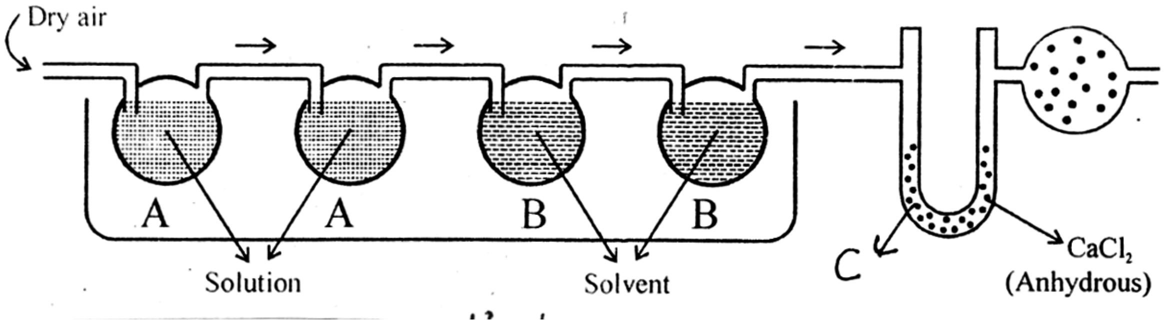


Fig. 9.8 : *Ostwalds dynamic method*

Dry air is passed through the solution bulbs first. The air carries with it some solvent (water) in the form of vapour. Hence there will be loss of weight in the solution bulbs. This loss is proportional to the vapour pressure of solution (P).

Now the air containing the solvent (water) vapour is allowed to pass through the solvent bulbs. The vapour pressure of solvent (P_O) is higher than the vapour pressure of solution (P). Therefore the air containing the vapour already, takes some more vapour from the solvent bulbs. This loss is proportional to (P_O - P).

Now the air saturated with solvent vapour is passed through the 'U' tube, 'U' tube absorbs the solvent vapour. (Water vapour, since water is solvent). The weight of 'U' tube increase.

Calculations and Results :

Loss (x) in 'A' bulbs (solution bulbs) α P

Loss (y) in 'B' bulbs (solvent bulbs) α P_O - P

Total Loss = gain (z) in weight of 'U' tube (C)

$x + y = P + (P_O - P) = P_O$

$P_O - P = y$

$P_O = (x+y) = z$

$$\therefore \quad \frac{P_O - P}{P_O} = \frac{y}{x+y} = X_s = \frac{n_s}{n_o}$$

$$\therefore \quad \frac{y}{x+y} = \frac{a}{M} \text{ X } \frac{W}{b}$$

$$M = \frac{aW}{b} = \frac{x+y}{y}$$

a = weight of solute

b = weight of solvent

M = mol. Wt. of solute

W = mol. Wt. of solvent.

9.7.4.b Cottrell's method of determining molecular weight of solute using elevation of Boiling point

This method require (1) accurate determination of elevaiton of boiling point. Hence conventional thermometers are not useful.

So, beckmann designed a thermometer which measures only the elevation in temperature ΔT but not absolute values of B.P. This thermometer contains a reservoir of Hg at one end of the capillary and as usual a bulb at the other end. These are internally connected through the capillary. At any level of temperature (-60^0C to 3000^C) the elevation can be measured by adjusting the amount of Hg in the bulb unlike conventional thermometer temperature. This adjustment is done with the help of the reservoir.

(2) The second requirement is elimination of super heating during boiling. For this, Cottrell used a special device (pumping device) which resembles an inverted funnel, whose stem is split into three symmetrically placed tubes as shown in the figure.

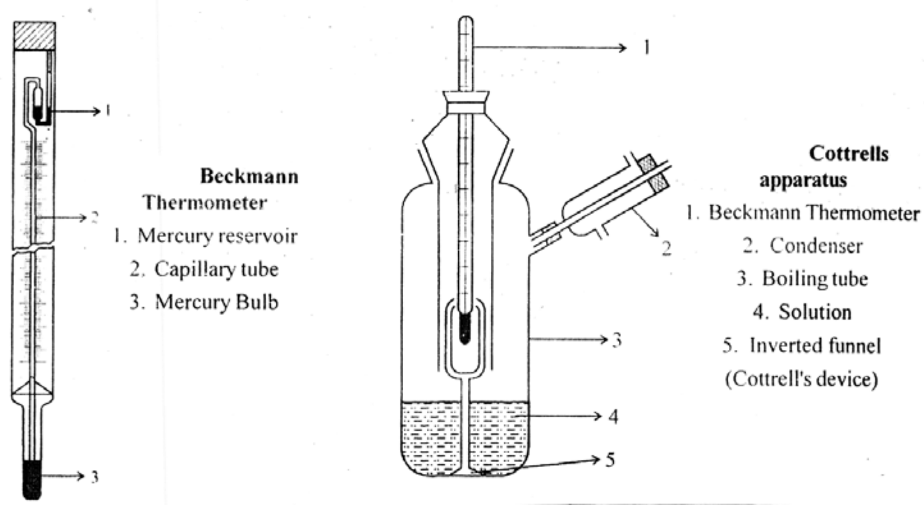


Fig. 9.9 : *Cottrell's method*

The apparatus consists of tube provided with a side tube. The tube contains another tube through which the thermometer is inserted. At the bottom of the outer tube a platinum wire is fused which is heated during boiling. The funnel like device is placed in the solution in the tube. This pumps the bubbles of the solution along with vapour on to the thermometer bulb. So, the liquid and the vapour will be in equilibrium on the surface of the bulb at the boiling point. This reduces super heating.

A known weight (b) of solvent (molecular weight - W) is taken in the Cottrell tube and the boiling point is determined (T_O). A known weight ('a' g) of the solute (molecular weight m) is introduced in the tube through the side tube in the form of a tablet. This dissolves completely and the boiling point of solution (T) is measured. Molar mass is calculated as follows.

Wt. of solvent = 'b' g

Wt. of solute = 'a' g

B.P. of solvent = T_O

B.P. of solution = T

Elevation in B.P. = $T - T_o = \Delta T$

$$\Delta T = K_b = \frac{a}{m} x \frac{1000}{b}$$

where K_b = molal elevation constant of solvent.

Problem : The boiling point of $CHCl_3$ was raised 0.325K when 5.141 x 10^{-4} kg. of anthracene is dissolved in 3.5 x 10^{-4} kg of $CHCl_3$. Calculate the molar mass of anthracene. (K_b = 3.9 $K.mol^{-1}$).

Solution :

$\Delta T = 0.325$ K

K_b = 3.9 Kg. mol-1

A = 0.5141 g ; b = 3.5 g

$$\therefore M = \frac{K_b \text{ x a x } 1000}{\Delta T_b \text{ x b}}$$

$$M = \frac{3.9 x 5.141 x 10^{-4} x 1000}{0.325 x 3.5 x 10^{-3}}$$

= 0.1763 kg of 176.3 g

9.7.4.c Rast's Method :

This method was developed by Rast for Camphor as a solvent. This method is thus generally used for solid solutions i.e., solid solute and solid solvent.

A known weight of campgor (b) is taken and finely powdered in dry mortar. To this a known weight (a) of solid solute is added. The mixture is mixed throughly. The mixture is melted to form a homogeneous solution, cooled dried and powdered. The mixture is taken in a capillary tube whose one end is sealed. The melting point is determined carefully by the conventional melting point determination method. The melting point of the pure sample of camphor is determined separately using another capillary tube. The difference in the melting point gives ΔT_f.

From the values a, b & , ΔT_f M is calculated (K_f for camphor = 40 K.kg mol^{-1})

Wt. of camphor - b.g.

Wt. of solute - a.g.

Mol. wf. of solute - m

$$\Delta T_f = K_f \quad x \ \frac{a}{m} \ x \frac{1000}{b}$$

$$\therefore \ M = \frac{K_f \ x \ a \ x \ 1000}{\Delta T_f \ x \ b}$$

9.7.4.d Berkeley and Hartley's Method of determining osmotic Pressure :

It is method of applying pressure to the solution which was just sufficient to stop osmosis. A porous pot, open at both the ends and having a copper ferrocyanide membrance fused in its walls, is sealed into the outer bronze cylinder. The bronze cylinder contains the solution and is fitted with a piston upon which weights may be placed to exert external pressure on the solution.

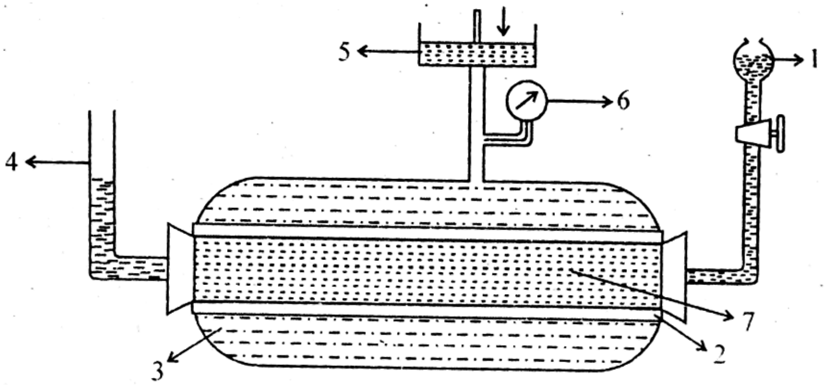


Fig. 9.10 : *Berkely - Hartley Method*
1. Solvent Reservoir 2. Semipermeable membrance
3. solution 4. Capillary tube 5. Piston 6. Pressure guage 7. Solvent

This porous pot is connected with a side tube (capillary tube) one end and a reservior containing water at the other end. The flow of water through the pot into the solution is indicated by the downward motion of the water meniscus in the side tube. This flow of osmosis of water into the solution can be stopped the application of external pressure on the solution with the help of the piston and this would be indicated when the water meniscus in the side tube becomes stationary. The pressure so applied on the piston is equal to the osmotic pressure of the solution. Thus substituting the values of osmotic pressure (π) molarity of the solution (C) and the temperature of the solution in Kelvin scale (T), in the equation.

$$\pi = CRT \ (C = \frac{n}{v})$$

R = Gas Constant

The molecular weight of the solute can be calculated.

Problem :

What is the osmotic pressure of a solution containing 0.1 mole of non-volatile solute in 100 cm^3 of solution at 27^0C.

Solution :

$\pi = \frac{n}{v} RT \qquad\qquad R = 0.82l.\text{atm}.K^{-1}\ \text{mol}^{-1}$

$\pi = \frac{0.1}{0.1} \times 0.0082 \times 300 \qquad V = 100\ cm^3 = 0.1l$

$\pi = 24.63\ \text{atm} \qquad\qquad V = 27^0C = 300\ K$

Intext Questions 9.3

1. Define colligative property. List two colligative properties.

   ....

2. What type of liquid pairs show (i) positive deviations (ii) negative deviations.

   ....

3. Why is the determination of osmotic pressure a better method as compared to other colligative properties of determining the molar masses of biomolecules.

   ....

9.8 Abnormal Colligative Properties

The colligative properties of the solutions depend only upon the number of solute particles present in the solution and not on their nature. But sometimes while measuring colligative properties abnormal results are obtained due to the following reasons :

i) If the solution is very concentrated, the particles of the solute start interacting with each other. Therefore, the solution should not be concentrated.

ii) In case of **association** two or more solute molecules associate to form a bigger molecule. The number of effective molecules in the solution, therefore decreases. Consequently the value of the collgative property (relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure) is observed to be less than that calculated on the basis of unassociated molecules. Since, the colligative property is inversely proportional to the molar mass, the molar mass of such solutes calculated on the basis of colligative property will be greater than the true molar mass of the solute.

iii) **In case of dissociation** of the solute in the solution, the number of effective solute particles increases. In such cases the value of the observed colligative property will be greater than that calculated on the basis of undissociated solute particles. The molar mass of the solute calculated from the measurement of colligative property will be lower than the true molar mass of the solute.

Van’t Hoff factor

In order to account for extent of association or dissociation Van’t Hoff introduced a factor ‘*i*’.

$$i = \frac{\text{Observed colligative property}}{\text{Normal (calculated or expected) colligative property}}$$

Since the colligative property is proportional to the number of solute particles or the number of moles of solute

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}}$$

Also, since colligative properties vary inversely as the molar mass of the solute, it follows that

$$i = \frac{\text{Normal (calculated or expected) molar mass}}{\text{Observed molar mass}}$$

Here the observed molar mass is the experimentally determined molar mass whereas the normal molar mass is the molar mass calculated on the basis of chemical formula of the solute. In case of association the value of van’t Hoff factor, i, is less than unity while for dissociation it is greater than unity. For example, benzoic acid association in benzene to form a dimer. The value of i is, therefore, close to 1/2. The value of *i* for aqueous NaCl is close to 2.0 because NaCl dissociates in water to form Na^+ and Cl^- ions.

The inclusion of van’t Hoff factor, *i*, modifies the equations for the colligative properties as follows :

$$\frac{P^O_A - P_A}{P^O_A} = i\,X_B$$

$$\Delta T_b = i\,K_b\,m$$

$\Delta T_f = i\, K_f\, m$

$\pi V = i$ CRT

Degree of Association

Degree of association may be defined as the fraction of the total number of molecules which associate to form a bigger molecule. Let us consider the association of benzioc acid in benzene. In benzene two molecules of benzoic acid associate to form a dimer. It can be represented as

$$2C_6H_5COOH \longrightarrow (C_6H_5COOH)_2$$

If *x* represents the degree of association of benzoic acid in benzene (i.e out of one molecule of benzoic acid, *x* molecules associate to form a dimer), then at equilibrium.

No. of moles of unassociated benzoic acid = 1 - *x*

No. of moles of associated benzoic acid = $\frac{x}{2}$

Total number of effective moles of benzoic acid = $1 - x + \frac{x}{2} = 1 - \frac{x}{2}$

According to definition, Van't Hoff factor is given by

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1-\frac{x}{2}}{1}$$

Example 9.8 : Acetic acid (CH_3COOH) associates in benzene to form double molecules 1.60g of acetic acid when dissolved in 100g of benzene (C_6H_6) raised the boiling point by 273.35 K. Calculated the van't Hoff factor and the degree of association of benzoic acid. Kb for C_6H_6 = 2.57 K kg mol^{-1}.

Solution : $\Delta T_b = i\, K_b\, m = \frac{1000i\, K_b\, W_B}{W_A\, M_B}$

Normal molar mass (M_B) of CH_3COOH = 60 g mol^{-1}

Van't Hoff factor, *i*, is = $\frac{\Delta T_b \text{ x } W_A \text{ x } W_B}{1000 \text{ x } K_b \text{ x } W_B}$

$$= \frac{0.35 \text{ x } 100 \text{ x } 60}{1000 \text{ x } 2.57 \text{ x } 1.60}$$

$$= 0.51$$

Since, acetic acid associates in benzene to form double molecules, the following equilibrium exists in the solution.

$$2CH_3COOH \longrightarrow (CH_3COOH)_2$$

If *x* represents the degree of association of the solute, then we would have (*1-x*) mol of acetic acid left unassociated and x/2 moles of acetic acid at equilibrium.

Therefore, total number of particles at equilibrium = 1 - x + x/2

$$= 1 - \frac{x}{2}$$

The total number of particles at equilibirum equal van't Hoff factor. But van't Hoff factor (i) is equal to 0.51.

$$\therefore \quad 1 - \frac{x}{2} = 0.51$$

$$\text{or} \quad \frac{x}{2} = 1 - 0.51 = 0.49$$

$$x = 0.49 \times 2 = 0.98$$

Therefore, degree of associaiton of acetic acid in benzene is 98%.

Degree of dissociation

Degree of dissociation may be defined as the fraction of the total number of particles that dissociate, i.e., break into simpler ions. Consider a solution of KCl in water. When KCl is dissolved in water, it dissociates into K^+ and Cl^- ions.

$$KCl \longrightarrow K^+ + Cl^-$$

Let *x* be the degree of dissociation of KCl, then at equilibrium, number of moles of undissociated KCl = 1 - *x*.

According to the dissociation of KCl shown above, when x mol of KCl dissociates, x moles of K^+ ions and x mol of Cl^- ions are produces.

Thus, the total number of moles in the solution after dissociation = 1 - x + x + x = 1 + x

$$\text{Hence, } i - \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1+x}{1}$$

Example 9.9 : A 0.5 percent aqueous solution of potassium chloride was found to freeze at 27.276K. Calculate the van't Hoff factor and the degree of dissociation of the solute at this concentration. (K_f for H_2O = 1.86 K kg mol^{-1}).

Solution : Normal molecular weight of KCl = 39 + 35.5 = 74.5 g mol^{-1}

$$\text{Observed molecular weight, } M_B = \frac{1000 \text{ x } W_B \text{ x } K_f}{\Delta T_f \text{ x } W_A}$$

$$= \frac{1000 \text{ x } 0.5\text{g x } 1.86 \text{ K kg mol}^{-1}}{(0.24 \text{ K}) \text{ x } 100 \text{ g}}$$

$$= 38.75 \text{ g mol-1}$$

$$\text{van't Hoff factor (i)} = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

$$= \frac{74.5 \text{ g mol}^{-1}}{38.75 \text{ g mol}^{-1}} = 1.92$$

Potassium chloride in aqueous solution dissociates as follow.

$KCl \longrightarrow K^+ + Cl^-$

Let *x* be the degree of dissociation of KCl. Thus at equilibrium.

No. of moles of KCl left undissociated = (1- *x*) mol

No. of moles of K^+ = *x* mol

No. of moles of Cl^- = *x* mol

Total number of moles at equilibrium = 1 - *x* + *x* + *x* = 1 + *x*.

$$\therefore \text{ Van't Hoff factor} = \frac{1+x}{1} = 1.92$$

or $x = 1.92 - 1 = 0.92$

$\therefore$ Degree of dissociation of KCl = 92%

What You Have Learnt

- Solution is a homogeneous mixture of to or more substances.
- solvent is that component of a solution that has the same physical state as the solution it self.
- solute is the substance that is dissolved in a solvent to form a solution
- Molarity is expressed as the number of moles of solute per litre of solution.

- Molality is expressed as the number of moles of solute per kilogram of solution.
- Normality is a concentration unit which tells the number of gram equivalents of solute per litre of solution.
- Mole fraction is the ratio of the number of moles of one component to the total number of moles in the solution.
- solutions can be solid, liquid or gaseous.
- Henry's law states that mass or mole fraction of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.
- Raout's law states that for a solution of volatile liquids, the partial pressure of each liquid in the solution is directly proportional to its mole fraction.
- A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.
- The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.
- Those properties of dilute solutions which depend only on the number of particles of solute and not on their nature are known as colligative properties.
- Molal elevation constant is the elevation in boiling point when one mole of solute is dissolved in one kilogram of the solvent.
- Boiling point of a liquid is the temperatures at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- Freezing point is the temperature at which the solid and the liquid forms of the substance have the same vapour pressure.
- Abnormal result are obtained when the solute associates or dissociates in the solution.
- Van't Hoff factor is defined as the ratio of normal molar mass to experimentally determined molar mass.

Terminal Exercise

1. What do you understand by ideal and non-ideal solutions ?
2. Define freezing point and boiling point.
3. Derive the relationship $\Delta T_b = K_b\, m$
4. A solution containing 7 g of a non-volatile solute in 250g of water boils at 373.26 K. Find the molecular mass of the solute.

5. 2g of a substance dissolved in 40g of water produced a depression of 274.5 K in the freezing point of water. Calculate the molecular mass of the substance. The molal depression constant for water is 274.85 K per molal.

6. Calculate the mole fraction of the solute in a solution obtained by dissolving 10g of urea (mol wt 60) in 100 g of water.

7. A solution containing 8.6g of urea (molar mass = 60 per dm^3) was found to be isotonic with a 5 per cent solution of an organic non-volatile solute. Calculate the molar mass of the non-volatile solute.

8. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25g of benzene shows a depression in freezing point equal to 1.62 K. Molar depression constant for benzene in 4.9 K kg mol^{-1}. What is the percentage association of C_6H_5COOH if it forms double molecules in solution.

9. The freezing point depression of 5.0×10^{-3} M solution of Na_2SO_4 in water was found to be $0.0265^{O}C$. Calculate the degree of dissociation of the salt at this concentration. (K_f for H_2O is 1.86K kg mol^{-1})

Answers to Intext Questions

9.1

1. Molarity, Molality, Normality, Mole fraction, Mass percentage.
   Molarity is the number of moles of solute dissolved per litre of the soltion.

2. Molality is the number of moles of solute dissolved per kg of the solvent.
   Normality is the number of gram equivalents of solute dissolved per litre of solution

9.2

1. For a solution of volatile liquids the partial vapour pressure of each liquid is proportional to its mole fraction.

2. The mass of a gas dissolved in a solvent is directly proportional to its partial pressure. Pressure should not be too high temperature should not be too low. The gas should not associate or dissociate.

9.3

1. Properties that depend upon the number of particles of solute and not on the nature of solute. e.g. Elevation of boiling point, depression of freezing point.

2. For which A-B molecular interactions are :

   i) weaker than A-A and B-B interactions.

   ii) stronger than A-A and B-B interactions.

3. At low concentration the magnitude of osmotic pressure is large enough for measurement.

10

COLLOIDS

You are familiar with solutions. They play an important role in our life. A large number of substances such as milk, butter, cheese, cream, coloured gems, boot polish, rubber, ink also play an important role in our daily life. They are also solutions of another kind. They are colloidal solutions. The term colloid has been derived from two terms, namely colla and oids. ‘Kolla’ means glue and ‘Oids’ means like i.e. glue-like. The size of the particles in colloidal solutions is bigger than the size of particles present in solutions of sugar or salt in water. In this lesson you will learn about the methods of preparation, properties and applications of colloidal solutions.

Objectives

After reading this lesson you will be able to:

- Explain the difference between true solution, colloidal solution and suspension;
- Identify phases of colloidal solution;
- Classify colloidal solution;
- Describe methods of preparation of colloids;
- Explain some properties of colloidal solutions;
- Recognize the difference between gel and emulsion and,
- Cite examples of the application of colloids in daily life.

10.1 Distinction between a True Solution, Colloidal Solution and Suspension.

You may recall that solution of sugar in water is homogeneous but milk is not. When you closely look at milk you can see oil droplets floating in it. Thus, although it appears to be homogenous it is actually heterogenous in nature. The nature of the solution formed depends upon the size of the solute particles. If the size of the solute particles is less than 1 nm it will form true solution but when the size is between 1 to 100 nm then it will form colloidal solution. When the size of solute particles is greater than 100 nm it will form a suspension. Therefore we may conclude that colloidal solution is an intermediate state between true solution and suspension (Table 10.1).

Table 10.1 : Some important properties of true solutions, colloids and suspensions

S.No.	Name of Property	True Solution	Colloids Solution	Suspension
1.	Size	Size of particles is less than 1 nm	Size of particles is between 1 nm and	Size of particles greater than 100nm
2.	Filterability	Pass through ordinary filter paper and also through animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper or animal membrane.
3.	Settling	Particles do not settle down on keeping	Particles do not settle down on their own but can be made to settle down by centrifugation.	Particles settle down on their own under gravity.
4.	Visibility	Particles are invisible to the naked eye as well as under a microscope	Particles are invisible to the naked eye but their scattering effect can be observed with the help of a microscope	Particles are visible to the naked eye.
5.	Separation	The solute and solvent cannot be separated by ordinary filteration or by ultra filteration.	The solute and solvent cannot be separated by ordinary filteration but can be separated by ultra-filteration.	The solute and solvent can be separated by ordinary filteration.
6.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse

10.2 Phases of Colloids Solution

Colloids solutions are heterogenous in nature and always consist of at least two phases: the **dispersed phase** and the **dispersion medium**.

- **Dispersed Phase**: It is the substance present in small proportion and consists of particles of colloids size (1 to 100nm).
- **Dispersion Medium**: It is the medium in which the colloids particles are dispersed.

For example in a colloidal solution of sulphur in water, sulphur particles constitute the 'dispersed phase' and water is the 'dispersion medium'.

Each of the two phases namely, dispersed phase and dispersion medium can be solid, liquid or gas. Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Different types of colloidal solutions and their examples are shown in Table 10.2. You should note that gases cannot form a colloidal solution between themselves, because they form homogenous mixtures.

Table 10.2 : Types of Colloidal Solutions

S.No.	Dispersed Phase	Dispersion Medium	Type of Colloidal Solution	Examples
1.	Solid	Solid	Solid Solution	Gemstones,
2.	Solid	Liquid	Sol	Paints, muddy water, gold sol, starch sol, arsenious sulphide sol.
3.	Solid	Gas	Aerosol of solids	Smoke, dust in air
4.	Liquid	Solid	Gel	Jellies, Cheese
5.	Liquid	Liquid	Emulsion	Milk, Cream
6.	Liquid	Gas	Aerosol	Mist, fog, cloud
7.	Gas	Solid	Solid foam	Foam rubber, pumice stone
8.	Gas	Liquid	Foam	Froth, whipped cream

Out of the various types of colloidal solutions listed above, the most common are sols (solid in liquid type), gels (liquid in solid type) and emulsions (liquid in liquid type). If the dispersion medium is water then the 'sol' is called a hydrosol; and if the dispersion medium is alcohol then the 'sol' is called an alcosol

Intext Questions 10.1

1. Classify the following into suspension, colloidal solution and true solution. Milk, sugar in water, clay in water, blood, boot polish, sand in water, face cream, jelly, foam.

   ....

2. Give one example each of
   (a) Sol (b) Gel (c) Aerosol (d) Emulsion

   ....

3. What is the difference between an alcosol and hydrosol?

   ....

4. How does colloidal solution differ from true solution?

   ....

10.3 Classification of Colloids

Colloidal solutions can be classified in different ways:

(a) On the basis of interaction between the phases.

(b) On the basis of molecular size.

10.3.1 Classification Based Upon Interaction

Depending upon the interaction between dispersed phase and the dispersion medium colloidal solutions have been classified into two categories.

(a) Lyophilic Colloids : The word Lyophilic means solvent lover. Lyophilic colloidal solutions are those in which the dispersed phase have a great affinity (or love) for the dispersion medium. Substances like gum, gelatin, starch etc when mixed with suitable dispersion medium, directly pass into colloidal state and form colloidal solution. Therefore, such solutions are easily formed simply by bringing dispersed phase and dispersion medium in direct contact with each other. However these colloidal solution have an important property i.e. they are reversible in nature. This means that once lyophilic colloidal solutions has been formed then dispersed phase and dispersion medium can be separated easily. Once separated these can again be formed by remixing the two phases. These sols are quite stable.

If water is used as dispersion medium then it is termed as hydrophilic colloid.

(b) Lyophobic Colloids : The word Lyophobic means solvent hating. Lyophobic colloidal solutions are those in which the dispersed phase has no affinity for the dispersion medium. Metals like Au, Ag and their hydroxides or sulphides etc., when simply mixed with dispersion medium do not pass directly into colloidal state. These sols have to be prepared by special methods. These sols can be readily precipitated and once precipitated they have little tendency to go back into the colloidal state. Thus these sols are irreversible in nature. Also they are not very stable and require a stability agent to remain in the colloidal form. In case water is used as dispersion medium it is called as hydrophobic sol.

10.3.2 Classification Based on Molecular Size

Depending upon the molecular size the colloids have been classified as

a) Marcromolecular colloids - In this type of colloids the size of the particles of the dispersed phase are big enough to fall in the colloidial dimension as discussed earlier (i.e.-100 nm)

Examples of naturally occuring macromolecular colloids are starch, cellulose, proteins etc.

b) Multi molecular colloids - Here individually the atoms are not colloidal size but they aggregate to join together forming a molecule of colloidal dimension. For example sulphur sol contains aggregates of S_8 molecules which fall in colloidal dimension.

c) Associated colloids - These are substances which behave as normal electrolyte at low concentration but get associated at higher concentration to form miscelle and behave as colloidal solution. Soap is an example. Soap is sodium salt of long chain fatty acid R COONa. When put in water, soap forms $RCCO^-$ and Na^+. These $RCCO^-$ ions associate themselves around dirt particles as shown below forming a miscelle (Fig. 10.1)

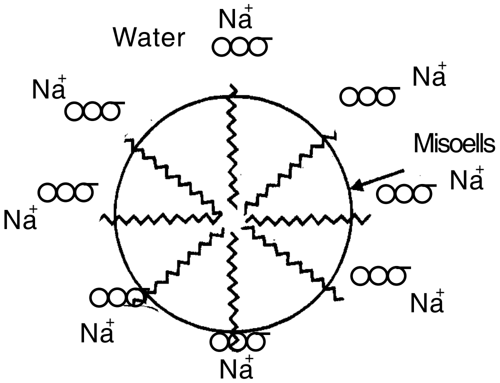


Fig. 10.1 : *Aggregating of RCCO$^-$ ions to form a micelle.*

10.4 Preparation of Colloidal Solutions

As discused earlier, the lyophilic sols can be prepared directly by mixing the dispersed phase with the dispersion medium. For example, colloidal solutions of starch, gelatin, gum etc. are prepared by simply dissolving these substances in hot water. Similarly, a colloidal sol of cellulose nitrate is obtained by dissolving it in alcohol. The resulting solution is called **Collodion**.

However, lyophobic colloids cannot be prepared by direct method.

Hence two types of methods are used for preparing lyophobic colloids. These are :

i) Physical methods

ii) Chemical methods

i) Physical methods

These methods are employed for obtaining colloidal solutions of metals like gold, silver, platinium etc. (Fig. 10.2)

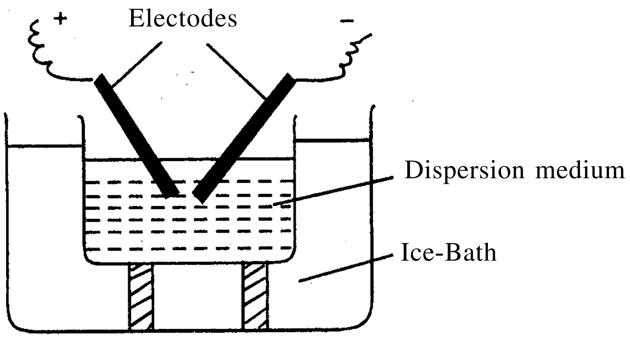


Fig. 10.2 : *Preparation of colloidal solution by Bredig's Arc Method*

An electric arc is struck between the two metallic electrodes placed in a container of water. The intense heat of the arc converts the metal into vapours, which are condensed immediately in the cold water bath. This results in the formation of particles of colloidal size. We call it as gold so.

Peptisation : Peptisation is the process of converting a freshly prepared precipitate into colloidal form by the addition of a suitable electrolyte. The electrolyte is called peptising agent. For example when ferric chloride is added to a precipitate of ferric hydroxide, ferric hydroxide gets converted into reddish brown coloured colloidal solution. This is due to preferential adsorption of cations of the electrolyte by the precipitate. When $FeCl_3$ is added to $Fe(OH)_3$, Fe^{3+} ions from $FeCl_3$ are adsorbed by $Fe(OH)_3$ particles. Thus the $Fe(OH)_3$ particles acquire + ve charge and they start repelling each other forming a colloidal solution.

ii) Chemical Methods : By oxidation

Sulphur sol is obtained by bubbling H_2S gas through the solution of oxidizing agent like HNO_3 or Br_2 water, etc. according to the following equation :

$$Br_2 + H_2S \rightarrow S + 2\,HBr$$

$$2\,HNO_3 + H_2S \rightarrow 2\,H_2O + 2\,NO_2 + S$$

$Fe(OH)_3$ SOl, $As_2\ S_3$ sol can also be prepared by chemical methods

10.5 Purification of Colloidal Solution

When a colloidal solution is prepared it contains certain impurities. These impurities are mainly electrolytic in nature and they tend to destabilise the colloidal solutions. Therefore colloidal solutions are purified by the following methods :

i) Dialysis

ii) Electrodialysis

Dialysis : The process of dialysis is based on the fact that colloidal particles cannot pass through parchment or celloplane membrance while the ions of the eletrolyte can. The colloidal solution is taken in a bag of cellophane which is suspended in a tub full of fresh water. The impurities diffuse out leaving pure coloidal solution in the bag (Fig. 10.3). This process of separating the particles of colloids from impurties by means of diffusion through a suitable membrane is called **dialysis**.

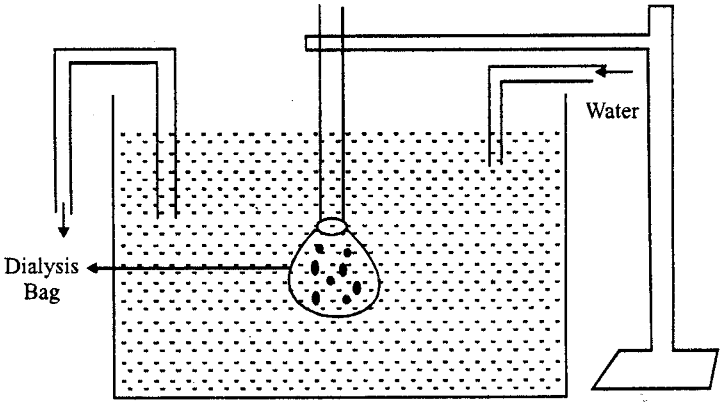


Fig. 10.3 : *A dialyser*

Electrodialysis : The dialysis process is slow and to speed up its rate, it is carried out in the presence of an electrical field. When the electric field is applied through the electrodes, the ions of the electrolyte present as impurity diffuse towards oppositely charged electrodes at a fast rate. The dialysis carried out in the presence of electric field is known as electrodialysis (Fig. 10.4).

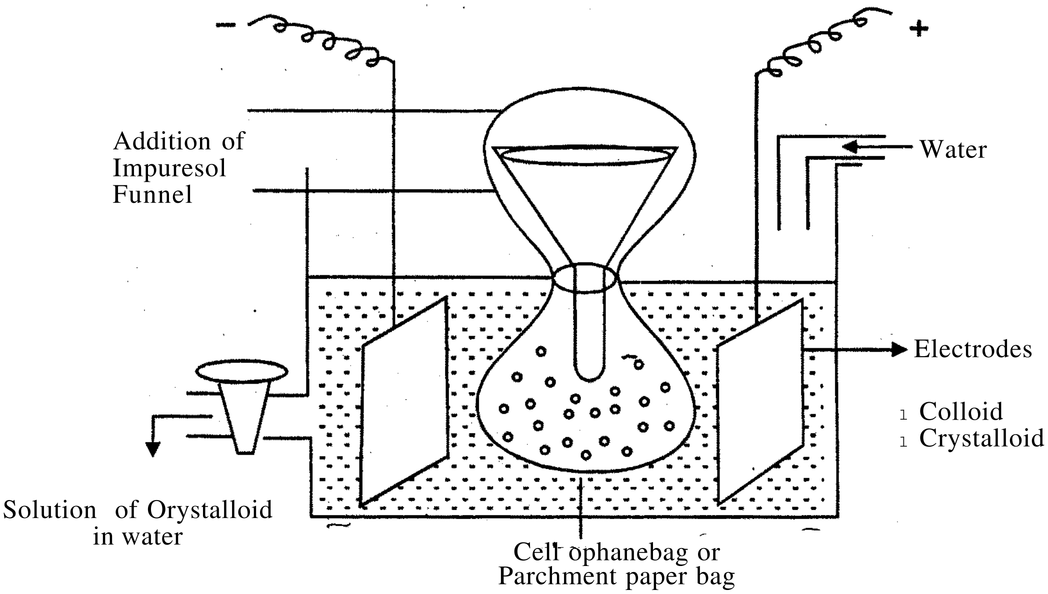


Fig. 10.4 : *Electrodialysis*

The most important use of dialysis is the purification of blood in the artificial kidney machine. The dialysis membrane allows the small particles (ions etc.) to pass through, whereas large size particles like haemoglobin do not pass through the membrane.

Intext Questions 10.2

1. Name two colloids that can be prepared by Bredig's Arc method.

   ....

2. Name two colloids that can be prepared by chemical methods.

   ....

3. Differentiate between (a) Lyophilic and Lyophobic sol. (b) macromolecular and multimolecular colloids.

   ....

4. Explain the formation of miscelle.

   ....

10.6 Properties of Colloids

The propeties of colloids are discussed below :

a) **Heterogeneous character** : Colloidal particles remain within their own boundary surfaces which separate them from the dispersion medium. So a colloidal system is a heterogeneous mixture of two phases. The two phases are dispersed phase and dispersion medium.

b) **Brownian movement :** It is also termed as Brownian motion and is named after its discoverer Robert Brown (a Botanist).

   Brownian Motion is the zig-zag movement of colloidal particles in continuous random manner (Fi.g 10.5). Brownian motion arises because of the impact of the molecules of the dispersion medium on the particles of dispersed phase. The forces are unequal in different directions. Hence it causes the particles to move in a zig-zag way.

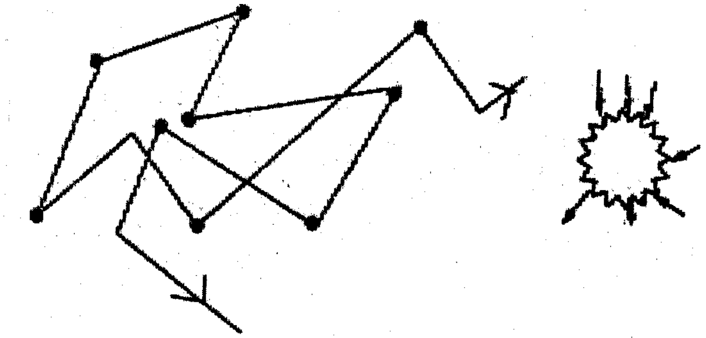


Fig. 10.5 : *Brownian Movement*

c) **Tyndall Effect :** Tyndall in 1869, observed that if a strong beam of light is passed through a colloidal solution then the path of light is illuminated. This phenomenon is called Tyndall Effect. This phenomenon is due to scattering of light by colloidal particles (fig. 10.6). The same effect is noticed when a beam of light enters a dark room through a slit and becomes visible. This happens due to the scattering of light by particles of dust in the air.

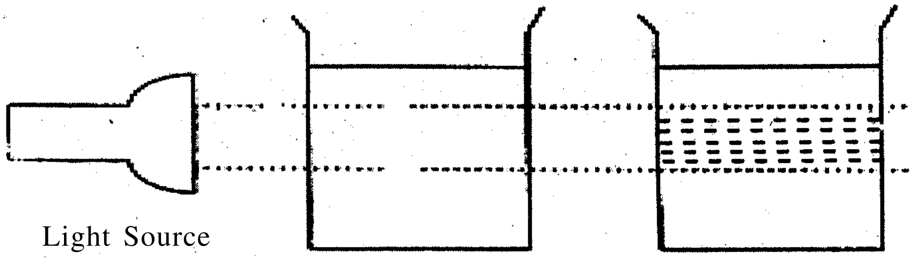


Fig. 10.6 : *The Tyndall Effect*

d) **Electrical Properties :** The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive. The dispersion medium has an equal and opposite charge. The colloidal particles therefore repel each other and do not cluster together to settle down. For example, arsenious sulphide sol, gold sol, silver sol, etc. contain negatively charged colloidal particles whereas ferric hydroxide, aluminium hydroxide etc. contain positively charged colloidal particles. Origin of charge on colloidal particles is due to :

a) Preferential adsorption of cations or anions by colloidal particles.

b) Miscelles carry a charge on them.

c) During the formation of colloids especially by Bredig arc method, colloidal particles capture electrons and get charged. The existence of charge on a colloidal particles is shown by a process called **electrophoresis**.

Electrophoresis is a process with involves the movement of colloidal particles either towards cathode or anode under the influence of electrical field. The apparants used is as shown in Fig. 10.7.

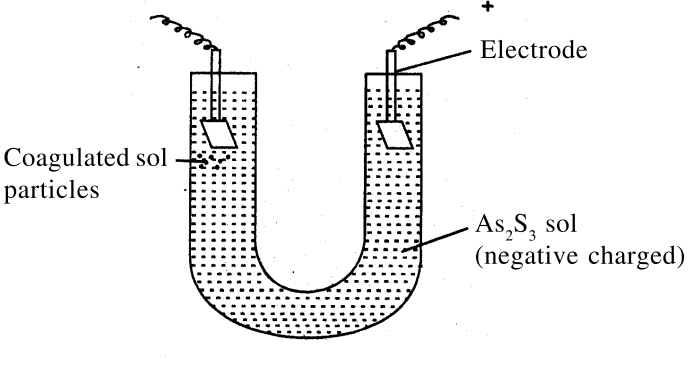


Fig. 10.7 : *A set up for Electrophoresis*

10.7 Applications of Colloidal Solutions

Colloids play a very important role in our daily life. Some of these applications are discussed below :

i) **Sewage disposal :** Colloidal particles of dirt, etc. carry elctric charge. When sewage is allowed to pass through metallic plates kept at a high potential, the colloidal particles move to the oppositely charged electrode and get precipitated there. Hence sewage water is purified.

ii) **Purification of Water in Wells :** When alum is added to muddy water, the negatively charged particles of the colloid are neutralized by Al^{3+} ions. Hence the mud particles settle down and the water can be filtered and used.

iii) **Smoke Precipitation** : Smoke particles are actually electrically charged colloidal particles of carbon in air. Precipitation of this carbon is done is a **Cottrell's Precipitator**. Smoke from chimneys is allowed to pass through a chamber having a number of metallic plates connected to a source of high potential as shown in Fig. 10.8 Charged particles of smoke get attracted to the oppositively charged electrode and get precipitated and hot purified air passes out.

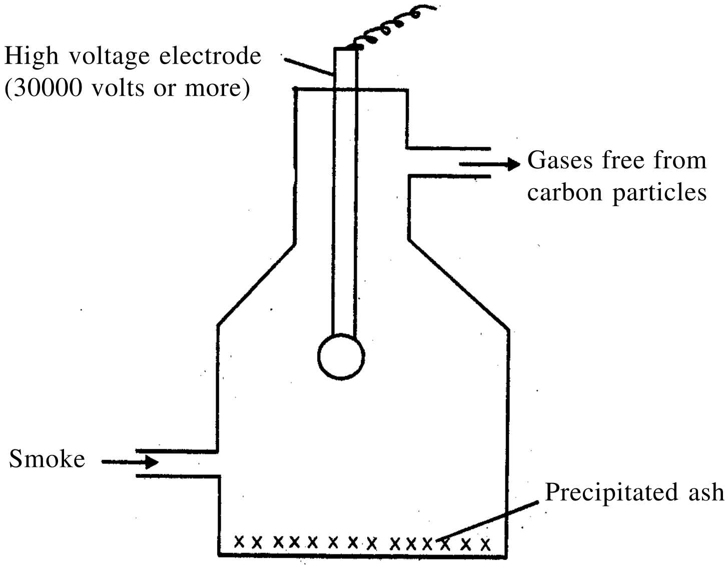


Fig. 10.8 : *Cottrell smoke precipitator*

Other applications in day to day life are :

i) **Photography :** A colloidal solution of silver bromide in gelatin is applied on glass plates or celluloids films to form photo-senstive plates in photography.

ii) **Clotting of Blood :** Blood is a colloidal solution and is negatively charged. On applying a solution of $FeCl_3$ bleeding stops and clotting of the colloidal particles of blood takes place.

iii) **Rubber Plating :** Latex is a colloidal solution of negatively charged rubber particles. The object to be rubber plated is made the anode in ther rubber plating bath. The negatively charged rubber particles move towards the anode and get deposited on it.

iv) **Blue Colour of Sky :** Have you ever wondered why is the sky blue? It is because the colloidal dust particles floating about in the sky scatter blue light, that makes the sky appear blue. In the absence of these colloidal particles the sky would have appeared dark throughout.

10.8 Emulsion and Gel

Emulsions are colloidal solutions in which both the dispersed phase and dispersion medium are liquids. However, the two liquids are immiscibel, as miscible liquids will form true solution.

Emulsion are of two kinds :

a) Oil-in-water emulsion : Here the dispersed phase is oil while the dispersion medium is water. Milk is an example of this kind as in milk liquid fats are dispersed in water. Vanishing cream is another example.

b) Water-in-oil emulsion : Here dispersed phase is water and dispersion medium is oil. Butter, cod-liver oil, cold creams are examples of this types.

The liquids forming emulsion i.e. oil and water will separate out on keeping as they are immiscible. Therefore an emulsifying agent or emulsifier is added to stabilise the emulsion. Soap is a common ***emulsifier***. The preparation of emulsion in the presence of an emulsifier is called emulsification.

How does an emulsifier work? It is believed that an emulsifier gets concentrated at the interface between oil and water i.e. the surface at which oil and water come in contact with each other. It acts as a binder between oil and water.

Application of Emulsions - Emulsions play very important role in our daily life. Some of the common applications are given below :

1. The cleansing action of soap and synthetic detergents for washing clothes, bathing etc is based upon the formation of oil in water type emulsion.
2. Milk is an emulsion of fat in water. Milk cream and butter are also emulsions.
3. Various cold creams, vanishing creams, body lotions etc. are all emulsions.
4. Various oily drugs such as cold liver oil are administered in the form of emulsion for their better and faster absorption. Some ointments are also in the form of emulsions.
5. The digestion of fats in the intestine occurs by the process of emulsification.

6. Emulsions are used for concentrating the sulphide ores by forth flotation process. Finely powedered or is treated with an oil emulsion and the mixture is vigorously agitated by compressed air when the ore particles are carried to the surface and removed.

Gels - Gels are the types of colloids in which the dispersed phase is a liquid and the dispersion medium is a solid. Cheese, jelly, boot polish are common examples of gel. Most of the commonly used gels are hydrophilic colloidal solution in which a dilute solution, under suitable conditions set as elastic semi solid masses. For example 5% aqueous solution of gelatin in water on cooling forms the jelly block.

Gels may shrink on keeping by loosing some of the liquid held by them. This is known as **syneresis** or resetting on standing.

Gels are divided in two caterogies elastic gels and non elastic gels. Elastic gels are reversible. When partly dehydrated on loosing water, they change back into the original form on addition of water. The non elastic gels are not reversible.

Gels are useful in many ways. Silica, cheese, jelly, boot polish, curd are commonly used gels. Solidified alcohol fuel is a gel of alcohol in calcium acetate.

What You Have Learnt

- Size of the particles in the colloidal state is intermediate between that of suspension and ture solution.
- There are eight different types of colloidal systems.
- Sols are classified on the basis of (a) interaction between dispersed phase and dispersion medium (b) molecular size of dispered phase.
- Colloidal solutions are prepared by physical and chemical methods.
- The zig zag motion of colloidal particles is called Brownian motion.
- Colloidal size particles scatter light and so the path of light becomes visible in a semi darkened room due to dust particles.
- Colloidal particles may carry electric charge.
- A colloidal dispersion of a liquid in another liquid is called an emulsion.
- A colloidal solution of liquid dispersed in a solid medium is called a gel.
- Colloids are extremely useful to mankind both in daily life and in industry.

Terminal Exercise

1. List three differences between a true solution and colloidal solution.
2. Describe one method of preparation of

a) a lyophilic colloid

b) a lyophilic colloid

3. What are associated colloids ?

4. What is Brownian motion ? How does it originate ?

5. Why bleeding from a fresh cut stops on applying alum ?

6. Two beakers A and B contain ferric hydroxide sol and NaCl solution respectively. When a beam of light is allowed to converge on them, (in a darkened room), beam of light is visible in beaker A but not in breaker B. Give the reason. What is this effect called ?

7. Define the following terms and give two examples of each
   - i) Gel
   - ii) Sol

8. Describe two important applications of colloidal solutions.

9. Give two examples of emulsions used in daily life.

10. Explain the role of emulsifier in an emulsion ?

Answers to Intext Questions

10.1

1. Suspension - Clay in water, Sand in water
   Colloidal - Milk, Blood, Boot polish, Face Cream, Jelly, Foam.
   True Solution - Sugar in water

2. Sol - Starch in water
   Gel - Silica gel
   Aerosol - Fog
   Emulsion - Milk

3. Alcosol - When alcohol is the dispersion medium.
   Hydrosol - When water is the dispersion medium.

4.

True solution	Colloidal solution
i) size of solute in less than 1 nm	i) Particle size (1-100) nm.
ii) Form transparent solution and allows light to pass through them.	ii) Path of light becomes visible.

10.2

1. Gol sol, Platinum sol
2. As_2S_3, Fe $(OH)_3$ (Arsenious sulphide sol, ferric hydroxide sol)
3. **a) Lyophilic sol :**

   1) easy to prepare

   2) affinity between dispersed phase and dispersion medium

   3) reversible

   Lyophobic

   1) special method used for preparation

   2) No affinity between the two phases.

   3) Not reversible

   b) Macromolecular - The size of the colloidal particles large enough to fall in the colloidal dimensions.

   Multimolecular - Individually the particles are not of colloidal dimensions but they aggregate to join together to form molecules of colloidal side.
4. Refer to 10.3.2 (c)

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;

---

* 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.

- 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.

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 active 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 or 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

Table 18.1 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 (Zinc blende, ZnS); Lead (Galena, PbS); Copper (Copper glance, Cu_2S); Silver (Silver glance or Argentite, Ag_2S); Iron (Iron pyrites, FeS_2)
Carbonate ores	Iron (Siferite, $FeCO_3$); Zinc (Calamine, $ZnCO_3$) , Lead (Cerrusite, $PbCO_3$)
Sulphate ores	Lead (Anglesite, $PbSO_4$)
Halide ores	Silver (Horn silver, AgCl); Sodium (Common salt or Rock salt, NaCl); Aluminium (Cryolite, Na_3AlF_6)
Silicate ores	Zinc (Hemimorphite, $2ZnO.SiO_2H_2O$)

18.1.1 Mineral Wealth of India

India possesses large deposits of minerals of some important metals such as iron, manganese, aluminium, magnesium, chromium, thorium, uranium, titanium and lithium. They constitute one-quarter of the world's known mineral resources. Mineral fuels (like coal ,petroleum and natural gas) constitute more than 80% while metallic minerals constitute only about 10% of the total volume of mineral production in a year. In this section, we shall list some of the important minerals of a few common metals such as Fe, Cu, Ag, Zn, Ti, Al, Sn, Pb and Na and their locations in India.

Important Ores of Some Common Elements

Iron	Iron ore reserves in the country are estimated at 1750 crore tonnes. Major iron ore mining is done in Goa, Madhya Pradesh, Bihar, Karnataka, Orissa and Maharashtra.
Aluminium	Its chief ore, bauxite is available in India in abundance. The annual production of bauxite is estimated to be more than 2 million tonnes. Important deposits of bauxite in the country occur in Bihar, Goa, Madhya Pradesh, Maharashtra, Tamil Nadu, Gujarat, Karnataka, Orissa, Uttar Pradesh, Andhra Pradesh, Jammu & Kashmir and Rajasthan.
Copper	India does not have rich copper ore deposits. The total reserves of the ore in the country are estimated around 60 crore tonnes. Major ore producing areas are Singhbum district (Bihar), Balaghat district (Madhya Pradesh) and Jhunjhunu district (Rajasthan).
Zinc and Lead	India has no significant deposits of lead ores. Lead and Zinc have been located at Zawar mines near Udaipur (Rajasthan) and at Hazaribagh

	(Jharkhand), Sargipalli mines in Orissa and Bandalamottu lead project in Andhra Pradesh. Some reserves have been located in Gujarat and Sikkim. The total reserves are estimated at about 360 million tonnes in which lead content is estimated to be around 5 million tonnes and zinc to be around 16 million tonnes.
Tin	Deposits of tinstone (SnO_2) are found in Hazaribagh (Jharkhand) and Orissa.
Silver	India does not possess rich silver deposits. Gold from Kolar fields and Hutti gold fields (Karnataka) and lead-zinc ores of Zawar mines (Rajasthan) contain some silver.
Titanium	Ilmenite ($FeTiO_3$) is recovered from beach sands of Kerala and Tamil Nadu. The estimated reserves are around 100 to 150 million tonnes.
Sodium	Tincal or Native borax ($Na_2B_4O_7.10H_2O$) is found in Ladakh and Kashmir.

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).

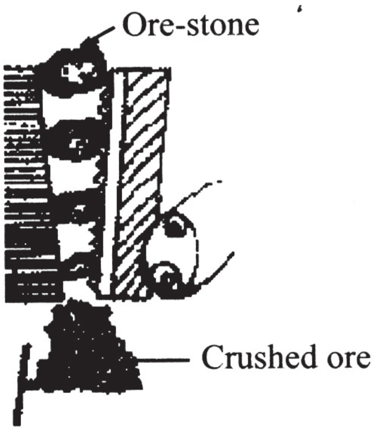


Fig. 18.1 : *Jaw Crusher*

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 are. The powdered are 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.

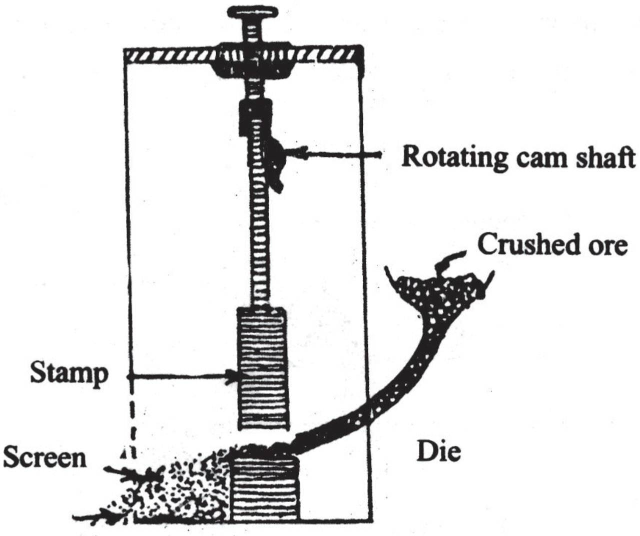


Fig. 18.2: *The Stamp mill*

18.2.2 Concentration or Dressing of the Ore

Generally, the ores are found mixed with earthy impurities like sand, clay, lime stone 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 (Fe_2O_3) tinstone (SnO_2) and gold (Au). In this method, as shown in the 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, tin stone (SnO_2) itself is non-magnetic but contains magnetic impurities such as iron tungstate ($FeWO_4$) and manganese tungstate ($MnWO_4$).

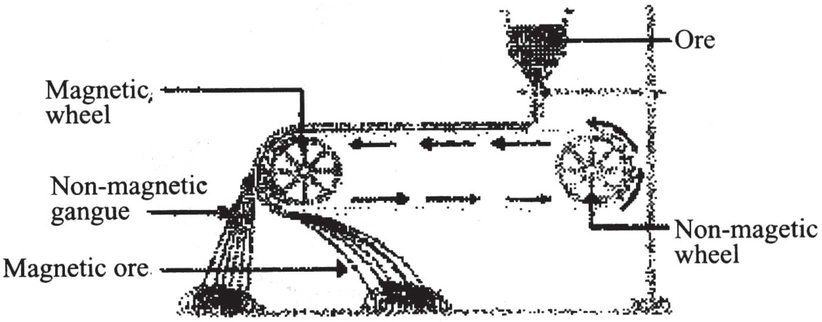


Fig. 18.4. : *Magnetic Separation*

The finely powdered ore is passed over a conveyer 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** ($CuFeS_2$). 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 weted 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).

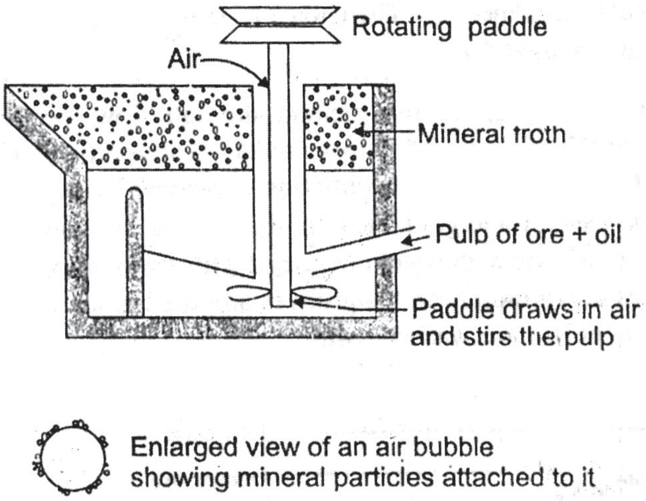


Fig. 18.5 : *Froth floatation*

(iv) Chemical method :

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 extraction of aluminium from bauxite ($Al_2O_3 .2H_2O$) . 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 aqueous solution of sodium hydroxide at 420 K under pressure. Aluminium oxide dissolves in sodium hydroxide, whereas, iron (III) oxide, silica and titanium (IV) oxide remain insoluble and are removed by filtration.

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

Sodium aluminate is diluted with water to obtain 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 Questions 18.1

1. Write the names of eight important metals. Give an example of one important ore of each metal.

   ....

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

   ....

3. Name some important methods of concentrating the ores.

   ....

4. Which method of concentration is applied in the following cases?

   (i) Magnetic ores (ii) Sulphide ores

   (iii) Bauxite ore

   ....

5. 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

$$ZnO_3 \longrightarrow ZnO + 2CO_2$$

(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.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$ZnO + C \longrightarrow Zn + CO$$

Although the ore has been concentrated in an earlier step, it is still contaminated with some gangue material which is finally removed in the reduction process by the addition of *flux* during smelting.

Flux is a chemical substance which combines with gangue at higher temperatures to form easily fusible material called *slag* which is not soluble in the molten metal. Flux are of two types :

Basic Flux :

On heating, lime stone is converted into calcium oxide used as basic flux which combines with acidic impurities like silica in metallurgy of iron and forms fusible calcium silicate ($CaSiO_3$) .

$$\underset{\text{(Limestone)}}{CaCO_3} \longrightarrow CaO + CO_2\ (g)$$

$$\underset{\text{(Basic flux)}}{CaO} + \underset{\text{(Acidic gangue)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

Acidic flux :

SiO_2 is used as acidic flux to remove basic impurity of FeO in metallurgy of Cu.

$$\underset{\text{(Acidic flux)}}{SiO_2} + \underset{\text{(Basic gangue)}}{FeO} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

The fusible slag, such as calcium silicate formed during smelting floats over the molten metal and is thus easily removed. Another advantage is that the slag provides a covering to the molten metal thus preventing it from getting oxidized by air.

(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. *Oxide* like chromium oxide (Cr_2O_3) or manganese oxide (Mn_3O_4) are reduced by aluminium powder is a highly exothermic reaction. This process is known as *Goldschmidt's Alumino-thennite reduction method.*

$$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3 + Heat$$

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

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 $TiC1_4$ (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 molybedenum 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) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

Copper glance

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

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

(Negative electrode)

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 1273 k. 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 Questions 18.2

1. Explain the following terms:
   Calcination, Roasting, Smelting, Flux and 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 into oxides.

   ....

4. How are oxide ores reduced ?

   ....

5. Name few materials which are used as flux in metallurgical processes.

   ....

6. 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 on 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.

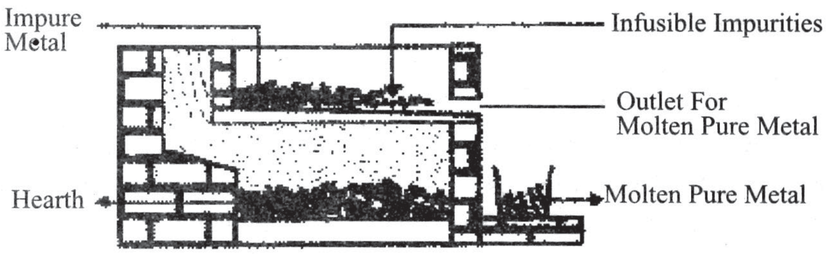


Fig. 18.6 : *Liquation*

(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).

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

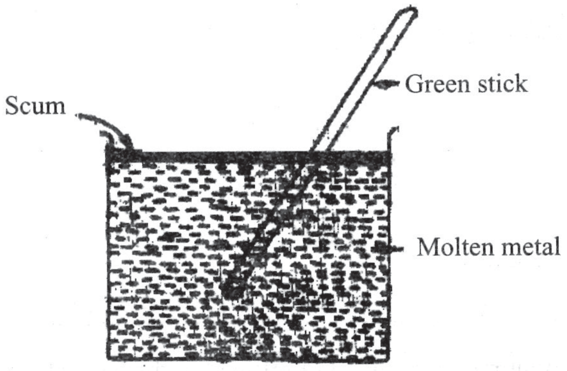


Fig. 18.7 : *Poling*

(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 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.*

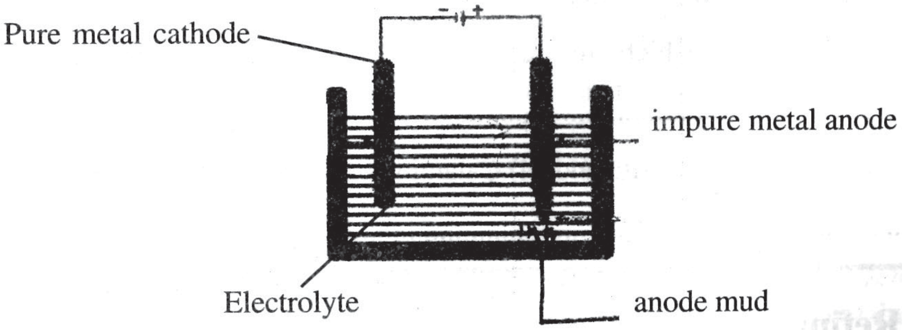


Fig. 18.8 : *Electrolytic Refining*

For example, in the electrolytic refining of crude copper (blister copper), a large piece of impure copper is made 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, anode becomes thinner while the cathode becomes thicker. The impurities like silver, gold settle down at the bottom of the cell as *'anode mud'*.

Intext Questions 18.3

1. State the nature of materials used for constructing cathodes and anodes in the electrolytic cell for refining of copper. Write chemical equations for the reactions which take place.

   ....

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

   ....

3. Which metals are refined by poling?

   ....

4. Name a metal which is purified by distillation.

   ....

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

   ....

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 *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 M_n^+ ions. Therefore, they are found in nature in association with some common anions, Le., 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 abundance of iron, aluminium and some amount of copper, tin, lead, silver and gold.
- Various steps involved in the extraction of metal are :
  (i) Crushing and pulverization
  (ii) Concentration or dressing of the ore
  (iii) Calcination or Roasting of the concentrated ore
  (iv) Reduction of the oxides to free metal

- The metals thus obtained are then purified by employing some suitable method, viz. *liquation, poling, distillation or electrolytic refining.*

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 metal sulphide 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 lime stone.
7. Describe the froth floatation method for the concentration of sulphide ore.
8. Give chemical equations involved in the self reduction method for the extraction of copper.

Answers to Intext Questions

18.1

1. Sodium (Na), Aluminium (Al), Silver (Ag), Iron (Fe), Zinc (Zn), Lead (Pb), Gold (Au), Mercury (Hg).

   Ores : rock salt, bauxite, argentite, haematite, zincite, galena, native gold, cinnabar, respectively.
2. *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.
3. Gravity separation, magnetic separation, froth floatation and chemical method.
4. (i) Magnetic separation method (ii) Froth floatation method (iii) Chemical method
5. 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. Oxide ores are reduced to metal by heating them with coke.
5. Silica, borax and other non-metallic oxides are acidic fluxes. Lime stone ($CaCO_3$) is a basic flux.
6. (i) $Al_2O_3 . 2H_2O \longrightarrow Al_2O_3 + 2H_2O$

   (ii) $ZncO_3 \longrightarrow ZnO + CO_2$

18.3

1. Cathode: Pure metal At Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

   Anode : Impure metal At Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

2. Liquation
3. Copper and tin
4. Zinc
5. Copper, Silver and Tin

18.3 Metallurgy

Some furnaces used in metallurgy

To obtain metals from the minerals, generally the minerals are mixed with other chemical substances and the reaction is carried out at high temperatures. These reactions take place in furnaces. The necessary heat is provided by either burning the fuels or by passing electricity. The furnaces are made with refractory bricks and then are covered with steel sheets outside. The furnaces are of different types depending on the chemical reactions that occur in them. The furnaces used in industry are of five types.

i.	Shaft furnace	ii.	Reverboratory furnace
iii.	Muffle furnace	iv.	Electric furnace
v.	Blast furnace and	vi.	Open Hearth furnace

Of these Reverboratory furnace and Blast furnace are of importance for the present study.

18.3.1.a Reverboratory furnace

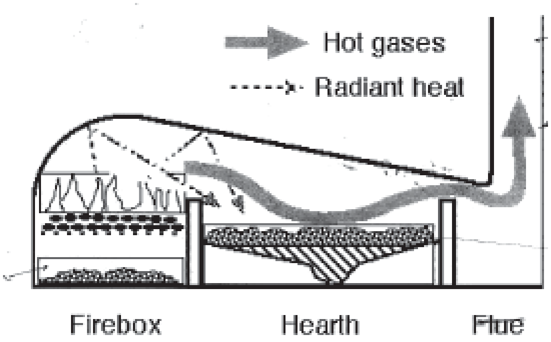


Fig. 18.3.1a Revorboratory Furnace

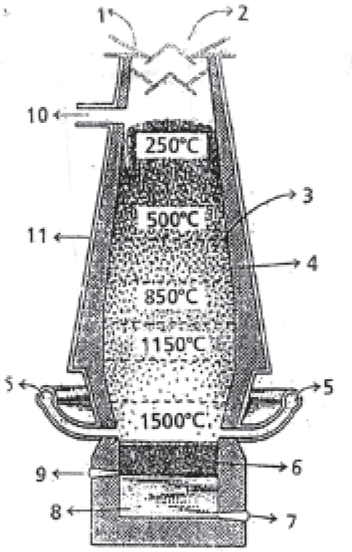
The reverboratory furnace is constructed with fire bricks. Its roof is a dome shaped and is constructed of silica bricks. The hearth is a spacious rectangular elevated space. All the reactions in the furnace take place in the hearth. A hopper is arranged at the top of the roof. Through this, the charge is dropped into the furnace. The charge may either be a solid or liquid. The fuel is burnt in ‘fire place’ or ‘fire box’. The hot gases produced in fire place rise to the roof of the furnace.

They are reflected on to the hearth to heat the charge. The waste gases formed in the furnace reactions leave the furnace through the chimney, heat content of the waste gases in this furnace cannot be used repeatedly. Hence, **the efficiency of the furnace is less.** This furnace is used to melt the charge or the metal. This furnace is used in the metallurgies of Cu, Steel and Pb.

18.3.1.b ii. Blast furnace:

Blast furnace is huge cylindrical furnace 100 feet tall and about 25 feet in diameter at widest part of the furnace. It is constructed of wrought iron. It is lined on the inside with fire bricks. The top of the furnace is fitted with a double cup and cone arrangement. By means of this device, the solid charge may be dropped into the furnace such that no gases escape from the furnace.

A conveyor belt, called a ‘skiphoist’ carries the charge to the top of the furnace and successive layers of ore, coke and lime stone are formed in the furnace. Near the bottom a series of pipes, called “tuyers are present. Through these tuyers hot air is blown. The reactions in the furnace result in waste gases that escape through the outlet at the top. The waste gases are burnt separately and the heat generated is utilized to heat the air that enters the tuyers. The receiver for the furnace products is present at the bottom of the furnace. This is known as “hearth” of the furnace. The products are obtained in the molten state. Connecting the cup and cone arrangement at the top with the hearth at the bottom, the body of the blast furnace is present. All the reactions, of the furnace take place in the body. The lowest temperature (400-500 ^{0}C) in the furnace is near the cup and cone arrangement, while the highest temperature (1500 ^{0}C) is noted near the tuyers.



1. Cone
2. Smelting material
3. Ore Reducing agent
4. Furnace brick lining
5. Hot air enterance
6. Gaugue
7. Hole
8. Liquid Material
9. Way to Gaugue
10. Blast furnacegas
11. Body

Fig. 18.3.1b Blast Furnace

Terminal Exercise

- Write about the furnaces used in metallurgy.
- Draw the Blast furnace diagram and label it.
- Draw the diagram of Reverboratory furnace and label it.

What you have learnt

- Furnaces used in metallurgy
- Blast furnace structure.
- Construction of Reverboratory furnace.

18.3.2 Copper

Occurrence:

Copper metal occurs in the elemental from to a little extent. It occurs mostly in the combined state as its oxy compounds or sulphur compounds. The important minerals are:

Name of the mineral	**formula**
Cuprite of ruby copper ore	Cu_2O
Copper glance	Cu_2S
Copper pyrites	$CuFeS_2$ or $Cu_2S.Fe_2S_3$

Extraction of copper:

The element copper is extracted from the sulphide ores mainly. The method of treatment of the ore depends on the kind of ore used.

Extraction from sulphide ore

Copper pyrites is the main source of copper metal. Copper metal is obtained by smelting process.

The various steps in the smelting process are given below.

1. The ore is first crushed in jaw crushers and in ball mills. The finely divided ore is concentrated by froath floatation process. The finely divided ore is suspended in water. A little pine oil is added and then the mixture is vigorously agitated by a current of air. The froth formed carries the ore particles almost completely. The gangue sinks to the bottom of the tank. The froath is separated and about 95% concentrated ore is obtained.

2. **Roasting** on the hearth of a reverboratory furnace in a free supply of excess air removes volatile impurities like As or Sb from the ore. And a mixture of sulphides of copper and iron is obtained. The sulphides are partially oxidized to the respective oxide. The reactions are as follows.

$$Cu_2. FeS_3 + O_2 \longrightarrow Cu_2S + FeS + SO_2$$

$$2\,Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2\,FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

3. **Smelting:** The roasted ore is mixed with a little coke and sand and smelted in a blast furnace and fused. A blast of air, necessary for the combustion of coke, is blown through the tuyeres present at the base of the furnace. The oxidation of the sulphides of copper and iron will be completed further. A slag of iron silicate is formed according to the reactions given below.

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$

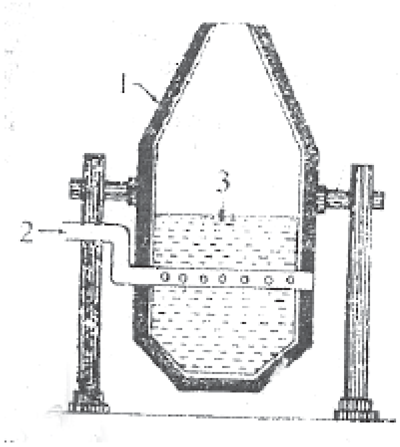
$FeO + SiO_2 \longrightarrow FeSiO_3$ (Slag)

$Cu_2O + FeS \longrightarrow Cu_2S + FeO$

The product of the blast furnace consists mostly of Cu_2S and a little of ferrous sulphide. This product is known as "Matte". It is collected from the outlet at the bottom of the furnace.

4. **Bessemerization:** The matte is charged into a Bessemer converter. A Bessemer converter is a pear-shaped furnace. It is made of steel plates. The furnace is given a basic lining with lime or magnesium oxide. The converter is held in position by trunnions and can be tilted in any position. A hot blast of air and sand is blown through the tuyers present near the bottom. Molten metal, the product in the furnace, collects at the bottom of the converter.

   Reactions that took place in blast furnace go to completion. Almost all of iron is eliminated as a slag. Cuprous oxide combines with cuprous sulphide and forms Cu metal

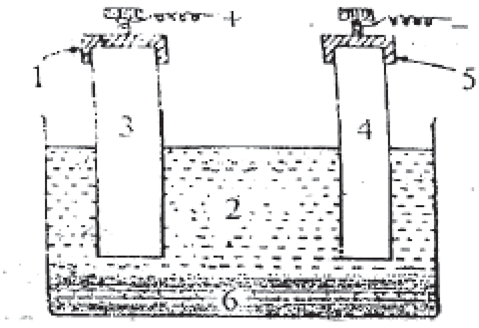


Fg. 18.3.2.a Bassemerization of matte.
1. Bessemer converter 2. Sand air 3. Molten Ali

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

The molten metal is cooled in sand moulds. SO_2 escapes. The impure copper metal is known as "Blister copper" and is about 98% pure.

5. **Refining:** The Blister copper is purified by electrolysis. The impure copper metal is made into plates. They are suspended into lead-lined tanks containing copper (II) sulphate solution. Thin plates of pure copper server as cathode. The cathode plates are coated with graphite. On electrolysis, pure copper is deposited at the cathode.



Fg. 18.3.2.b Electrolytic refining of Cu.

1. Anode 2. Copper sulphate solution 3. impure Cu (or) Blister Cu
4. Pure copper 5. Cathode 6. Anode mud.

18.3.3. Zinc-Occurrence and extraction

Ancients used zinc in the form of its alloys with copper. They called the metal by the name **Yashada** in Ayurveda medicine.

a) **Occurrence:** Zinc is not found in the native state. Its important minerals are given below.

Name of the mineral	**Formula**
Zinc blend	ZnS
Zincite	ZnO
Calamine	$ZnCO_3$

Other minerals are Franklinite ($ZnO.Fe_2O_3$) Willemite (Zn_2SiO_4). These are of minor importance.

b) **Extraction of zinc:** The metal Zn can be extracted from its minerals in different ways depending on the ore.

Reduction process.

Zinc blend ore is treated in the following states.

i) **Crushing:** The ore is crushed to a fine powder in ball mills.

ii) **Concentration of the ore:** The ore is concentrated first by gravity process. The crushed ore is washed with a stream of water on a Wilfley's table. The tables have a corrugated top and are under a rocking motion. Due to this motion, the lighter gangue particles are washed away by the stream. The heavier ore particles settle to the bottom of the table.

The partially concentrated ore is further concentrated by froth floatation process. The ore particles go with the froth.

The concentrated ore is subjected further to electromagnetic separation if iron oxide is present in the gangue. Iron oxide is magnetic and so forms a heap nearer to the magnetic pole.

iii) The concentrated ore thus obtained is roasted in rotary shelf burner which is provided with horizontal shelves and raking arms. The ore is added at the top and zinc oxide is collected from the bottom. The following reactions take place.

$$2\,Zn\,S + 3O_2 \longrightarrow 2\,Zn\,O + 2\,SO_2$$

$$Zn\,S + 2\,O_2 \longrightarrow Zn\,SO_4$$

$$2\,Zn\,SO_4 \longrightarrow 2\,ZnO + 2\,SO_2 + O_2$$

If calamine is the starting material for extraction, the ore is directly calcined to get zinc oxide.

$$Zn\,CO_3 \longrightarrow ZnO + CO_2$$

iv) Reduction: Three methods are in practice for the reduction of the oxide to the metal. The most commonly used method is the Belgian process. In this process, the roasted ore is mixed with coal or coke intimately and is taken in fireclay or earthen ware retorts. The retorts are made of fireclay which are bottle shaped tubes. These closed at one end. The other end in connected to air cooled earthen ware condenser. A large number of retorts are placed in tiers in large furnace and heated in 1100^0C by burning the gas. 'Prolongs' made of sheet iron are attached to the condensers. The metal condenses in these earthen ware condensers and the prolongs. The metal powder collected is mixed with some zinc oxide and is known as "zinc dust". Some of the zinc metal is collected in the fused state. This is solidified in moulds. This metal is called "zinc spelter".

$$ZnO + C \;\text{——}\; Zn + CO$$

$$ZnO + CO \;\text{——}\; Zn + CO_2$$

Spelter contains some impurities such as cadmium and lead.

A second method for reduction of the oxide consists in heating a mixture of zinc oxide and coke in an electric furnace at 1200^0C. The charge is introduced at the top of the furnace and the spent material is taken off at the bottom. Zn vapour and CO escape at the top and from these the metal condensed in earthen ware vessel.

v) Electrolytic refining: Very pure zinc is obtained by electrolysis. The electrolyte is zinc sulphate solution containing a little H_2SO_4. Impure zinc is made as anode and the pure zinc plates are made as cathode.

vi) Other methods of refining: Commercial Zn contains 1.3% of lead. Of iron and traces of cadmium and arsenic. This is purified by liquation or fractional distillation process.

18.3.4. Silver – Occurrence and principles of Extraction

Silver is known to man from times immemorial. It is used in ornamental and other household valuable.

1. Occurrence

Silver occurs in native state associated with copper and gold as alluvial sands. It occurs in the combined state. Some of the important minerals are given below.

Name of Mineral	Formula
Argentite or Silver glance	$Ag_2 S$
Horn Silver or Chlorargyrite	$Ag Cl$
Pyrargyrite of Ruby silver ore	$[Ag_3 SbS_3]$

2. Extraction of silver

Silver is mostly worked out from sulphide ores. The commonest procedure is the cyanide process. This is also known as Mac Arthur Forrest process. The different steps involved in the process are:

1. Crushing: the ore, Argentite, is crushed to a fine powder in ball mill

2. Concentration of the ore: The finely powdered ore is concentrated by froth floatation process. The ore is suspended in water. Suitable oil like pine oil and little sodium carbonate is added to it. The suspension is agitated by a current of air. The ore particles are wetted more by oil and so go With the forth. The concentrated ore is separated from the foam.

3. Treatment with sodium cyanide: The concentrated ore is digested with a dilute solution (1%) of sodium cyanide for many hours. The silver gradually passes into solution as a complex sodium. argentocyanide,

$$Ag_2S + 4\,NaCN \longrightarrow \underset{\text{Sodium argento cyanide}}{2\,Na\,[Ag\,(CN)_2\,]} + Na_2S$$

The air blown in oxidizes the sodium sulphide to sodium thio sulphate and then to sodium sulphate. This forces the above reaction to go to completion.

$$2Na_2\,S + 2O_2 + H_2O \longrightarrow Na_2\,S_2\,O_3 + 2NaOH.$$

$$Na_2\,S_2O_3 + 2O_2 + 2NaOH \longrightarrow 2\,Na_2\,SO_4 + H_2O.$$

4. Displacement of Silver: The silver in now precipitated from the sodium argento cyanide solution by the addition of zinc dust. The precipitation of Ag is due to the noble nature 9 Ag. Metal.

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

5. Fusion: The silver that is precipitated is filtered off. Then it is fused with KNO_3 or fusion Mixture to oxidize any zinc present as impurity.

6. Purification Ag: The silver obtained in fusion is refined by electrolytic process to get very pure metal. Impure silver (contains Zn, Cu & Au as impurities) is made as the anode in the electrolytic bath containing $AgNO_3$ with a little HNO_3. The cathode is made of pure silver metal.

18.3.5. Process of molten electrolysis.

Alluminium – Process of molten electrolysis.

In 1827 Wohler obtained the metal Al by the action of potassium on aluminium chloride. It is the 3rd most abundant element on earths crus.

a. Occurrence

Al is an active metal. So it does not occur free in nature. The important minerals of Al are given below:

Nature of mineral	Formula
Corundum	Al_2O_3
Diaspore	$Al_2O_3 . H_2O$
Bauxite	$Al_2O_3 . 2 H_2O$
Gibbsite	$Al_2O_3 . 3 H_2O$
Cryolite	$3NaF . AIF_3$, (or) Na_3, AIF_6
Felspar	$K Al Si_3 O_8$
Spinels	Aluminates of Mg, Fe & Mn.

(spinels have the formula AB_2O_4 where 'A' is a group II A element or a transition metal in the +2 Oxidation state and B is a group IIIA metal or transition metal in +3 oxidation state.

Example: $Mg Al_2O_4$

b. Extraction

For the purpose of extraction of Al, bauxite is the best source. From bauxite Al is obtained by electrolysis. For this purpose pure bauxite is necessary. The following steps are used in the extraction of Aluminium.

i. Purification of Bauxite

The method of purification of bauxite depends on the nature of the impurity present. If bauxite contains iron oxide as impurity, it can be purified by either Baeyer's process or Hall's process. When the bauxite contains more SiO_2 as impurity, it is purified by Serpeck's process.

Baeyer’s Process:

The finely powdered ore is roasted. Ferrous oxide present in ore is converted into ferric oxide. Then roasted ore is digested with a concentrated solution of sodium hydroxide under pressure at 423 K for a few hours in an autoclave. It dissolves in water while the impurity, Fe_2O_3 and clay, remains unaffected. They are removed by filteration.

$$Al_2O_3\ ,\ 2H_2O_{(s)} + 2\ NaOH_{\ (aq)} + 2Na\ AlO_{2(aq)} + 3H_2O_{(1)}$$

The filtered sodium meta aluminate is diluted with water when hydrated aluminium oxide is precipitated. To hasten the process of precipitation a crystal of Al $(OH)_3$ is added. The crystal acts as a seeding agent. Sodium meta-aluminate undergoes hydrolysis and forms aluminium hydroxide.

$$2Na\ AlO_{2(aq)} + 4H_2O \longrightarrow 2NaOH_{\ (aq)} + Al_2O_{3\ –}\ 3H_2O \downarrow$$

(hydrated Al_2O_3)

Or $2Al(OH)_3 \downarrow$ (aluminium hydroxide)

The precipitate thus obtained is collected and washed. It is ignited at 1200^0C to get pure anhyfrous Aluminium oxide alumina, $Al_2O_{3.}$

$$2Al\ (OH)_{3(s)} \longrightarrow Al_2O_{3(s)} + 3H_2O_{(l)}$$

Hall’s process

In this method the bauxite ore is fused with sodium carbonate.. Al_2O_3 is converted sodium meta-aluminate. It is extracted with water. Sodium meta-aluminate goes into the solution. The impurities of Fe_2O_3 or silica are left behind. The extracted sodium meta aluminate is separated by filtration. This solution is saturated with CO_2 at 323 – 333K. Aluminium hydroxide is precipitated as a result of the hydrolysis of sodium meta-aluminate. The precipitate is filtered off and washed. It is dried and ignited to get alumina.

$$Al_2O_3\text{-}2H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$$

$$2NaAlO_{2(aq)} + 3H_2O_{(l)} + CO_{2(g)} \longrightarrow 2Al(OH)_{3(s)}\ {}^{-}\ Na_2CO_{3(aq)}$$

Serpek’s process:

This method of purification is employed for bauxite which contains silicon dioxide as the main impurity (in large amount).

In this process powered bauxite is mixed with coke and is then heated to 2075k in a current of nitrogen. Alluminium nitride is formed. Silicon dioxide is reduced to silicon and it escapes as vapour.

$$SiO_2 + 2C \downarrow \longrightarrow Si \uparrow + 2CO \uparrow$$

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

The aluminium nitride, formed in the above reactions is hydrolysed to get hydrated aluminium oxide. This is washed, dried and then ignited as in Hall's process or Baeyer's process.

$$AlN + 3H_2O \longrightarrow Al\,(OH) \downarrow + NH_3 \uparrow$$

$$2Al\,(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

Pure aluminium oxide obtained by any of the above methods is subjected to electrolytic reduction to get aluminium.

18.3.5.a Electrolytic reduction of alumina:

Pure alumina is a bad conductor of electricity. Its fusion temperature 2050^0C is also very high. So, it is not easy to electrolyse alumina. Cryolite, $Na_3\,AlF_6$ is added to increase the conductivity of the fused alumina. To lower the melting point of alumina fluorspar is added. Then it is electroysed.

Electrolysis is carried out in an iron or steel tank. The tank is lined inside with graphic (carbon)

That acts as cathode. Anode consists of number of carbon or copper rods suspended from the top of the cell. The anodes are immersed partially into the electrolyte. The electrolyte consists of a fused mixture of alumina, cryolite and fluorspar. The surface of the electrolyte covered with powdered coke. This prevents the oxidation of the metal formed in the electrolysis. Heat produced by the current keeps the mass in fused state at 1175 to 1225k. the following reactions take place in the electrolytic cell under these conditions.

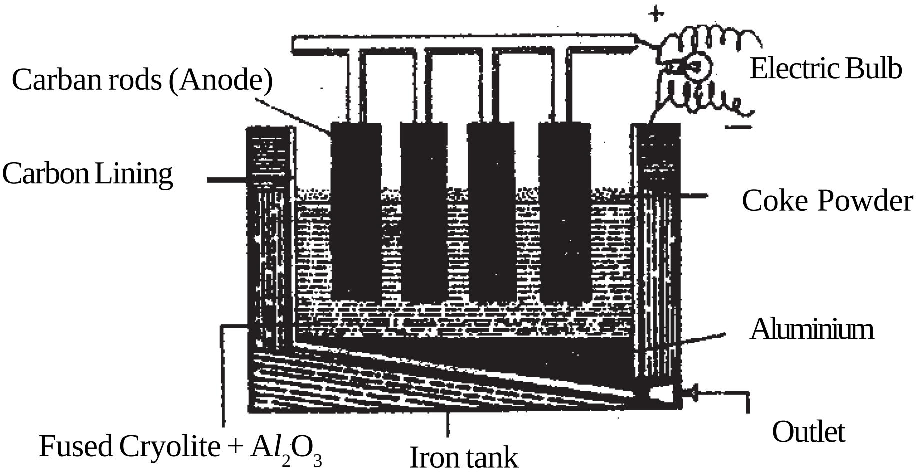


Fig. 18.3.5.a Electrolytic reduction of Alumina

$$Na_3AlF_6 \longrightarrow 3NaF + AlF_3 \quad \text{(cryolite)}$$

$$4AlF_3 \longrightarrow 4Al^{3+} + 12F$$

Aluminium ions move towards the cathode (i.e. carbon lining) and they are discharged. Aluminium metal is formed. Flouride ions are discharged to give fluorine at the anode.

At cathode : $4Al^{3+} + 12e^- \longrightarrow 4\,Al.$

At anode : $12F^- \longrightarrow 12F + 12e^-$

$$2\,Al_2O_3 + 12F \longrightarrow 4AlF_3 + 3O_2$$

Aluminium, produced at the cathode, sinks to the bottom of the cell. It is removed from time to time through tapping hole (Th). Fluorine formed at the anode reacts with alumina. Oxygen is displaced with the formation of aluminium fluoride. Oxygen which is evolved at the anode either escapes or reacts with the carbon electrodes (i.e., anode). CO and CO_2 are formed corroding the electrodes. For this reason only the electrodes have to be frequently replaced Alumina is added at intervals. In the process, 99% pure aluminium is obtained.

18.3.5.b Refining of Aluminium:

Aluminium obtained by the above process contains impurities like Si, Cu, Mn, etc. It is refined by Hoope's electrolytic method.

The electrolytic cell used for refining of aluminium consists of an iron tank lined inside with carbon. It contains three layers of fused masses. These layers differ in their specific gravities. The upper layer is of pure aluminium. A number of graphite rods act as cathode. They are suspended from the fop into the upper layer. The middle layer consists of fused mixture of fluorides of sodium, barium and aluminium. The layer acts as an electrolyte. The bottom layer contains impure aluminium and carbon lining of the tank acts as anode. To increase the density of fused impure A1 in this layer copper and silicon are added.

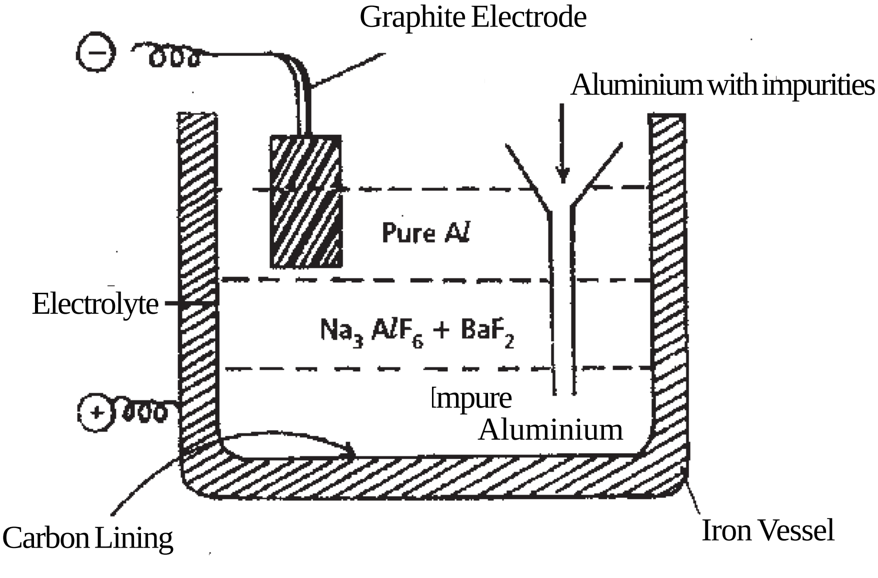


Fig. 18.3.5b Purification of Aluminium in Hoopmethod.

On passing current, aluminium ions from the middle layer are discharged at the cathode layer (upper layer). Pure A1 is deposited in the layer. At the same time an equivalent amount of aluminium passes into the middle layer from the bottom layer. 99.89% is the result of this process.

18.3.6.a Magnesium – Process of molten Electrolysis

a. Occurrence

Magnesium does not occur free in nature. It is widely distributed in nature in the combined state. It is present in sea water as halides, in animal blood, in vegetable kingdom as chlorophyll, in certain spring water as magnesium sulphate.

The important mineral of magnesium are given below:

Name of the Mineral	**Formula**
Magnesite	$MgCO_3$
Dolomite	$CaCO_3$, $MgCO_3$
Carnallite	KCl , $MgCl_2$, $6H_2O$
Keiserite	$MgSO_4$, H_2O
Epsom salt or Epsomite	K_2SO_4 , $MgSO_4$, $MgCl_2$, $6H_2O$
Asbestos	$CaMg_3(SiO_3)_4$

b. Extraction

Magnesium is prepared on a large scale by the electrolysis of either magnesium chloride or magnesia. These materials are obtained from carnallite, magnesite or sea water.

i. Electrolysis of fused magnesium chloride (from Carnallite)

The magnesium chloride necessary for electrolysis is obtained from Carnallite. To get magnesium from Carnallite, the mineral must be dehydrated to get anhydrous MgCl. Then only the $MgCl_2$ can be electrolyzed. To prepare anhydrous mineral, the mineral is heated to lose four molecules of water directly and easily. Removal of the other two molecules of water is very difficult. The reason is that $MgCl_2$ undergoes hydrolysis forming electrically on conducting Mg compounds. Then it becomes difficult for the electrolysis to be carried out. However, if the mineral is heated in the presence of large amounts of HCl gas, the following hydrolysis reaction can be carried out.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

$$MgCl_2 + H_2O \longrightarrow MgO + 2HCl$$

This also increases the conductivity of the fused mass. During the last stages of dehydration of carnallite, mineral is heated to 350^0C in a current of HCl. Afterwards, the mineral is mixed with an equal amount of NaCl and heated to 700^0C. the presence of KCl, NaCl in anhydrous $MgCl_2$ prevents hydrolysis and also increases the electrical conductivity. The $MgCl_2$ obtained in this way is electrolyzed.

The electrolysis is carried out in an iron tanks. The electrolyte is anhydrous magnesium chloride or Carnallite prepared as described above. The temperature of the electrolytic bath is maintained at 970^{0}C by external heating. The iron tank itself acts as cathode. The anode consists of a carbon graphite coated with lead rod. The anode is covered by a porcelain tube. The electrolysis is carried in an atmosphere of coal gas or H_2 in order to prevent the oxidation of magnesium metal. The metal obtained is 99% pure. The reactions take place as follows.

The reactions that take place are

Ionization : $MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$

At Cathode (deduction) : $Mg^{2+} + 2e^- \longrightarrow Mg$

At Anode (oxidation) : $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$

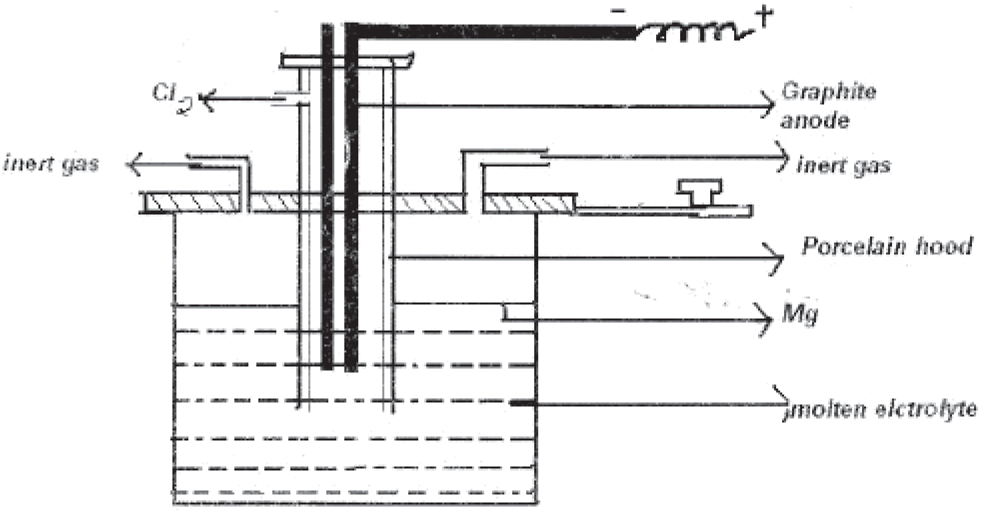


Fig. 18.3.6.a Preparation of magnesiun from carnalite

The chlorine gas rises through the porcelain pipe and is collected. By maintaining the temperature at 967^{0}C, not only the mineral is fused but also the metal obtained is in the molten state. The magnesium metal being lighter than the electrolyte, rises to the surface and there is solidifies. It is skimmed off with perforated ladles from time to time. The metal is 99.99% pure. It can be further purified for higher purity of the metal.

18.3.6.b Extraction of Mg from Magnesite: Electrolytic method.

Magnesium metal can also be obtained from magnesite. The magnesite mineral is calcined and the magnesia (MgO) thus obtained is melted and electrolyzed. In the commercial preparation, magnesia is mixed with the fluorides of Mg, Ba and Na in a steel tank at 1170K to 1220K. A set of cast iron rods are projected from the bottom of the tank into the electrolyte. The anode consists of carbon suspended from the top of the tank. Magnesium metal is liberated at the cathode in the molten state. It is lighter than the electrolyte and so rises to the top and solidifies due to cooling by air. This solid scum prevents the oxidation of the molten metal by atmospheric air. The metal is removed periodically and fresh amounts if magnesia are added simultaneously to the tank. The reactions in the process can be written as follows.

The reactions that take place are

Ionization : $MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$

At Cathode (reduction) : $Mg^{2+} + 2e^- \longrightarrow Mg$

At Anode (oxidation) : $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$

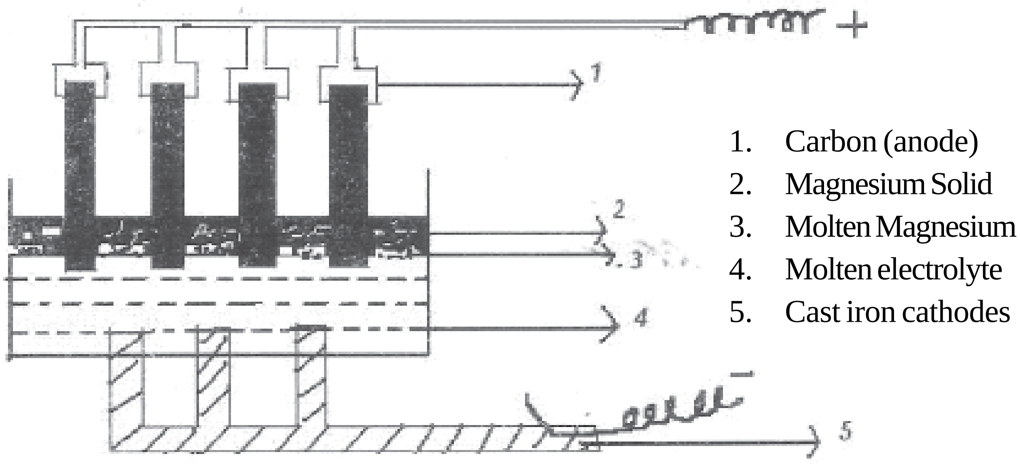


Fig. 18.3.6.b Extraction of Magnesium from Magnesite

18.3.7 Sodium

a. Occurrence

Sodium is a very reactive metal. So, it does not occur in the native state. It occurs only in the combined state. It is distributed abundantly in the nature. Some important minerals are given below.

Name of the mineral	**Formula**
Common salt or rock salt in sea water	$NaCl$
Chile salt petre of Caliche	$NaNO_3$
Borax or tincal	$Na_2B_4O_7\ \ 10H_2O$.
Mirabilite	Na_2SO_4.

b. Extraction of Sodium

The compounds of alkali metals are to thermal treatment and hence such methods are useless to prepare these metals. The common methods of extraction of the metals are not applicable to alkali metals. Electrolytic reduction of their fused compounds is the only alternative for the extraction of alkali metals. They are

i. Castner process and ii. Down's process.

18.3.7.a. i. Castner process:

The type of the electrolytic cell used in the process for the electrolysis of fused caustic soda is shown in fig.

Fused sodium hydroxide is taken in a cylindrical iron tank. It works as the electrolyte. The electrolyte is fused by heating to about 330^{0}C with a ring of burners. From the bottom of the tank a cylindrical iron rod is introduced into the fused electrolyte. This rod functions as anode. A hollow cylindrical nickel anode surrounds the iron cathode. The anode and cathode are separated by a nickel wire gauze. It is provided with a receiver fitted with a loose cap at the top. During the process of electrolysis, the sodium ions migrate to the cathode and get deposited. Since the molten sodium is heavier than sodium hydroxide it rises to the surface. The nickel wire gauze prevents the passage of sodium to the anode. Sodium is removed by the perforated ladles from time to time.

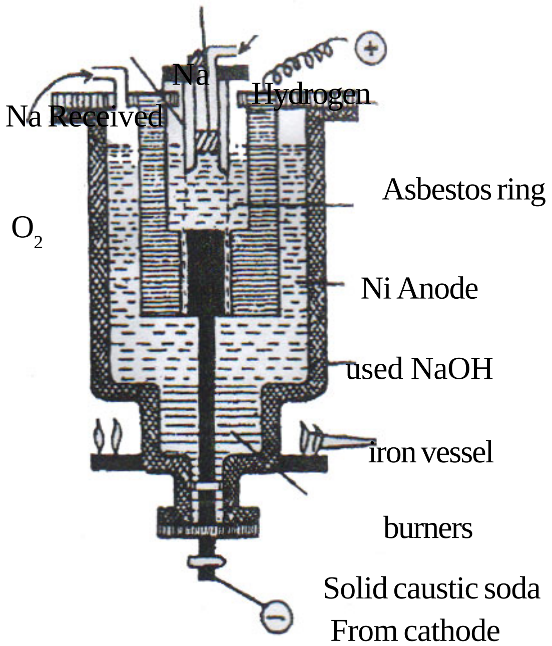


Fig. 18.3.7.a Preparation of Sodium - Castner process

The following electrode reactions take place. Na is liberated at the cathode and oxygen at the anode. Na metal reacts with the small amounts of water produced at the anode give H_2

Ionization : $4NaOH \longrightarrow 4Na^{+} + 4OH^{-}$

At Cathode (Reduction reaction) : $4Na^+ + 4e^- \longrightarrow 4Na$

At anode (Oxidation reaction) : $4OH^- \longrightarrow 2H_2O + O_2 + 4e$

$$2\,Na + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$$

The impurities settle down at the bottom of the tank. The temperature in the cell should be maintained around 330^{0}C to prevent any sodium metal from going into fused sodium hydroxide. This might reduce the yield of sodium.

18.3.7.b. ii. Down's process.

The manufacture of sodium by previous process is costly and moreover the sodium hydroxide necessary for the process is prepared from sodium chloride by electrolysis. Pure sodium chloride melts at 803^{0}C. At this temperature, separation of sodium from fused electrolyte (sodium hydroxide) is difficult. So, the melting point of the electrolyte is brought down to a temperature between 500^{0}C and 600^{0}C. This can be achieved by the addition of $CaCl_2$, CaF_2 or KCl to the electrolyte. By doing this there are three advantages.

a. the melting point of NaCl is decreased. So, the fuel wastage is reduced very much and hence the probability of sodium catching fire is avoided.

b. at lower temperatures, the vapour pressure of sodium in air is reduced. Therefore, loss by evaporation of sodium is minimized.

c. At lower temperature loss of sodium due to its dissolution in fused electrolyte is also reduced. Moreover, the process of electrolysis takes place smoothly and the yields are improved. The reactions that take place in the cell can be written as given below.

In the Down's process, the electrolytic cell is made of an iron or steel tank. It is lined with refractory material inside. These bricks are also acid resistant in nature. A graphite rod introduced from the bottom of the tank acts as anode. The anode is surrounded by a ring shaped iron cathode. A conical connecting hood is placed above the anode. The iron gauze acts as partition and separates the anode and the cathode. The wire gauze prevents the passage of sodium liberated at the cathode and anode. Also the Na is not allowed to mix up with Cl_2 that is produced at anode.

Ionization : $2NaCl \longrightarrow 2Na^+ + 2Cl^-$

At Cathode (reduction reaction) : $2Na^+ + 2e^- \longrightarrow 2Na$

At Anode (oxidation reaction) : $2\,Cl^- \longrightarrow Cl_2 + 2e^-$

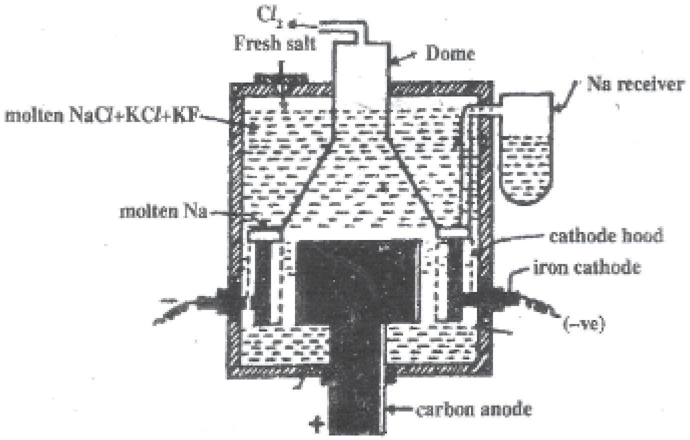


Fig. 18.3.7.b Preparation of Sodium - Down's process

Calcium is possible impurity in this method. Inspite of this, the metal obtained is very pure.

18.3.8.a. Iron – occurrence and principle of extraction

Iron is known to ancient Indians. Many monumental works were done with iron and steel. Ashoka pillar in Delhi; Puri Jagannath temple are good examples for this.

Occurrence:

Iron element is present in meteorites. But Fe occurs mostly in the combined state. The important minerals are given here below

Haematite (reddish brown colored) - Fe_2O_3
Magnetite (Magnetic oxide) - Fe_3O_4
Limonite (hydrated oxide) - $2Fe_2O_3 \cdot 3H_2O$
Siderite (spathic iron ore) - $FeCO_3$
Iron pyrites - FeS_2

The chemistry of iron can be studied under three sections depending upon the type on iron required. The sections are:

A. manufacture of cast iron

B. manufacture of wrought iron and

C. manufacture of steel

A. Manufacture of cast iron

The manufacture of cast iron from the ores involves several steps. They are given in the following steps.

i. Dressing of the ore:

Hematite or magnetite is used for the preparation of cast iron. The ore needs no concentration on most of the occasions. Only in a few cases the ore is washed with water.

ii. Preliminary roasting or calcinations:

the ore is mixed with a small amount of coal and heated in a free supply of air. The following changes occurs in the kilns.

$$2FeO_3 . 3H_2O \longrightarrow Fe_2O_3 + 6H_2O$$

$$FeCO_3 \longrightarrow FeO + CO_2$$

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

Volatile materials like water, CO_2 , S & As are removed either directly or by oxidation. Any ferrous oxide present in the mineral is oxidized to ferric oxide. The most important of all the mass becomes porous.

iii. Blast furnace treatment:

The roasted ore, coke (no sulphur present in it) and lime stone are mixed in 8:4:1 parts by weight. The change is fed into the blast furnace. A blast of hot air is sent into the furnace through the tuyeres. The tuyeres are cooled by water circulation around them in pieces. The temperature range in the furnace is 500^0-2000^0 k. various reactions take place in the blast furnace are given in the next lines.

Sno.	Temperature range & name of the zone	Changes Occuring	Chemical equations
1	4000-7000^{0}C Zone of reduction	Spongy iron is formed. Iron oxide is reduced	$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
2.	800 C - 1000 C	CO_2 is reduced to CO Limestone decomposes to lime and CO_2. Lime Combines with SiO_2 to from the slag, $CaSiO_3$	$CO_2 + C \rightarrow 2\ CO+163\ kj$ $CaCO_3 \rightarrow CaO+CO_2$ $CaO + SiO_2 \rightarrow CaSiO_3$
3.	12000C Zone of fusion	Coke burns to CO_2 Porous iron melts. Any iron oxide remaining is completely reduced to	$C + O_2 \rightarrow CO_2$
4.	Above 130000C near the hearth.	Fe. Molten iron collects in the bottom of the hearth. Slag floats on iron liquid.	

Table 18.3.8

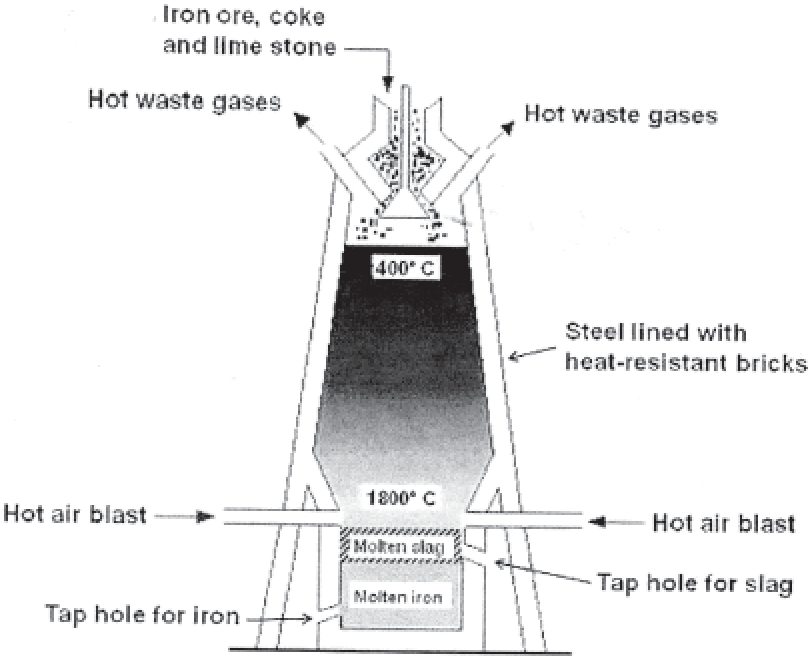


Fig. 18.3.8.a Blast Furnace

The waste gases known as the "blast furnace gas", escape from the outlet at the top. They are burnt and the heat generated is utilized to heat the blast of air entering the tuyeres. The iron obtained is known as "Pig Iron". The pig iron is melted and poured into moulds. The solid iron obtained by cooling pig iron is called as "cast iron". It contains nearly 4% C.

18.3.8.b Manufacture of Wrought iron

Wrought iron is the purest form of iron containing about 0.2%C. It is prepared by heating cast iron in a reverboratory furnace. The furnace is given a basic lining of iron oxide. The impurities and the carbon present in cast iron combine with the lining. The impurities form a slag and carbon is oxidized to 'CO' and escapes and burns with a blue flame. The flames are known as "puddler's Candles".

Hence the process is known as puddling process. The molten mass on the hearth of the furnace is stirred with iron rods. The plastic iron gathers at the end of the rods as balls. The balls contain the slag and are hammered out.

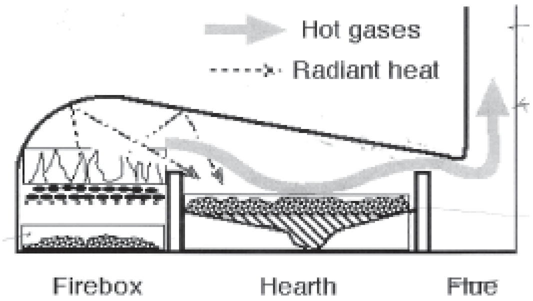


Fig. 18.3.8.b Reverboratory Furnace

18.3 Intext Questions

1. Mention the types of roasting.

   ....

2. Mention two types of minerals & formulae of iron.

   ....

3. Write the names of following minerals.

   i) $ZnCO_3$ ii) Zn_2SiO_4 iii) $ZnO . Fe_2O_3$

   ....

4. For which minerals calcination is applied?

   ....

5. Write the equations for the reaction between silver glance and sodium cyanide.

   ....

6. Write the formulae for the following.

   1) Mirabilite 2) Tinkal

   ....

What you have learnt

1. Furnaces used in the extraction of metals.
2. Extraction of Zn, Cu, Ag, Al, Na, Mg, Cast iron and wrought iron
3. Purification of metals

Terminal Exercise:

1. Mention two minerals of Al and write its extraction.
2. How do you extract chlorine from its Chloride ore?
3. Explain the industrial manufacture of Sodium by castners method.
4. Explain the extraction of silver.
5. Write the extraction of Al from bauxite.
6. Explain froath floatation.

18.3. Answers to intext Questions:

1. Oxidation, sulphatising and chloridising roasting.
2. i) Haematite Fe_2O_3, ii) Magnetite Fe_3O_4
3. i) calamine ii) willemite iii) Frank lenite
4. For the minerals of carbonates and bicarbonates, calcination is applied.
5. $Ag_2S + 4NaCN \qquad 2\,Na\,[Ag\,(CN)_2] + Na_2S$
6. i) Na_2SO_4 ii) $Na_2B_4O_7 . 10H_2O$.

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. Yellow glow of street light 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 of bone fracture.

In this lesson we shall study occurrence, physical and chemical properties and uses of hydrogen and s-block elements (alkali metals 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 basic nature of oxides and hydroxides and
- explain the solubility and thermal stability of their carbonates and sulphates.

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 $1s^1$.

19.1.1 Position in the Periodic Table

Where is hydrogen placed in periodic table?

Elements are place in the periodic table according to their outermost electronic configuration. So hydrogen ($1s^1$) may be placed with alkali metals (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 ${}^{1}_{1}H$ or H, deuterium ${}^{2}_{1}H$ or D and tritium ${}^{3}_{1}H$ 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 ${}^{1}_{1}H$ isotope, 0.014% of D and $7 \times 10^{-16\%}$ of T, therefore the properties of hydrogen are essentially those of the lightest isotope. Tritium is radioactive and emits low energy β particles ($t_{1/2}$ = 12.33yrs).

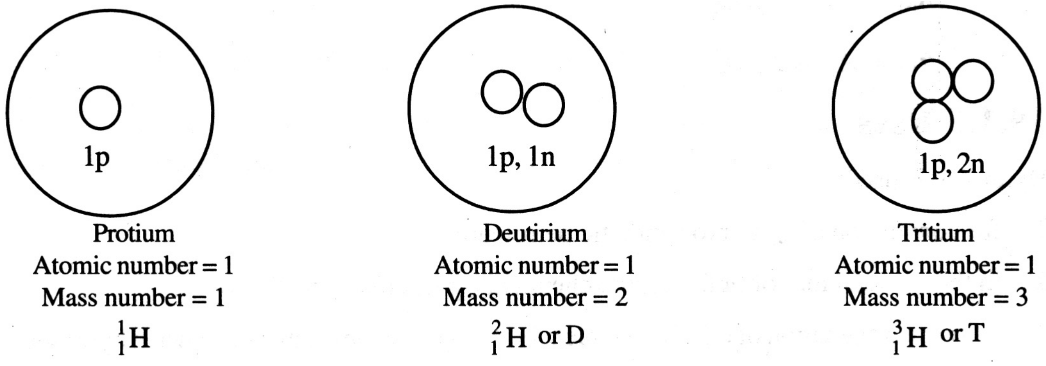


Fig 19.1: *Isotopes to hydrogen*

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

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.

19.1.3 Physical properties

Hydrogen is a diatomic gas, H_2. It is colourless and has no smell. It is 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.

   $$2H_2 + O_2 \rightarrow 2\,H_2O$$

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

   $$ZnO + H_2 \rightarrow Zn + H_2O$$

   $$CuO + H_2 \rightarrow Cu + H_2O$$

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.

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

   $$2H_2 + C \rightarrow CH_4$$

   $$2H_2 + O_2 \rightarrow 2H_2O$$

$H_2 + Cl_2 \rightarrow 2HCl$

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

$2Na + H_2 \rightarrow 2NaH$

$2Li + H_2 \rightarrow 2LiH$

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 443K in presence of nickel as 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.

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?

   ....

5. Name the gas which is used for the production of fertilizers.

   ....

6. How are vegetable oils changed into vegetable ghee?

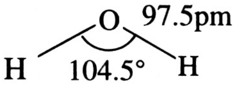
   ....

19.2 Compounds of Hydrogen

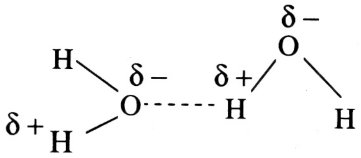
Hydrogen forms a large number of compounds: here we will consider only two of them, namely water (H_2O) and hydrogen peroxide (H_2O_2).

19.2.1 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 (δ^+) 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 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.

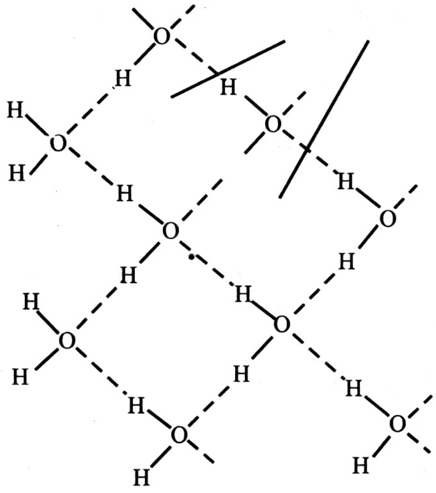


Fig. 19.2: *Tetrahedral arrangement of oxygen atoms in ice.*

19.2.2 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 O–D 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:

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

$$SO_3 + D_2O \longrightarrow D_2SO_4$$

19.2.3 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 At cathode:

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

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

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 clolourless 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:

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

(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:

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

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

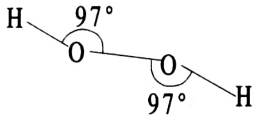
Uses:

Hydrogen peroxide is used:

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

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.

19.3.1.1 Electronic configuration

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

Table 19.1: Electronic configuration of alkali metals

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	$ls^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^2p^6, 5s^1$
Caesium	Cs	55	ls^2, 2s2p6, $3S^2p^6d^{10}, 4s^2p^6d^{10}, 5s^25p^6, 6s^1$

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 outermost shell.
4.	Electronegativity	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 outermost electron absorbs 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 not able to come in contact with 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 E^o, its reaction with water is considerably less vigorous than that of sodium which has the least negative E^o 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.

$$2M + H_2 \rightarrow 2MH$$

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

$$2M + X_2 \rightarrow 2MX (X = F, Cl, Br, I)$$

19.3.1.4 Stability and Solubility of Carbonates and Sulphates:

The carbonates and sulphates of alkali metals are generally soluble in water and thermally stable. The carbonates are highly stable to heat and melt without decomposing. As the electropositive character increases down the group, the stability of the carbonates increases. Carbonate of lithium is not so stable to heat due to the small size of lithium.

Intext Questions 19.3

1. Name the important ores of sodium.

   ....

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

   ....

3. Which of the alkali metals forms only monoxide?

   ....

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

   ....

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

   ....

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

   ....

19.4 The Alkaline Earth Metals

You have seen a gradual increase in the size of the alkali metals as we move 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.

Table 19.4: Physical properties of the alkaline earth metals

Symbol	Ionic Radius (pm)	First Ionization enthalpy (kJ mol^{-1})	Electro negativity	Density (gcm^{-3})	M.P. K	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

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.

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 occur native. 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.

Table 19.5: Electronic configuration

Element	Symbol	Atomic number	Electronic configuration
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 outermost shell.
4.	Electronegativity	Be > Mg > Ca > Sr > Ba As the electropositive character increases from top to bottom due to decrease in ionization energy, electronegativity 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. The reactivity 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 bum 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.

$$2Mg + O_2 \rightarrow 2MgO$$

$$2Be + O_2 \rightarrow 2BeO$$

$$2Ca + O_2 \rightarrow 2CaO$$

$$Ba + O_2 \rightarrow 2BaO$$

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) **Solubility and stability of carbonates and sulphates:**

Carbonates: The carbonates of alkaline earth metals are sparingly soluble in water. They decompose if heated strongly. Their thermal stability increases with increase in the size of the cation. Decomposition temperatures of carbonates are given below:

$BeCO_3$	**$MgCO_3$**	**$CaCO_3$**	**$SrCO_3$**	**$BaCO_3$**
< 373K	813K	1173K	1563K	1633K

Sulphates: The sulphates of alkaline earth metals are white solids, stable to heat. The sulphates, $BeSO_4$ and $MgSO_4$ are readily soluble and the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration energies of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore, their sulphates are soluble.

The sulphates decompose on heating, giving the oxides.

$$MSO_4 \rightarrow MO + SO_3$$

The thermal stability of sulphates increases with the increase in the size of cation. This is shown by the temperature at which decomposition occurs:

$BeSO_4$	**$MgSO_4$**	**$CaSO_4$**	**$SrSO_4$**
773K	1168K	1422K	1647K

(vii) Complex compounds: Smaller ions of the group 2 elements form complexes. For example chlorophyll is a complex compound of magnesium. Beryllium forms complexes like $[BeF_4]^{2-}$.

Intext Questions 19.4

1. Name the common ore for K and Mg.

   ....

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

   ....

3. Name an amphoteric oxide of alkaline earth metals.

   ....

4. Arrange the carbonates of alkaline earth metals in order of thermal stability.

   ....

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 .
- Thermal stability and solubility of carbonates and sulphates.

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 ice less dense than water and what kind of attractive forces must be overcome 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
11. Explain the trends of solubility and stability of the carbonates and sulphates of alkaline earth metals.

Answers to Intext Questions

19.1

1. Three isotopes of hydrogen are (a) protium ${}^{1}_{1}H$, deuterium D or ${}^{2}_{1}H$ and (c) tritium T or ${}^{3}_{1}H$.
2. Tritium.
3. It is lightest of all the gases known.
4. Methane (CH_4).

5. Ammonia (NH_3).

6. Vegetable oils $+H_2 \xrightarrow[Ni]{443K}$ Vegetable ghee.

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. $BaO_2.8H_2O + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 + 8H_2O$
4. (a) as a bleaching agent.

   (b) germicide and disinfectant.
5. H_2O_2 reduces $KMnO_4$

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

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

19.3

1. NaCl and $NaNO_3$.
2. Cs < Rb < K < Na < Li
3. Lithium
4. $2Na + 2H_2O \rightarrow 2NaOH + H_2$
5. Ionic.
6. (i) Sodium (ii) potassium

19.4

1. Carnallite ($KCl.MgCI_2.6HP$).
2. Be < Mg < Ca < Sr < Ba
3. BeO
4. $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

19.2.1.a Hard & Soft Water

Water which does not give stable 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 harness 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.

$$Mg(H\,CO_3)_{2(aq)} \xrightarrow{\text{boiling}} MgCO_{3(s)} \downarrow + H_2O_{(1)} + CO_{2(g)}$$

$$Ca(H\,CO_3)_{2(aq)} \xrightarrow{\text{boiling}} Ca\,CO_{3(s)} \downarrow + H_2O_{(1)} + CO_{2(g)}$$

b) **Clarke's process:** Requisite quantity of milk of lime is added to the water sample to remove temporary hardness.

$$Ca(HCO_3)_{2(aq)} + Ca(OH)_{2(aq)} \longrightarrow 2Ca\,CO_{3(s)} \downarrow + 2H_2O_{(1)}$$

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

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 can not 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.

$$Na_2Al_2Si_2O_8\,x\,H_2O$$

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 as shown in the figure 19.2.1.a

Chemical reaction during softening of water is

$$Na_2Al_2Si_2O_8xH_2O + Ca^{2+}{}_{(aq)} \longrightarrow Ca\,Al_2Si_2O_8xH_2O_{(s)} + 2\,Na^{+}{}_{(aq)}$$

$$Na_2Al_2Si_2O_8xH_2O + Mg^{2+}(aq) \longrightarrow Mg\,Al_2Si_2O_8xH_2O_{(s)} + 2\,Na^{+}{}_{(aq)}$$

After some use, all the sodium ions (Na^+) in the permutit are replaced by Ca^{2+} or Mg^{2+} ions and then it is said that the permutit is "exhausted". The exhausted permutit can be "revived or regenerated "for subsequent use by soaking it with 10% brine (Na Cl solution) then washing away the chlorides of calcium and magnesium.

Chemical reaction during "revival" of exhausted permutit is

$$Ca\,Al_2Si_2O_8xH_2O_{(s)} + 2\,Na^{2+}{}_{(aq)} \longrightarrow Na_2\,Al_2Si_2O_8xH_2O + Ca^{2+}{}_{(aq)} \text{ or } Mg^{2+}(aq)$$

(or)

$Mg\,Al_2Si_2O_8xH_2O_{(s)}$

Exhausted permutit

Thus, the exhausted permutit can be revived and used again for softening water.

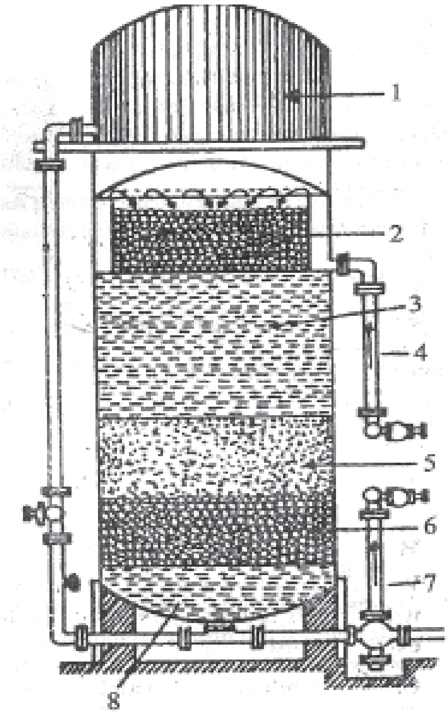


Fig. 19.2.1.a Permutit Process - softening of water

1. Brine Tank 2. Pre Filter 3. Hard Water 4. Raw Water Inlet 5. Permutit
6. Gravel 7. Soft Water Outlet 8. Soft Water

b) Calgon Process:

Cal.gon is sodium hexametaphosphate $Na_2 [Na_4(PO_3)_6]$ or $(NaPO_3)_6$
This doe.s 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 exchange resin which consists of giant organic molecules having – COOH groups.

$$2RCOOH + Ca^{2+} \longrightarrow (RCOO)_2 Ca + 2H^+_{(aq)}$$

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.

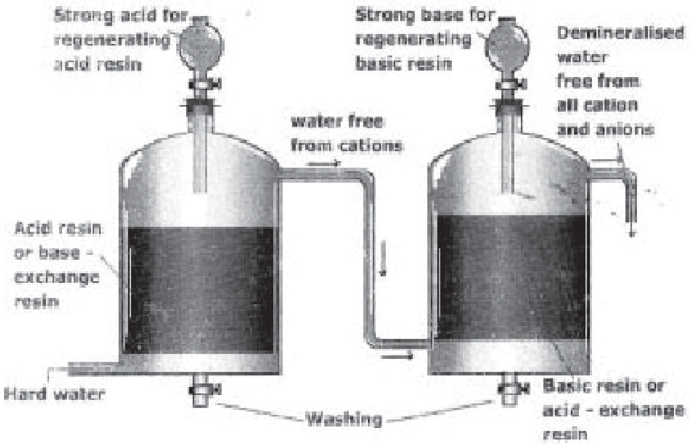


Fig. 19.2.1.a Ion exchange method

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

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

$$2(RNH_3) OH + SO^{2-}_4 \longrightarrow (RNH_3)_2 SO_4 + 2OH$$

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

From step I   From step II
Released   Released

Deionised 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.

19.2.1 a 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?

19.2.1.a 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 sulphates.
3. 2 Na Soap(aq) + $\frac{Ca^{2+}{}_{(aq)}}{Mg^{2+}{}_{(aq)}} \rightarrow \frac{Ca}{Mg} Soap \downarrow + Na^{+}{}_{(aq)}$
4. Boiling Water

19.2.1.b Hydrogen Peroxide

Industrial preparation of H_2O_2

i) Electrolysis:

Hydrogen peroxide is manufactured by the electrolysis of 50% sulphuric acid solution. The product is this subjected to vacuum distillation. The distillate is 30% solution of H_2O_2. The first product formed in the course of electrolysis is peroxy disulphuric acid. Which is formed by trhe electrolytic oxidation of sulphuric acid. The reactions are

$$2H_2SO_4 \longrightarrow 2HSO^-_4 + 2H^+$$

$$2H_2SO^-_4 \longrightarrow H_2S_2O_8 + 2e \text{ (at anode)}$$

Peroxy disulphuric acid reacts with water during distillation to form H_2O_2

$$H_2S_2O_{8(aq)} + 2H_2O_{(l)} \longrightarrow 2H_2SO_{4(aq)} + H_2O_2$$

$$2H + 2e \longrightarrow H_2 \text{ (at cathode)}$$

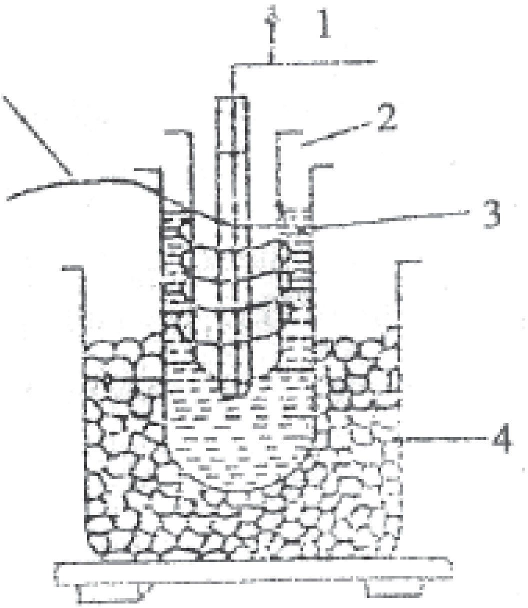
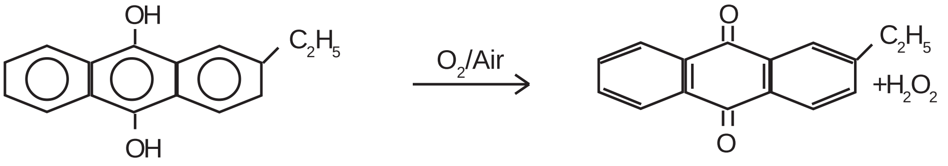


Fig. 19.2.1.b Manufacture of H_2O_2 by Electrolytic process
1. Platinum anode 2. Diaphragm 3. 50% H_2SO_4 4. Ice pieces 5. Lead cathode

Hydrogen peroxide is also obtained by the electrolysis of an aqneous solution of ammonium sulphate and sulphuric acid in molar proportions. The electrolysis is carried out at a low temperature in a cell provided with a platinum anode and a lead cathode. The two electrodes are separated by a porous stone ware diaphragm.

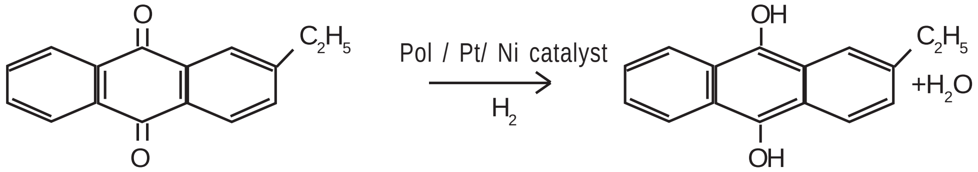
ii) By auto – oxidation:

The modern process for the manufacture of H_2O_2 is based on the auto oxidation of 2- ethyl anthraquinol. This method involves alternative oxidation and reduction steps of 2-ethyl anthra quinol. A 10% solution of the compound is prepared in a mixture of benzene and an alcohol



2- ethylanthra quinol **2- ethylanthra quinone**

Air is passed through the mixture. The resulting 2-ethyl anthraquinone is then reduced by passing hydrogen under a pressure of 1 to 3 atmospheres at 4^0C with catalyst pt pdorni. This gives back 2-ethyl anthraquinol. The H_2O_2 formed in this reaction is extracted with water and the dilute solution of H_2O_2 is concentrated to obtain H_2O_2 of the required strength.



19.2.1.b Intext questions:

1. What is the electrolyte used in the manufacture of H_2O_2 by electrolysis?

   ....

2. What is the organic compound used in the preparation of H_2O_2 by auto oxidation?

   ....

What you have learnt:

- Preparation of H_2O_2 by electrolysis.
- Preparation of H_2O_2 by auto oxidation.

Terminal exercise:

1. Explain the preparation of H_2O_2 by electrolysis.
2. How do you prepare H_2O_2 by auto oxidation.

19.2.1.b Answer to in text questions.

1. 50% sulphuric acid.
2. 2- ethyl anthraquinol.

19.3.1.5.a Preparation and properties of NaOH

NaOH is also known as caustic soda. It is a highly useful chemical in a number of industries. The manufacture of this compound is done in two methods.

1) Causticizing Process, 2) Electrolytic Process.

1. **Causticizing Process:** When milk of lime $Ca(OH)_2$ is added to a warm, dilute solution of sodium carbonate at 80-85^{0}C, sodium hydroxide is formed.

   $Ca(OH)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaOH$ (caustic soda)

   Calcium carbonate is slightly soluble and separates out as a mud at the bottom this process is called causticization

   NaOH formed is 98% pure solution.

2. **Electrolytic process:** in electrolytic process very pure caustic soda can be obtained. The principle used in the various process can be summarized by follows.

   Brine Solution (an aqueous solution of NaCl) is electrolysed. The following changes take place during electrolysis.

   $2\ NaCl \longrightarrow 2\ Na^+ + 2\ Cl^-$ (ionization)

   At Cathode $2H_2O + 2e^- \longrightarrow 2\ OH^- + H_2$ (reduction)

   $2\ Na^+ + 2OH^- \longrightarrow 2\ NaOH_{aq}$

   At anode $4\ OH^- \longrightarrow 2H_2O + O_2 + 4e^-$ (oxidation)

   $2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$ (oxidation)

   Two cells are used for the manufacture of NaOH

   1) Nelson Cell, 2) Castner – kellner cell.

(a) Nelson (Cell) Process:

Nelson cell based for the manufacturing of sodium hydroxide.

Principle: On electrolysis of Brine solution the following reaction take place

$2\ NaCl \longrightarrow 2\ Na^+ + 2\ Cl^-$ (Ionization)

At anode $2Cl^- \longrightarrow Cl^2 + 2e^-$ (oxidation)

At cathode $2H_2O + 2e^- \longrightarrow 2\ OH^- + H_2$ (reduction)

$2\ Na^+ + 2OH^- \longrightarrow 2\ NaOH$

Hydrozen gas liberated at cathode and Cl_2 gas liberated at anode. The solution becomes rich with NaOH and is collected in the receiver.

Process: A perforated steel U-tube lined inside with asbestos is used as cathode brine solution taken in U-tube and it is mounted in an iron tank. A carbon rod suspended into the brine solution acts as anode. The cathode and the anode are separated by the asbestos lining present inside the U-tube.

On passing electric current Cl_2 is liberated at the anode and is led out. NaOH is collected at the bottom. Na^+ ions are attracted towards the cathode they pass through the asbestos and reach the cathode and reacts with the steam to form NaOH.

The steam blown when electrolysis is carried out gives two advantages.

1. to keep the solution hot and
2. to clear the perforation of the asbestos lining

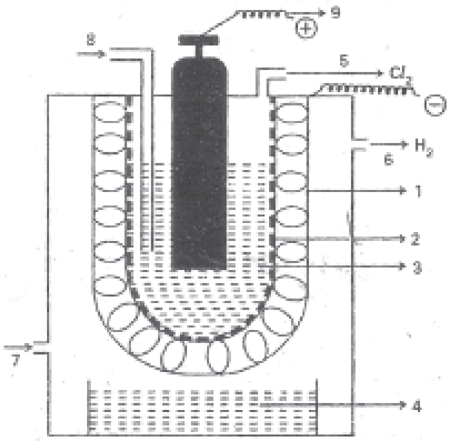


Fig. 19.3.1.5.a Nelson cell

1. Perforated steel U-tube & cathode (perforations blown up for easy understanding of the student) 2. Asbestos lining 3. Brine Solution 4. NaOH solution collected 5. Cl_2 outlet 6. H_2 outlet 7. Steam inlet 8. Brine inlet 9. Graphite anode

Castner – Kellner Process:

This process is also known as mercury cathode process.

Principle: Brine solution is subjected to electrolysis using mercury as cathode. Cl_2 gas evolves at anode. Sodium Amalgam formed at cathode when sodium amalgam reacts with water NaOH is formed evolving H_2 gas.

Electrode reaction in the cell

a) In the outer comportments

$$2\,NaCl \longrightarrow 2\,Na^+ + 2\,Cl^- \text{(ionization)}$$

At graphite anode

$$2\,Cl^- \longrightarrow Cl_2 + 2e^- \text{ (oxidation)}$$

At mercury cathode

$$Hg + 2\,Na^+ + 2e^- \longrightarrow Na_2Hg.$$

b) in the central compartments

at anode $Na_2Hg-2e^- \longrightarrow 2\,Na^+ + Hg$

at cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2\,Na^+ + 2OH^- \longrightarrow 2\,NaOH$

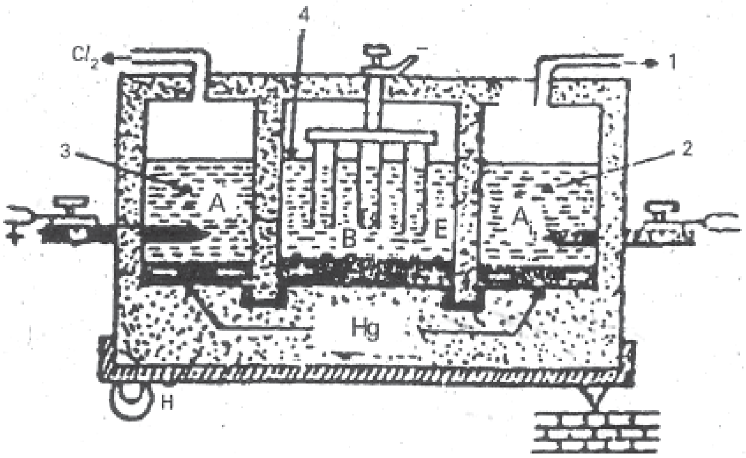


Fig 19.3.1.5.b Castner - Kellner Process.
1. Cl_2 2 & 3. Brine Solution 4. Caustic Soda

Process: A rectangular iron tank is divided into three comportments by the suspended slate partitions. The partitions do not reach the bottom of the tank. The bottom of the tank is covered with mercury.

In two outer comportments, Brine solution is taken. The two graphite rods projected into brine solution acts as anode.

In central comportment di NaOH solution is taken. A bunch of iron rods are suspended in the central comportments which acts as cathode.

When electricity is passed the mercury layer at the bottom functions as cathode in the outer comportments and as anode is the central comportment (Hence the mercury layer at bottom is called as intermediate, electrode by induction). Cl^- ions are discharged at anode and Cl_2 gas evolved from outer comportments. Na^+ ions lose their charge at the mercury and form Na metal. Na metal forms sodium amalgam with mercury. The amalgam is then brought into the central compartment by the use of eccentric wheel sodium amalgam forms NaOH with water and H_2 gas is released.

Properties of Sodium Hydroxide:

a) Physical Properties:

NaOH is hygroscopic substance of realy dissolve in H_2O. An exothermic change take place forming a hydrated compound. NaOH x H_2O. It is soapy to touch. It absorbs CO_2 from atmosphere.

b) Chemical properties

i) It is very strong alkali it is neutralized by acids to give salts.

Ex: $NaOH + HCl \longrightarrow NaCl + H_2O$

ii) Reaction with metals

Zn, Al and Sn are anphoteric metals they displace H_2 from NaOH

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

Sodiumzincate

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

Sodium alluminate

iii) Reaction with non metals

1) **With Fluorine:** Fluorine react with dilute NaOH and gives oxygen difluoride

$2\ NaOH + 2\ F_2 \longrightarrow 2\ NaF + OF_2 + H_2O$

With conc. NaOH

$4\ NaOH + 2F_2 \longrightarrow 4\ NaF + 2\ H_2O + O_2$

2) **With chlorine and other halogens:**

Cold & dilute

$2\ NaOH + X_2 \longrightarrow Nax + NaOX + H_2O$

Hot and concentrated NaOH

$6\ NaOH + 3\ X_2 \longrightarrow 5\ Nax + NaOX_3 + 3\ H_2O$

3) **With C and Si Fused NaOH gets reduced by C:**

$6\ NaOH + 2\ C \longrightarrow 2\ Na + 2\ Na_2CO_3 + 3H_2\uparrow$

Concentrated NaOH reacts with Si on heating to give sodium silicate

$2NaOH + Si + H_2O \longrightarrow Na_2SiO_3 + 2H_2$

4) **With Ammonium salts:**

Ammonium salts react with NaOH liberates NH_3

$NaOH + NH_4Cl \longrightarrow NaCl + NH_3 + H_2O$

5) **With acidic oxides:** Acidic oxides react with NaOH and give their salts.

$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$

6) **With compounds:**

When hydroxides are unstable oxides are precipitate out.

$2\ AgNO_3 + 2\ NaOH \longrightarrow 2\ AgOH + 2\ NaNO_3$

$$2\,AgOH \longrightarrow Ag_2O \downarrow + H_2O$$

$$ZnSO_4 + 2NaOH \longrightarrow Na_2SO_4 + Zn(OH)_2$$

$$Zn(OH)_2 + NaOH \longrightarrow Na_2ZnO_2 + ZH_2O$$

Uses of NaOH

1. Soap, paper and rayon industries use NaOH.
2. In the manufacture organic coloring matter.
3. In the preparation sodium compounds like NaOX, $NaXO_3$.
4. In petroleum refining.
5. In the laboratory as a reagent and as a cleansing agent.

19.3.1.5.c Salts of Alkali metals:

Alkali metals form oxo – salts like carbonates, bicarbonates, nitrates and nitrites, some compounds of interest are studied here.

Sodium nitrate ($NaNO_3$)

This is naturally available as chile salt petre. It can be prepared by action of HNO_3 on Na_2CO_3

$$Na_2CO_3 + 2\,HNO_3 \longrightarrow 2\,NaNO_3 + H_2 + CO_2$$

1) It is white deliquescent, crystalline, solid, soluble in water.
2) It is stable but on strong heating decomposes

$$2\,NaNO_3 \longrightarrow 2NaNO_2 + O_2$$

Uses:

1) $NaNO_3$ used as nitrogenous fertilizer in agriculture.
2) It is used in the manufacture of HNO_3, $NaNO_2$ and KNO_3

Preparation of Na_2CO_3 & $NaHCO_3$

Na_2CO_3 : The hydrated $Na_2CO_3 . 10H_2O$ is known as washing soda. The anhydrous salt is known as soda or soda ash. It is mainly prepared by two methods 1) Leblanc Process, 2) Ammonia – Soda process.

19.3.1.5.d. 1. Leblanc Process:

It is important for its principle and the by products. The raw meterals used in the process are NaCl, C, H_2SO_4 limestone etc. reaction sequence is as follows.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCL$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

$$Na_2SO_4 + 4\,C \longrightarrow Na_2S + 4\,CO$$

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + CaS \text{ (Black ash)}$$

19.3.1.5.e. 2. Ammonia – soda or Solvay process

This process came into prominence due to the low cost of products of sodium carbonate.

Principle: Into Brine solution NH_3 gas is passed and saturated to result in ammonical brine. Brine is saturated with CO_2 as a result formation of relatively less soluble $NaHCO_3$. The thermal dissociation of $NaHCO_3$ gives Na_2CO_3.

$$H_2O + CO_2 + NH_3 \longrightarrow NH_4^+ + HCO_3^-$$

$$Na^+ + HCO_3 \longrightarrow NaHCO_3$$

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

The CO_2 required for the process obtained from line stone.

Process:

i) **Saturation of Brine with ammonia:** The ammonia absorption tower is filled with brine solution. Then ammonia gas containing a small amount of CO_2 is passed into it. The solution when allowed to settle down, precipitates the impurities (Ca, Fe. Mg hydroxides or carbonates)

$$2\,NH_3 + H_2O\,.CO_3 \longrightarrow (NH_4)_2\,CO_3$$

$$Mg\,Cl_2 + (NH_4)_2\,CO_3 \longrightarrow MgCO_3 + 2\,NH_4Cl$$

The precipitates are filtered & the filtrate is sent to 'carbonation tower'

ii) **Carbonation of ammonical brine:** The carbonation tower is cylindrical iron tower which contains perforated plates arranged on and above the other.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

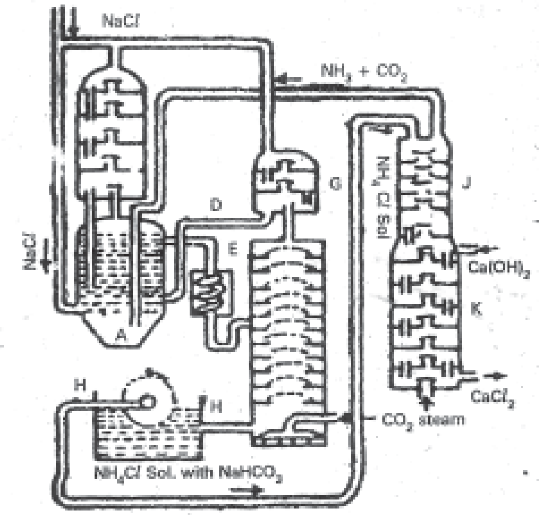


Fig No. 19.3.1.5.e Preparation of sodium carbonate - Solvay process

iii) **Filtration:** The liquid from the carbonation tower is sent into vacuum filter where $NaHCO_3$ is filtered off. The filtrate containing ammonia salts is pumped into ammonia regeneration tower.

iv) **Ammonia regeneration:** The milk of lime $Ca(OH)_2$ for regeneration of NH_3 is produced as follows

$$CaCO_3 \longrightarrow CaO + CO_2$$

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

The filtrate is run down from the top of the ammonia regeneration tower is mixed with $Ca(OH)_2$ to liberate NH_3 gas which is sent back to saturation tank.

$$NH_4HCO_3 \longrightarrow NH_3 + H_2O + CO_2$$

$$Ca(OH)_2 + 2\ NH_4Cl \longrightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O$$

v) **Decompositions of $NaHCO_3$ at high temperatures**

The $NaHCO_3$ obtained in the filter is heated to give Na_2CO_3

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

Properties of Na_2CO_3

Physical properties:

1. Na_2CO_3 is white crystalline solid
2. It is an efflorescent substance and loses water of crystallization when exposed to air.

$$Na_2CO_3.10H_2O \longrightarrow Na_2CO_3.7H_2O \longrightarrow Na_2CO_3.H_2O$$

3. It melts at 852.1^{0}C
4. It dissolves in water with liberation of heat.

$$Na_2\ CO_3 + H_2O \longrightarrow 2NaOH + H_2CO_3$$

Chemical Properties:

1. Reaction with acids: Acids liberates CO_2 from sodium carbonate.

$$Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + CO_2$$

2. Reaction with non-metals and their compounds Na_2CO_3 reacts with S and SO_2 to give sodium thio sulphate.

$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2$$

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

3. Water glass in formed when Na_2CO_3 is fused with silica (SiO_2)

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

4. Reaction with compounds: in soluble metal carbonates are precipitated from solution on addition of sodium carbonate solutions.

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2\,NaCl$$

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnCO_3\downarrow + Na_2SO_4$$

Uses of Na_2CO_3:

1. Na_2CO_3 is used in the manufacture of glass, water glass.
2. In softening of hard water
3. In the petroleum industry in refining process
4. In laundries, paper industry
5. In the laboratory as a reagent in qualitative and quantitative analysis.

Preparation of $NaHCO_3$:

In the manufacture of sodium carbonate by solve process the sodium bicarbonate is obtained this is commercially used as it is the sodium carbonate is converted into the sodium bicarbonate by saturation of aquons Na_2CO_3 with CO_2

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

Properties:

1. It is white crystalline solid. It is less soluble compared to Na_2CO_3 in water.
2. It gives an alkaline solution due to hydrolysis

$$NaHCO_3 + H_2O \longrightarrow NaOH + H_2CO_3$$

3. $NaHCO_3$ does not gives any coloration with phenol phthalein but gives coloration with methyl orange. This property used in the quantitative estimation of HCO^-_3 and CO_3^{--} in this mixture.

Uses:

1. In medicine as an antacid
2. In the fire extinguishers to liberate CO_2
3. In cooking as a backing powder.

Preparation and uses of NaCl

Common salt 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.

Properties:

1) Ordinary NaCl is slightly hygroscopic due to presence of Ca and Mg chlorides.
2) Solubility of NaCl has little effect with change in temperature.

Uses:

1) It is essential constituent of our diet
2) It is starting material for the manufacture Na or Cl_2, Caustic Soda
3) In the preparation of freezing mixture with ice
4) As a preservative for meat and fish.

Biological importance of Na and K

There are 27 metals and non metals in living systems out of them Na, Ka, Mg and Ca are required in major quantities.

The presence of Na^+ and K^+ ions inside and outside the cell produce an electrical potential across the cell membrane.

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.

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.

19.3.1.5.a Intext questions:

1. Draw a neat diagram of Nelson cell and label it.
2. Write equation for reaction of NaOH with Al metal.
3. Write equations involved in preparation of NaOH by electrolysis.
4. How Na_2CO_3 converted to NaOH.
5. How Na_2CO_3 is use full in the removal hardness of water.

What you have learnt:

1. Preparation of NaOH by causticizing method Nelson process, Castner-Kellner method.
2. Reactions of NaOH with, metals, non metals with some compounds discussed.
3. Ampotesic metals gives hydroxides with NaOH, which dissolve in excess NaOH.
4. Na_2CO_3, $NaHCO_3$ are commercially important compounds.
5. Sodium, Potassium are important elements in cell biology.

Terminal Exercises:

1. Give the equation for the NaOH with halogens.
2. Write equations involved in the manufacture of Na_2CO_3 by solve process.
3. What is the role of alkali metals in cell biology.

4. What is role of mercury in the manufacture NaOH by castner-Kellner process.
5. Write equation for the reaction of NaOH with carbon and silicon.

19.3.1.5.a Answers to Intext Questions:

1. See the diagram
2. $6\ NaOH + 2\ Al \rightarrow 2\ Na_3AlO_3 + 3\ H_2$
3. $Nacl \rightarrow Na^+ + Cl^-$

   At anode $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

   At Cathode $2H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$

   $2\ Na^+ + 2\ OH \rightarrow 2\ NaOH$
4. $Na_2CO_3 + Ca(OH)_2 \rightarrow 2\ NaOH + CaCO_3$
5. Na_2CO_3 reacts with chlorides, sulphate of heavy metals present hard water and converts them into insoluble carbonate.

   Ex:- $MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2\ NaCl.$

19.4.4.a Alkaline earth metals

CaO, $CaCO_3$ lime, limestone

Preparation and uses of CaO

Calcium oxide also known as quick time is prepared from line stone by calcination.

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

Reverse reaction also takes place. To prevent back ward reaction CO_2 is removed from reaction mixture.

Uses of lime and lime stone :

CaO is used in the manufacture of mortar cement and calcium chloride. 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.

$CaCO_3$: It is available in nature in different forms like chalk, marble, pumice stone etc. line stone is used as a flux in metallurgies. Marble is used for building purposes, manufacture of cement.

Biological importance of Mg and Ca

Role of Mg^{+2} ions

1) Mg^{+2} are concentrated in animal cells
2) Enzymes like 'phospho hydrolyses' and phospho transferases 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.

19.4.4.a Intext questions :

1. A mixture of 1 part of slacked time, 3 parts of sand and water is known as lime mortar when mixed sand hardens due to formation of calcium silicate.
2. Enzymes like phospho hydrolysis and phaspho transferases contain Mg^{+2}. These enzymes participate in ATP reactions and release energy in process. Mg^{+2} is constituent of chlorophyll.

19.4.4.a Answer's to Intext questions:

1. What is mortar? How it is harness?
2. What is the importance of Mg^{+2} ions in biology.

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 characterised 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), nitroglycrine, 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 organism.

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 enhalpy;
  - (iii) electronegativity;
  - (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^{1-6}.

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	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$
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	$2s^22p^1$	+5	+2.60	88
Aluminium	$3s^23p^1$	+13	+ 11.60	118
Gallium	$4s^24p^1$	+31	+29.60	124
Indium	$5s^25p^1$	+49	+47.60	152
Thallium	$6s^26p^1$	+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) $_{9}F$ and $_{17}CI$ (ii) $_{6}C$ and $_{14}Si$ (iii) $_{5}B$ and $_{6}C$

   (iv) $_{6}C$ and $_{7}N$

   ....

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 $_{17}CI$ (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 mol^{-1}

B	**C**	**N**	**O**	**F**
–0.30	–1.25	+0.20	–1.48	–3.6
Al	Si	P	S	Cl
–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. Interelectronic 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 CI – CI 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 (3p) 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 BE_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
$(AlH_3)x$	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
TlH_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

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

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 the 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) ${}_{9}F$ (ii) ${}_{6}C$ (iii) ${}_{6}C$ (iv) ${}_{7}N$
2. ${}_{4}Be$ (ii) ${}_{17}Cl$ (iii) ${}_{2}He$ (iv) ${}_{8}O$
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*-orbitals
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. $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$
5. The bond angle decreases from 107° to almost 90°.
6. (i) $4Al_{(s)} + 3O_{2(g)} \rightarrow 2AlO_{3(s)}$

   (ii) $Si_{(s)} + 2Cl_{2(g)} \rightarrow SiCl_4(l)$

   (iii) $C_{(s)} + 2Cl_{2(g)} \rightarrow CCl_4(l)$
7. (i) BCl_3 (ii) $PbCl_4$

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 Group 13 of the periodic table. Though the outermost 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 orthoboric 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 ions (H_3O^+). Thus

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

When heated, it decomposes to metaboric 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 van der Waals forces which are responsible for the cleavage of solid structure into flakes.

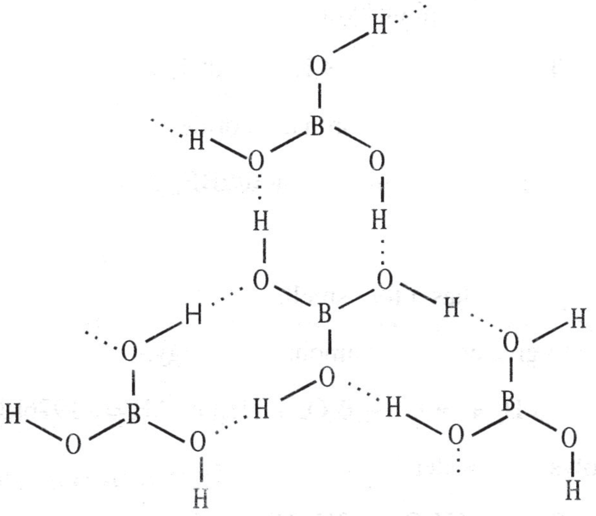


Fig. 21.1: *Structure of boric acid; the dotted lines represent hydrogen bonds*

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

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

(ii) By the action of lithium hydride on boron trifluoride

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

Properties:

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

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O;\ \Delta H = -1976\text{kJ mol}^{-1}$$

- It is readily hydrolysed by water

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

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 B–H 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 multi centre bonds, i.e., 3c – 2e or three centre two electron B–H–B bonds and four normal B-H bonds.

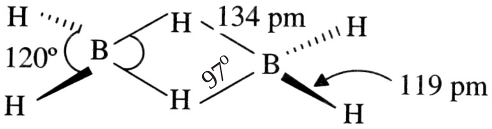


Fig.21.2: *Structure of diborane,* B_2H_6

21.1.4 Boron Trifluoride

Boron forms halides BX_3 (X = F, CI, 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 hydrofluoric 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; infact 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 trifluoride 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:

B–F bond in BF_3 has a multiple bond character since its structure is a resonance hybrid of three resonating structures.

Note that in the resonating structures boron completes its octet.

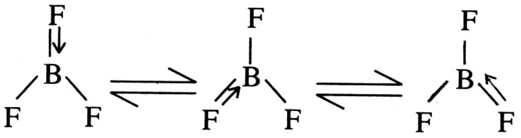


Fig 21.3 : *Resonating structures of boron trifluoride*

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.

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

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

When pure, it is a white solid which sublimes at 453K. Aluminium 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.

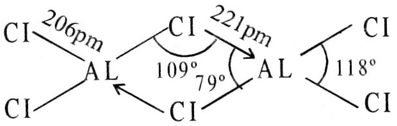


Fig.21.4: *Structure of $AlCl_3$*

When treated with water it gives hydrated aluminium ions and Cl^- ions:

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

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, $K^+ Al^{3+} (SO_4^{2-})_2 \cdot 12H_2O$ 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 $(NH_4) Al (SO_4)_2 \cdot 12H_2O$

Chrome alum $KCr(SO_4)_2 \cdot 12H_2O$

Ammonium chrome alum $(NH_4)Cr(SO_4)_2 \cdot 12H_2O$

Ferric alum $K Fe (SO_4)_2 \cdot 12H_2O$

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 $K_2SO_4.Al_2\ (SO_4)_3\ .24H_2O$.

Intext Questions 21.1

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 van der 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 973 K giving carbon tetrafluoride. Alkalies and acids have no action on diamond. It is the hardest natural substance.

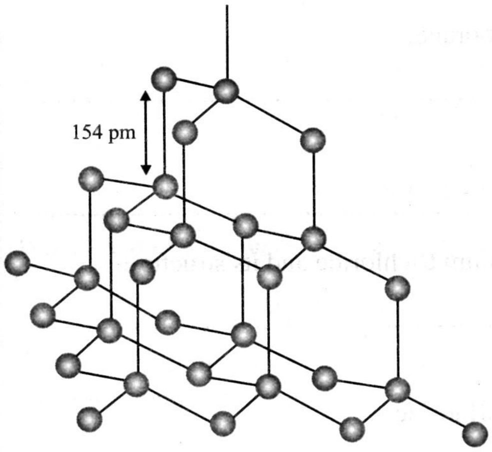


Fig.21.5: *Structure of diamond*

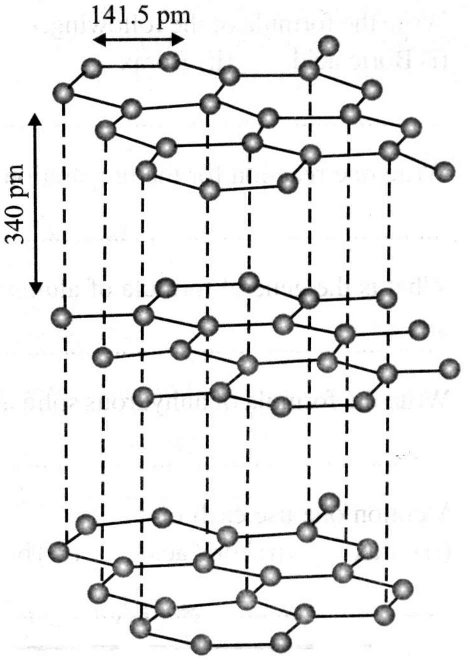


Fig. 21.6 : *Structure of graphite*

Graphite, on the other hand, is reactive. It burns in air at 873 K 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.

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

The structure of carbon dioxide on the other hand is linear O = C = O. There are two σ bonds and two π bonds in the molecule CO_2. The carbon atom uses sp hybrid orbitals to form σ 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 2p 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 in fused alkalies or fused carbonates forming silicates. Silica also reacts with fluorine and HF to form silicon tetrafluoride

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

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

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 tetrachloromethane and silicon tetrachloride as tetrachlorosilane.

- 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

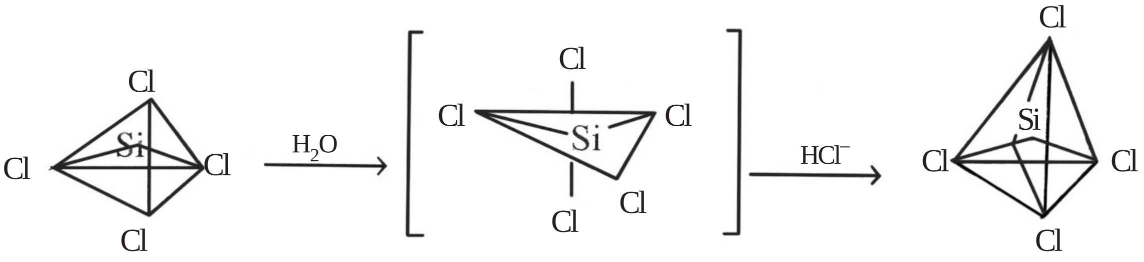
$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

Carbon tetrachloride is not hydrolysed by water whereas 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 *3d* 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 Questions 21.2

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.

21.3.1 Ammonia

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

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

or

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

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 750 K and under a pressure of about 200 atmospheres (Haber's process).

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

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 into 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 10 per cent 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

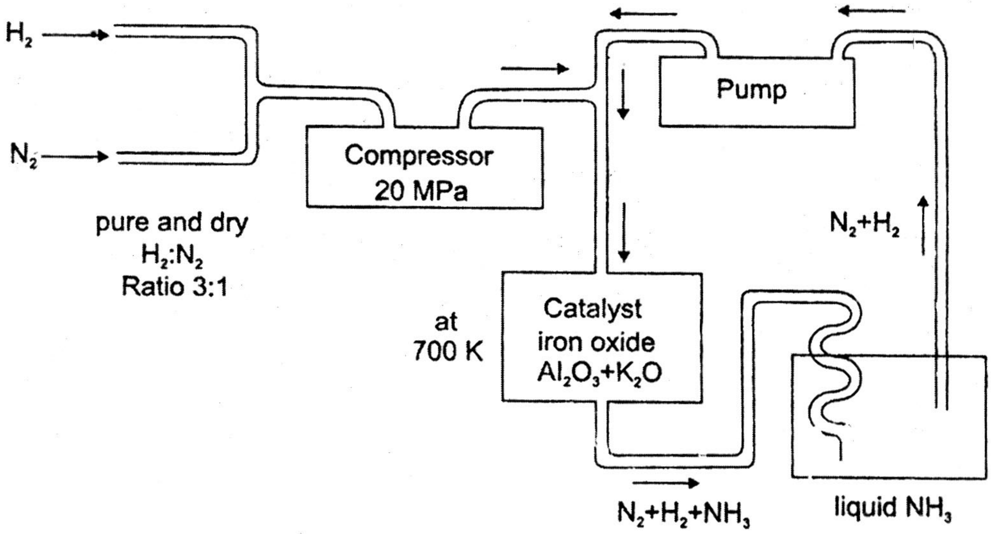


Fig.21.7: *The Haber process for the manufacture of ammonia*

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

(ii) **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.:

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

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

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

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

(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 tetraamrnine 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 $[Ni\,(NH_3)_6]^{2+}$ are well known.

Uses:

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

(i) In the manufacture of ammonium sulphate for use as a fertilizer.

(ii) In the manufacture of nitric acid (Ostwald process)

(iii) In the manufacture of sodium carbonate by Solvay process.

(iv) Liquid ammonia is used in refrigerators.

(v) 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 $H\hat{N}H$ becomes 107° instead of 109° (in CH_4) due to lone pair-bond pair repulsion (Fig. 21.8).

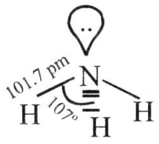


Fig. 21.8 : *Structure of ammonia*

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 these 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 1.50 g cm^{-3} at 248 K. 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 NO_2

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

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

(i) $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

(ii) $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

(iii) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(iv) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(v) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
cone.

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

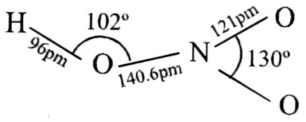
(vi) $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$
dil.

(vii) $Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$
dil.

(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.

(ix) $C_3H_5(OH)_3 + 3HNO_3 \xrightarrow{\text{conc. } H_2SO_4} C_3H_5(NO_2)_3 + 3H_2O$
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 nitric acid 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 aqua regia (HNO_3 : HCl = 1 : 3)
- HNO_3 (100%) is a constituent of rocket propellant.

21.3.3 Nitrogen Fixation

Any process by which atmospheric nitrogen is converted into a useful nitrogen compound is referred to as a method of *Nitrogen Fixation.*

The importance of fixation of atmospheric nitrogen is to make up for the loss of nitrogen from soil, created by cultivation. The chief sources of making up this loss of nitrogen are:

(a) Natural fixation

(b) Artificial fixation

(a) **Natural fixation of nitrogen:** The natural agencies which bring about the fixation are as following:

(i) *Lightning storms:* The nitric oxide produced in the lightning is oxidised to nitrogen dioxide.

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO$$

$$2NO + O_2 \xrightarrow{\text{air}} 2NO_2$$

The dioxide dissolves in rain water to give nitric acid which is carried to the soil and used by plants in the form of nitrates.

(ii) *Symbiotic bacteria:* The other natural agency is nitrogen fixing bacteria, **symbiotic bacteria**. These bacteria appear to live as 'guests' on the rootlets of leguminous plants, 'the hosts'. The bacteria convert atmospheric nitrogen into a form available as food for the plant on which they live. It is thus a cooperative affair; the plants furnish home and food for the bacteria and the bacteria in turn furnish nitrogen drawn from air as an essential food to the plants.

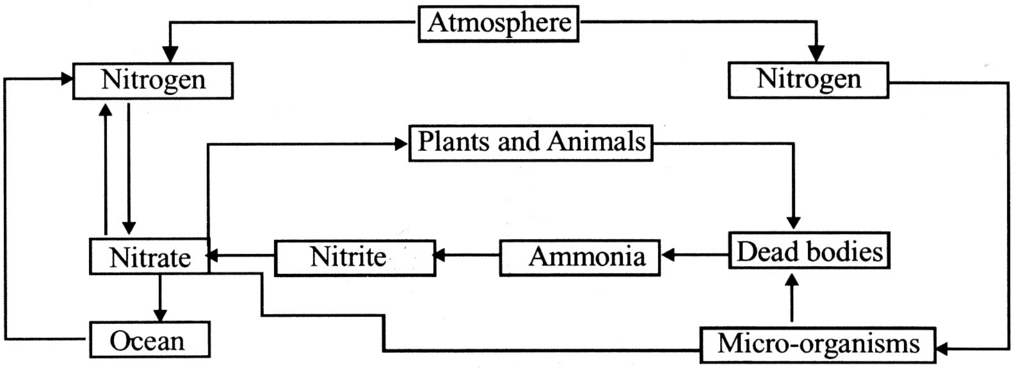


Fig. 21.10 : *Fixation of Nitrogen*

(b) Artificial Fixation of Nitrogen: The important artificial methods of fixing nitrogen are as follows :

(i) *Conversion to ammonia by Haber s process* : This is by far the most important method of fixing atmospheric nitrogen.

Ammonia is supplied to the soil as its salts, e.g. $(NH_4)_2 SO_4$. It may also be oxidised to nitric acid and nitrate salts (e.g. KNO_3) which may be used for the purpose.

(ii) *Conversion into calcium cyanamide:* When calcium carbide is heated to l373K in a stream of nitrogen the following reaction occurs

$$CaC_2 + N_2 \xrightarrow{1373K} \underset{\textbf{calcium cyanamide (nitrolim)}}{CaNCN} + C$$

The mixture of calcium cyanamide and carbon is directly used as a fertilizer under the name *nitrolim*

(iii) *Conversion into nitric acid:* In Birkeland and Eyde process nitrogen is made to combine with oxygen at a very high temperature (~3000K). The nitric oxide formed is converted into the dioxide

$$N_2 + O_3 \xrightarrow{3300K} 2NO$$

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

The dioxide is dissolved in water in the presence of air to form nitric acid. In this method electric sparking is used to generate that high temperature, so the method is good only where electricity is cheap.

(iv) *Conversion into nitride.* Certain metal oxides, e.g. Al_2O_3.MgO and BaO when heated with coke to ~l800K in a current of atmospheric nitrogen, give metal nitrides

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

The heated mass is reacted with water when the nitride is hydrolysed to produce ammonia

$$AlN + 3HOH \longrightarrow Al(OH)_3 + NH_3$$

Ammonia may be supplied to the soil in the form of ammonium salts.

21.3.4 Fertilizers

Chemical compounds directly supplying the elements of primary importance, i.e. nitrogen, phosphorus and potassium to soil are known as fertilizers. A chemical compound acting as fertilizer may supply one or more than one of these elements. Thus the following broad classification of fertilizers emerges

1. Nitrogenous fertilizers
2. Phosphatic fertilizers
3. Potassium fertilizers
4. Mixed fertilizers

1. Nitrogenous fertilizers: The chief compounds which act as nitrogenous fertilizers include

(i) ammonium sulphate, (ii) urea and (iii) calcium cyanamide

(i) Ammonium sulphate is one of the best nitrogenous fertilizers. It is prepared either by the action of sulphuric acid on ammonia (obtained from destructive distillation of coal)

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

or from gypsum by the action of aqueous ammonia and carbon dioxide

$$2NH_3 + H_2O + CO_2 + CaSO_4 \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

Ammonium sulphate is manufactured in our country at Sindri (Bihar) and Alwaye (Kerala).

(ii) **Urea:** It is usually made by the action of carbon dioxide and liquid ammonia at 453K under a pressure of 200 atm. The reaction occurs in two steps

$$2NH_3 + CO_2 \longrightarrow \underset{\textbf{ammonium carbamate}}{NH_2COONH_4}$$

$$NH_2COONH_4 \xrightarrow{\text{heat}} \underset{\textbf{urea}}{NH_2CONH_2} + H_2O$$

Large quantities of urea are manufactured at Nangal (Punjab) in our country. Of all the nitrogenous fertilizers urea has the maximum nitrogen content hence it is widely used.

(iii) **Calcium cyanamide, Ca (NCN):** It is manufactured by heating calcium carbide in nitrogen at 1373 K

$$CaC_2 + N_2 \longrightarrow CaNCN + C$$

It is used in the commercial name of nitrolim. When supplied to the soil it hydrolyses to ammonia which gets oxidised to nitrate and is used up by plants.

$$CaNCN + 3HOH \longrightarrow CaCO_3 + 2NH_3$$

2. **Phosphatic fertilizers:** Calcium phosphate, $Ca_3(PO_4)_2$ is converted into superphosphate, $Ca\,(H_2PO_4)_2$, by the action of sulphuric acid.

$$Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

The product containing superphosphate and calcium sulphate is used in the name or *superphosphate of lime.*

3. **Potassium fertilizers. T**he chief compound serving as potassium fertilizer is potassium chloride.

4. **Mixed fertilizers :** These are also known as NPK fertilizers. The important mixed fertilizers are $(NH_4)_3PO_4$. KNO_3, and ammonium super phosphate, $(NH_4)H_2PO_4$.

Rating of fertilizers. The rating of fertilizers is done on the basis of the percentage of N_2, P_2O_5 and K_2O in them. For example a fertilizer containing 2% N_2, 8% P_2O_5 and 2% K_2O has a rating of 2, 8, 2. For different crops different ratings are required. For example, some crops and required ratings are

Potato: 4, 8, 10; wheat: 2, 12, 6; sugar: 4, 12, 6.

Intext Questions 21.3

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.

   ....

5. Write the formula of superphosphate of lime.

   ....

6. Name two compounds which are considered as nitrogenous fertilizers.

   ....

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.
- The salient features of nitrogen fixation.
- Fertilizers: nitrogenous, phosphatic, potassium and mixed. Their methods of preparation and their importance.

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 CO_2 molecules.
4. Why does BF_3 act as a Lewis acid?
5. What is catenation ? Why does carbon show catenation but silicon does not?
6. Compare the structure of CO_2 and SiO_2.
7. Describe briefly the Haber process for the manufacture of ammonia.
8. Why is graphite a conductor of electricity but diamond is not?
9. What type of fertilizers are the following?

   (i) Nitrolim (ii) Urea (iii) Superphosphate of lime

Answers to Intext Questions

21.1

1. (i) $B(OH)_3$

   (ii) $Na_2B_4O_7.10H_2O$
2. $4BCl_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$
3. $NM(SO_4)_2 .12H_2O$

Where N = monovalent large cation like K^+ or NH_4^+ and M = trivalent 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. $SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$

21.3

1. No. Nitrogen cannot increase its covalency beyond 4.
2. 107°.
3. sp^3
4. N, P and K
5. $Ca\,(H_2PO_4)_2$ along with $CaSO_4$ is known as superphosphate of lime.
6. Ammonium sulphate, Urea.

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

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

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

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 de oxidizer 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% 85-99%	Cheap balances, utensils in the laboratory
2.	Aluminium bronze	10-12% Al 88-90% Cu	Cheap Jewellery, Photo Frames, Making coins.
3.	Duralumin	95% Al 4% Cu 0.5% Mg 0.5% Mn	Making airship
4.	Y-alloy	92.5% Al 4% Cu 2% Ni 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:

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

21.2.1.a Similarities between Carbon and Silicon:

1. Both carbon and silicon have similar outer shell configuration i.e.ns^2np^2
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_2	SiO_2
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 mineral.
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 tetra chlorides 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 carbon monoxide (CO), Carbon oxide (CO_2) and carbon sub oxide (C_3O_2) are

Uses of CO and CO_2

S.No.	Carbon monoxide		Carbondioxide
1.	CO is an important component fuels like produceer gas, Water gas and coal gas.	1.	Solid CO_2 is called dry ice. it is used a refrigerant.
2.	CO is a good reducing agent.	2.	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	3.	It is used in the manufacture of urea and in neutralising alkalies.
4.		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, tridymite 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.

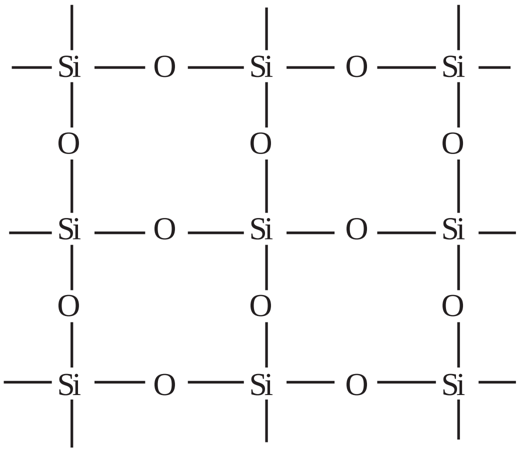
Uses:

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 $[Na_3(Al_6Si_6O_{24})S_2]$

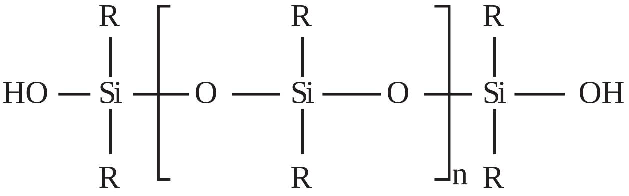
Uses:

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 be long chain linear compounds (or) cyclic and branched chain compounds. They are prepared from carbon silicon halides.

$$2R\text{-}Cl + Si \xrightarrow[300^0C]{Cu} R_2SiCl_2$$



$$HO - \underset{R}{\overset{R}{|}}\!\!\!\underset{|}{\overset{|}{Si}} \left[O - \underset{R}{\overset{R}{Si}} - O \right]_n \underset{R}{\overset{R}{Si}} - OH$$

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.

21.2.1.b Fuel gases:

Any substance which liberates energy when burnt in oxygen is called a fuel.

Fuels produce less ash and give more energy when burnt.

Producer gas:

It is essentially a mixture of CO and N_2 composition is 33% CO; 64% N_2; 3% CO_2; H_2

It is prepared in an furnace called Gas producer.

Coke is burnt at the bottom of the producer. Air is blown from the bottom. The following reactions takes place in the producer and producer gas is formed.

$$C + O_2 \longrightarrow CO_2 ; \qquad \Delta H = -394.0 \text{ KJ/mol}$$

$$CO_2 + C \longrightarrow 2\,CO ; \qquad \Delta H = +163.0 \text{ KJ/mol}$$

$$2C + O_2 \longrightarrow 2\,CO; \qquad \Delta H = -231.0 \text{ KJ/mol}$$

At the bottom CO_2 is formed which is passed through red hot coke and is reduced to carbon monoxide.

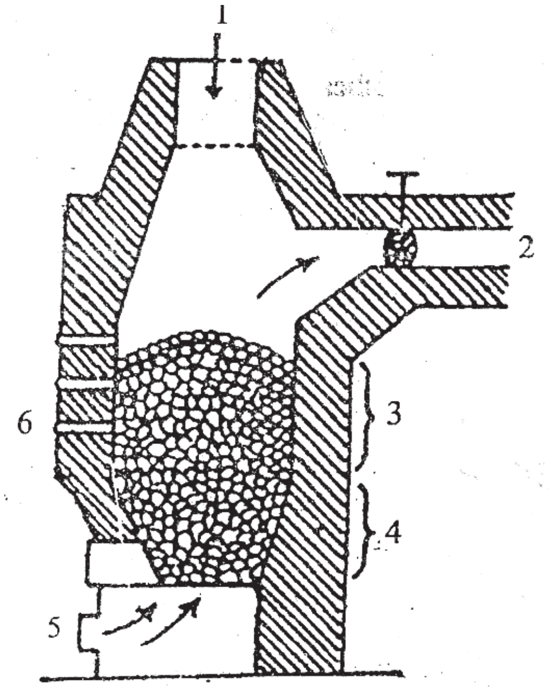


Fig. 21.2.1.b Manufacture of Producer Gas - "Gas Producer" Structure.
1. Charging hopper 2. Producer Gas 3. CO from CO_2 (reduction)
4. CO_2 from C (oxidation) 5. Air 6. Coke

The calorific value of producer gas is 5439.2 KJ M^{-3}

Uses:

1. It is used in gas engines.
2. It is used as an industrial fuel in the manufacture of steel and glass.

Water gas:

It is a mixture of Carbon monoxide and Hydrogen.

Composition of water gas 40-50% CO; 45-50% H_2. In the furnace coke is burnt to red hot and over it super heated steam is passed until it turns into white.

$$C + H_2O \longrightarrow CO + H_2 \quad \Delta H = +121.22 \text{ KJ/mol}$$

It is an endothermic reaction and the temperature of the coke comes down. When hot air is passed over the coke the temperature increases. Alternatively hot air and steam are blown into red hot coke. When hot air is passed over coke, the temperature increases due to exothermic reaction. The CO_2 and N_2 that are formed are sent outside.

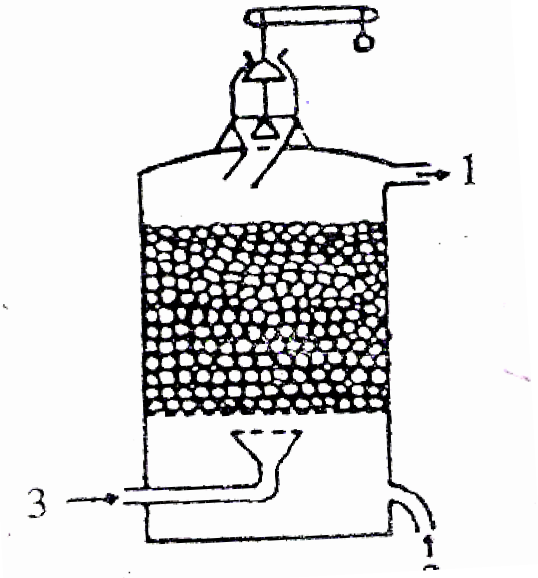


Fig. 21.2.1.b Manufacture of Water Gas

1. Water gas 2. Air 3. Water Vapour

It's calorific value is 13000 KJ M^{-3}. If the water gas burnt with blue flame, it is called as blue gas.

Uses:

1. It is used as fuel in industries.
2. Used in NH_3 preparation by Haber's process.
3. Used in Preparation of methyl alcohol.

21.2.1.a,b. Intext questions :

1. What is dry ice ?
2. What is the nature of C, Si oxides ?
3. What is carborundum ? How its prepared ?
4. What are silicons ? Write its one use ?
5. What is blue gas ? Why its called as blue gas ?
6. How much is the calorific value of producer gas ?

21.2.1.a,b. Answers to intext Questions

1. Solid CO_2 is called as dry ice.
2. The oxides of C, Si (CO_2, SiO_2) have acidic nature.
3. SiC (Silicon carbide) is carborundum. When silica is heated with coke in an electric furnace gives carborundum.
4. Poly Organo silicon compounds are silicons. There are used in aeroplanes as lubricants and to prepare grease.
5. Water gas is called as blue gas because it burnt's with blue flame.
6. The calorific value of producer gas is 5439.2 KJM^{-3}.

21.3.3.a Oxyacids of Phosphorous

After reading the lesson, you will be able to know

* The preparation and structures of oxy acids 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)

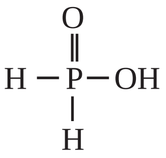
It is prepared in the laboratory by the interaction of yellow or white phosphorous and dilute solution of $Ba(OH)_2$ on heating.

$$6\,H_2O + 2P_4 + 3Ba(OH)_2 \longrightarrow \underset{\text{Barium hypo phosphoric}}{3\,Ba(H_2PO_2)_2} + \underset{\text{+ Phosphine}}{2\,PH_3\uparrow}$$

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 hypo phosphorous acid is represented is follow.



$$H-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OH$$

H_3PO_2 is monobasic acid

Meta phosphorous acid (HPO_2)

Meta phosphorous acid is very less 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.

$HO - P = O \quad HPO_2$

Ortho phosphorous acid (H_3PO_3)

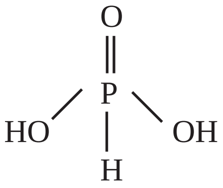
Ortho phosphorous acid is prepared by dissolving phosphorous (III) oxide P_4O_6 in cold H_2O

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3 \text{ or } P(OH)_3$$

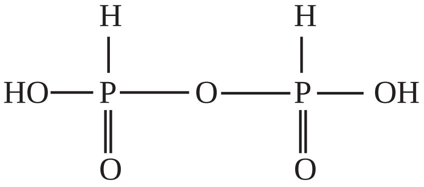
a. H_3PO_3 contains two acidic hydrogens. i.e. its basicity is two. It gives two series of salts. They are primary phosphates (containing $H_2PO_3^-$) or dihydrogen phoshates. Secondary phosphates (containing HPO_3^{-2}) or mono hydrogen phosphites.

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



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-OH$$

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

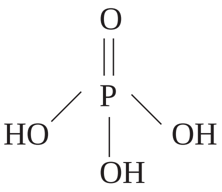
1. It is prepared by dissolving P_4O_{10} in water. $P_4O_{10} + 6H_2O \longrightarrow 4\,H_3PO_4$
2. It is weak tribasic acid and has no oxidizing or reducing properties. It gives three series of salts. These are dihydrogen phosphates (example NaH_2PO_4); mono hydrogen phosphates (example Na_2HPO_4) 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

$$H_3PO_4 \xrightarrow[-H_2O]{520K} H_4P_2O_7 \xrightarrow[-H_2O]{870K} HPO_3$$

Pyro Phosporic acid meta phosphoric acid

And then Meta phosphoric acid.

5. Orthophosphates are indentified in qualitative analysis by ammonium phospho molybdate formation. (Molybdate test). The canary yellow ammonium phospho molybdate has the formula $\{(NH_4)_3PO_4\ 12(Mo\ O_3)\}$
6. The structure of H_3PO_4 is represented in the figure shown



b. Meta phosphoric acid (HPO_3)

It is formed by heating pyro phosphoric acid or ortho phosphoric acid to 870K.

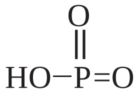
It is a glassy transparent solid. Hence it is called as glacial phosphoric acid.

It is a monobasic acid. Its salts are known as meta phosphates. There is no evidence for the existence of free mono phosphate ions (PO_3^-) or of the dimeta phosphate

$(P_2O_6)^{-2}$ or $(PO_3)_2$

But tri and tetra meta phosphates form a family of ring compounds.

The structure of meta phosphoric acid is represented as



$$HO-\overset{\overset{\displaystyle O}{\|}}{P}=O$$

c. Pyro phosphoric acid ($H_4P_2O_7$)

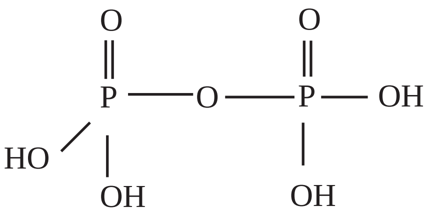
Pyro phosphoric acid is formed by heating an equimolecular mixing of the ortho and meta phosphoric acids at 373K

It is tetra basic acid but gives only two series of salts.

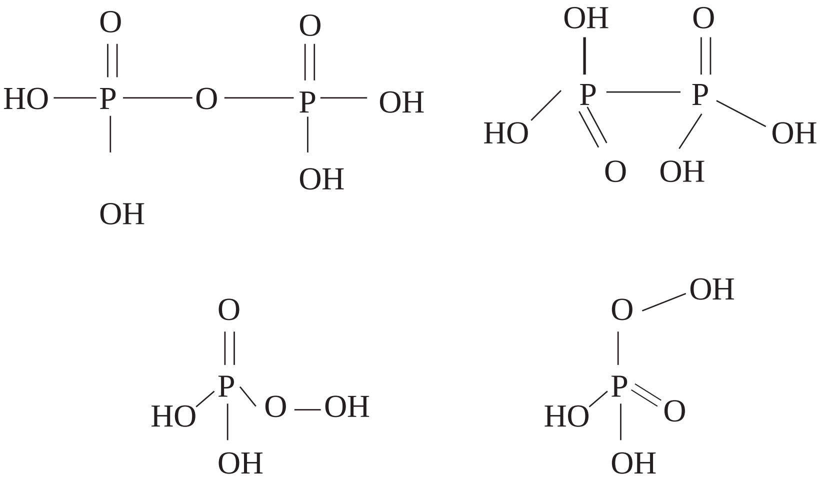
Example: $Na_2H_2P_2O_7$ $Na_4P_2O_7$

Pyrophosphates give positive answer to the molybdate test i.e. they give ammonium phosphor molybdate $(NH_4)_3PO_4\ 12(Mo\ O_3)$.

The structure of Pyro phosphoric acid is written as



Structures of Hypo phosphoric acid $H_4P_2O_6$ and peroxy phosphoric acid H_3PO_5



Some important characteristics of oxy acids 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. The P H bonds are responsible for the reducing properties of the acids.

iv. 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 atleast 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 tow 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. Hypo phosphorous acid, Pyro phosphorous acid and meta phosphorous acid
2. Meta phosphorous 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.

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 chloro fluoro 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}, $C1_2O_7$, Mn_2O_7, etc. These oxides combine with water to form acids whereas 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 Groups 1 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 *amphoteric oxides.* 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 into 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 behaviour of ZnO.

   ....

4. Name the compound formed when the oxide of an element of Group 1 or 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.

Ozone is formed around high voltage electrical installations. Traces of ozone are formed in forests by decay of organic matter. Ozone is prepared industrially by Siemen's ozonizer.

Siemens ozonizer : In this apparatus metal electrodes are used to produce an electric field. Two coaxial glass tubes are fused together at one end. The outer tube has an inlet for oxygen or air and an outlet for ozone (with oxygen or air). The inner side of the inner tube and the outer side of the outer tube are coated with tinfoil (T). These are connected to the terminals of an induction coil or high voltage transformer.

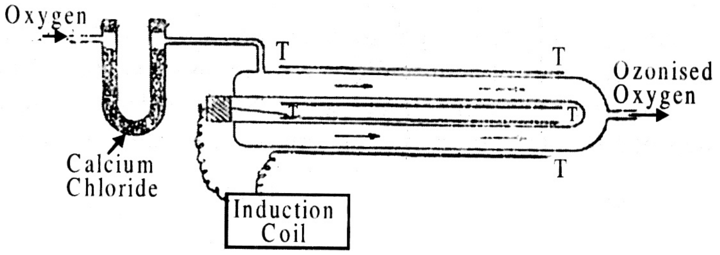
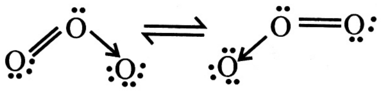


Fig. 22.1 : *Siemen s Ozonizer*

Pure, dry and cold oxygen or air is passed through the inlet in a slow current. Electrical energy is absorbed and about 5 to 10 percent of oxygen is converted into ozone.

All rubber and cork fittings are avoided because of the corrosive action of ozone on these materials.

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^o)



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 oxidi.zes 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.

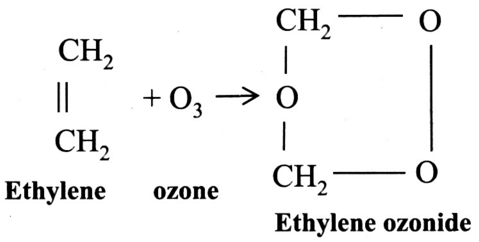
$$O_3 + 2Hg \rightarrow Hg_2O + O_2$$

The 'tailing' effect can be removed by washing with dilute acid.

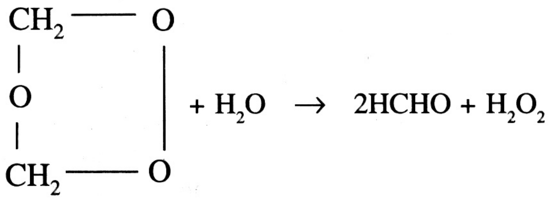
(v) Ozone oxidizes stannous chloride to stannic chloride. Note that no oxygen is produced in this reaction.

$$O_3 + 3SnCl_2 + 6HCl \rightarrow 3SnCl_4 + 3H_2O$$

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 set up. 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 ozonolyses 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 and (2) the Contact process. Nowadays 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 sulphur dioxide in then oxidized by atmospheric oxygen to sulphur trioxide in the presence of a catalyst, vanadium (V) oxide, V_2O_5 heated to 720K.

$$2SO_2 + O_2 \xrightarrow[720K]{V_2O_5} 2SO_3$$

The plant is operated at a pressure of 2 atmosphere 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 H_2SO_4, water must not be added to conc. H_2SO_4. Dilute sulphuric acid is prepared by adding Conc. H_2SO_4 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 electronegative 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.

$$2HX + F_2 \rightarrow 2HF + X_2 \text{ (X = CI, Br or I)}$$

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 by product in the electrolysis of sodium chloride. Chlorine is a greenish yellow gas and can be liquified 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, HCI, 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 < HCI < 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.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Hydrogen chloride is made by heating a mixture of NaCl and conc. H_2SO_4 at 423 K.

$$NaCl + H_2SO_4 \xrightarrow{423K} HCl + NaHSO_4$$

$$NaCl + NaHSO_4 \xrightarrow{823K} HCl + Na_2SO_4$$

High purity HCl is made by the direct combination of the elements (H_2 and $C1_2$)

$$H_2 + Cl_2 \longrightarrow 2HCl$$

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. 293 K), whereas HCl, HBr and HI are gases.
- The boiling point of HF is unexpectedly high as compared to HCI (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).

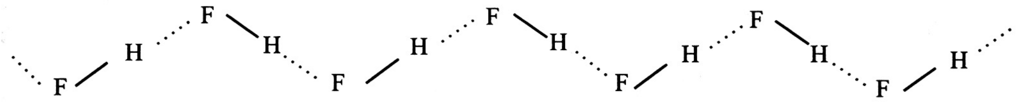


Fig. 22.2 : *Hydrogen bonded chain in HF*

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, hydrobromic acid 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 sand 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 hypochlorous acid. $Cl_2O + H_2O \longrightarrow 2HOCl$

It is a powerful oxidizing agent.

Chlorine dioxide, 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

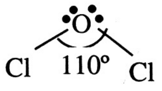
$$Cl_2O_6 + 2OH^- \longrightarrow ClO_3^- + ClO_4^- + H_2O$$

Chlorine heptoxide, Cl_2O_7 is prepared by the action of phosphorus pentoxide on anhydrous perchloric acid at 263 K.

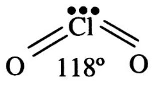
$$P_4O_{10} + 4HClO_4 \longrightarrow 4HPO_3 + 2Cl_2O_7$$

It is a colourless oil which explodes on heating or striking.

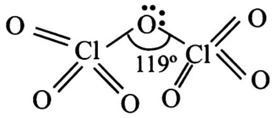
The structures of chlorine oxides are as follows :



Cl_2O



ClO_2



Cl_2O_7

Oxoacids of chlorine

Chlorine forms four oxoacids, HOCl, HOClO, $HOClO_2$ and $HOClO_3$

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.

$$\underset{\textbf{barium chlorate}}{Ba\,(ClO_3)_2} + H_2SO_4 \longrightarrow HClO_2 + BaSO_4$$

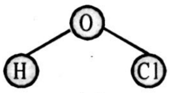
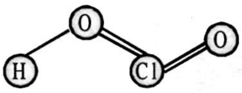
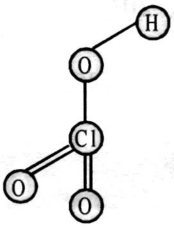
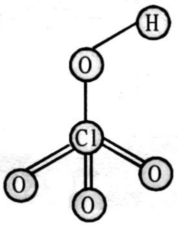
Perchloric acid, $HOClO_3$, is prepared by distilling potassium perchlorate with concentrated sulphuric acid under reduced pressure

$$\underset{\textbf{potassium perchlorate}}{2KClO_4} + H_2SO_4 \longrightarrow 2HClO_4 + K_2SO_4$$

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.

Table 22.1 : 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 then 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 whereas $HOClO_3$ is the strongest acid, thus the acid strength increases in the order.

$$HOCl < HOClO < HOClO_2 < HOClO_3$$

22.4.3 Chlorofluorocarbons (CFC)

Chlorofluorocarbons 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 tonnes 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 Interhalogen 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 can be prepared by direct reaction between the halogens. They can also be prepared by the action of a halogen on a lower interhalogen.

$$Cl_2 + F_2 \text{ (equal volumes) } \xrightarrow{473K} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess } F_2\text{) } \xrightarrow{573K} 2ClF_3$$

$$I_2 + 5F_2 \xrightarrow{293K} 2IF_5$$

$$I_2 + 7F_2 \xrightarrow{523\text{–}573K} 2IF_7$$

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 gases 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 np6. 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 Bartlett in 1962 by the reaction of xenon with PtF_6. Since then several other xenon compounds, mainly with the most electronegative elements (fluorine and oxygen), have been prepared. He, Ne and Ar do not form any compounds whereas 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

$$Xe + F_2 \xrightarrow{873K, 1bar} XeF_2(s)$$

(2:1 ratio)

$$Xe + 2F_2 \xrightarrow{873K, 7bar} XeF_4(s)$$

(1 : 5 ratio)

$$Xe + 3F_2 \xrightarrow{573K, 60\,bar} XeF_6\ (s)$$

(l : 20 ratio)

XeF_2, XeF_4 and XeF_6 are all white solids. They readily sublime at 298 K. They differ in their reactions with water

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 xenon trioxide and hydrogen fluoride.

$$6\ XeF_4 + l2H_2O \longrightarrow 4\ Xe + 2XeO_3 + 24\ HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

XeF_6 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.

$$XeF_6 + MF \longrightarrow M^+[XeF_7]^- \text{ (M = Na, K, Rb, Cs)}$$

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 cone. 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.

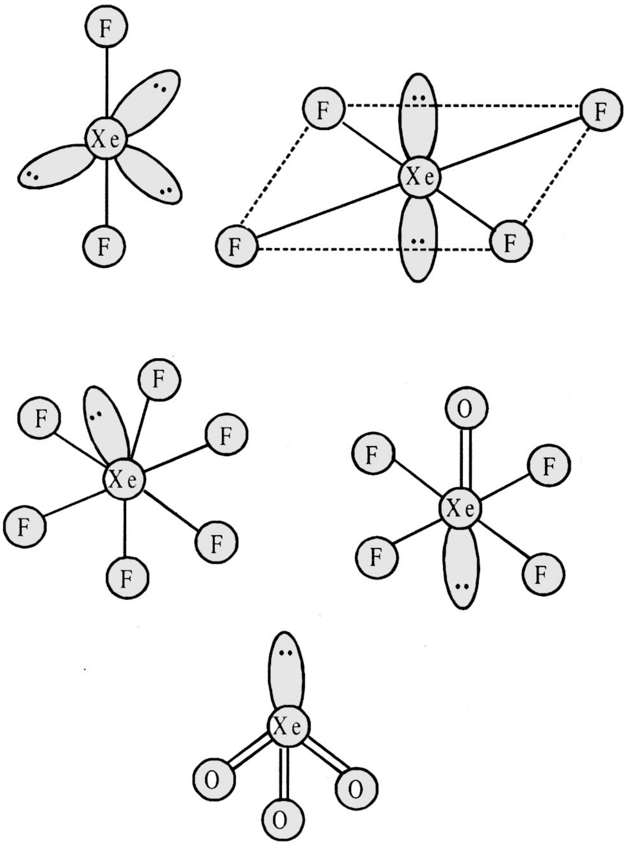


Fig. 22.3: *The structures of* XeF_2, XeF_4, XeF_6, XeO_3 *and* $XeOF_4$

What You Have Learnt

- While sulphur exists as S_8 molecules oxygen exists as O_2 molecules. Both these elements form divalent anions however 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 oxoacids : HOCl, $HClO_2$, $HClO_3$ and $HClO_4$.
- The binary compounds of halogens with one another are called inter halogen 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 other halogen forming interhalogens. Halogen (Fluorine) can even react with noble gases. Halogens react with hydrogen forming hydracids.
- Fluorochlorocarbons 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 do not react with either acids or alkalies. Which type of oxides are they?
3. Is ozone 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_4^-.
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. $ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$

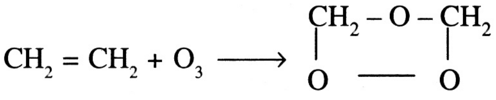
   $ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$
4. An oxide of group 1, K_2O and of Gr 2 BaO

   $K_2O + 2HCl \longrightarrow 2KCl + H_2O$

   $BaO + H_2SO_4 \longrightarrow BaSO_4 + H_2O$

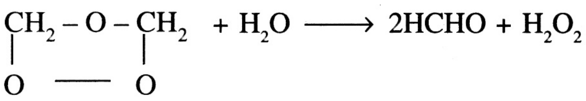
22.2

1. When ethene combines with O_3, an ozonide is formed, thus



$$CH_2 = CH_2 + O_3 \longrightarrow \begin{array}{l} CH_2 - O - CH_2 \\ \,| \qquad\qquad\; | \\ O \;\text{——}\; O \end{array}$$

On hydrolysis it gives HCHO,



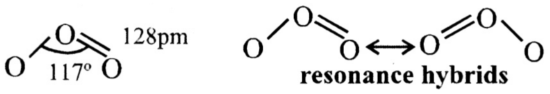
$$\begin{array}{l} CH_2 - O - CH_2 \\ \,| \qquad\qquad\; | \\ O \;\text{——}\; O \end{array} + H_2O \longrightarrow 2HCHO + H_2O_2$$

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.

4^0



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. Hl > HBr > HCl > HF
5. Chlorofluorocarbons (or freons)

22.1.a Sodium thiosulphate (HYPO)

Preparation of sodium thiosulphate.

Crystalline hydrated sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is known as 'hypo'

1. In the laboratory sodium thiosulphate is prepared by boiling alkaline or neutral sodium sulphate with 'flowers of sulphur'

$$Na_2SO_3 + S \xrightarrow{\text{Boiling}} Na_2S_2O_3$$

The unreacted excess sulphur is filtered off and the filtrate off and the filtrate is concentrated to the crystallization point. $Na_2S_2O_3.5H_2O$ crystallizes out.

2. Hypo is prepared by the oxidation of sodium sulphide or sodium polysulphide with air.

$$2Na_2S_5 + 3O_2 \xrightarrow[\text{in air}]{\text{heating}} 2Na_2S_2O_3 + 6S$$

3. Sodium sulphide solution can also react with SO_2 to form $Na_2S_2O_3$

$$2Na_2S + SO_2 \longrightarrow 2Na_2S_2O_3 + S$$

4. Hypo is manufactured industrially by a combination of the principle of oxidizing Na_2S with SO_2 and the laboratory technique.

Properties of Hypo

I. Physical properties:

a. Sodium thiosulphate is a colorless, crystalline efflorescent substance.

b. It is highly soluble in H_2O. It is one of the few common laboratory chemicals which form super saturated solutions.

II. Chemical properties:

a. Action of heat: Hypo loses all the molecules of water (water of crystallization)when heated to about 48K.

On heating it undergoes thermal decomposition to give H_2S, SO_2 and S.

b. Reaction with dilute acids: with dilute mineral acids (HCl or H_2SO_4), hypo produces SO_2 and S.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2 + S$$

c. Reactions with $AgNO_3$ solution: When hypo reacts with $AgNO_3$ solution, two types of reactions may take place.

First type of reaction:

When very dilute solution of sodium thiosulphate is added to $AgNO_3$ solution, a white precipitate of $Ag_2S_2O_3$ is formed which readily changes to black solid (Ag_2S). the reactions are:

$$Na_2S_2O_3 + 2AgNO_3 \longrightarrow 2NaNO_3 + \underset{\text{White ppt}}{Ag_2S_2O_3\downarrow}$$

$$H_2O + Ag_2S_2O_3 \longrightarrow H_2SO_4 + \underset{\text{Black ppt}}{Ag_2S\downarrow}$$

Second type of reaction:

When con. Hypo is added to $AgNO_3$ solution, a white precipitate $Ag_2S_2O_3$ is formed first. The precipitate readily dissolves in excess of sodium thiosulphate due to the formation of a complex compound $\{Na_2Ag(S_2O_3)_2\}$. The reactions are as follows:

$$Na_2S_2O_3 + 2AgNO_3 \longrightarrow \underset{\text{White ppt}}{Ag_2S_2O_3 \downarrow} + 2NaNO_3$$

$$Ag_2S_2O_3 \downarrow + 3Na_2S_2O_3 \longrightarrow \underset{\text{Sodium argento thiosulphate complex}}{2Na_3[Ag(S_2O_3)_2]}$$

d. **Reaction with iodine:**

Sodium thiosulphate is converted into sodium tetrathionate by l_2

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

This reaction is used in volumetric analysis. At the end point iodine gives an indigo blue color with starch indicator.

e. **Reaction with salts:**

Sodium thiosulphate reacts with ferric chloride, cupric chloride or auric chloride etc. and converts them into complex thiosulphate.

f. **Reaction with exposed photographic film or AgBr:**

In photography, the fixing is done by washing the film with hypo solution. Thus hypo is used as a photographic fixer making use of the following reaction. The silver bromide (or the silver halide) on the film reacts with sodium thiosulphate forming a complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$$

g. **Reaction with more Cl_2:**

Hypo reacts with Cl_2 giving Na_2SO_4 and HCl.

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + S + 2\,HCl.$$

This reaction is used in removing excess chlorine in some industrial processes. (Example: Textile industry) Hence t is known as ‘antichlor’

Uses of Hypo:

Hypo is used

I. In photography for fixing.

II. As an antichlor in textile industry.

III. In the volumetric analysis in the laboratory.

IV. As an antiseptic in medicine.

22.1.a Intext questions

1. Write the equation for the preparation of hypo in laboratory.

   ....

2. Mention any four uses of hypo.

   ....

3. What happens when hypo is heated?

   ....

4. How hypo is useful in photography?

   ....

What you have learnt

- Laboratory preparation of Hypo
- Physical & Chemical properties of Hypo
- Uses of Hypo

22.1.a Answers Intext questions

1. $Na_2SO_3 + S \longrightarrow Na_2S_2O_3$
2. 1. As Photographic fixel
   2. As Antichlov in cloth Industry
   3. As a reagent in Volumetric Analysis in the lab.
   4. As antiseptic in medicine.
3. Hypoloses water upto 488K. It decomposes into H_2S, SO_2 and S
4. Hypo is used as fixel in Photography.

   $AgBr + Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Terminal Exercise

1. Write about preparation of Hypo and Physical Properties.
2. Write the reactions of Hypo with the following

   a) Iodine b) AgBr c) Chlorine

22.1.b 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 sulphur trioxide SO_3

$$2SO_2 + O_2 \xrightarrow[\Delta]{\text{Catalyst}} 2SO_3$$

III. Sulphur trioxide is absorbed in H_2SO_4.

The pure SO_3 formed is absorbed in 98% conc. Sulphuric acid to get oleum or pyro sulphuric 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. SO_2 converts into SO_3 by Oxidation. This is a reversible reaction. It is an exothermic reaction

$$2SO_2 + O_2 \longrightarrow 2SO_3 \qquad H = -189 \text{ K J}$$

The equation reveals the following points:

I. 3 volumes of the reactants convert into 2 volumes of SO_3. 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_3 yields.

According to Le Chatelier's principle

I. A decrease in volume of the system is favored 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 withstand 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 SO_2 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 Pt deposited on $MgSO_4$ and a mixture of Fe_2O_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.

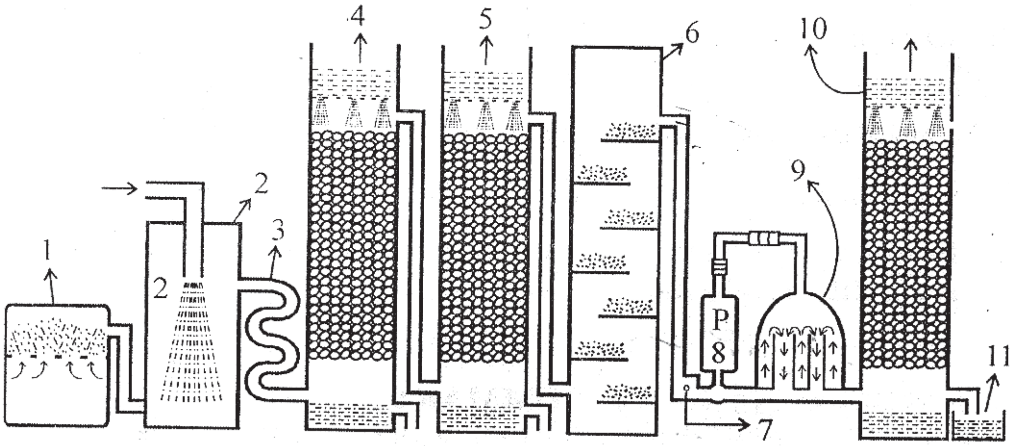


Fig. 22.1.b Manufacture of Sulphuric acid - Contact Process

1. Pyrites burners 2. Dusting tower 3. Cooling Pipes 4. Scribbing tower 5. Drying tower 6. Arsenic purifier 7. Testing box 8. Preheater 9. Catalytic chamber 10. Absorption tower

1. Pyrites burners or suphur burners: here S or iron 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. Preheater: 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, V2O5 maintained at the required temperature. SO_2 in 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 H_2SO_4

   ....

What you have learnt :

1. Preparation of Sulphuric acid by contact process.

22.1.b. 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.c Oxyacids of Sulphur

Sulphur oxoacids are numerous and more important than the oxyacids 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

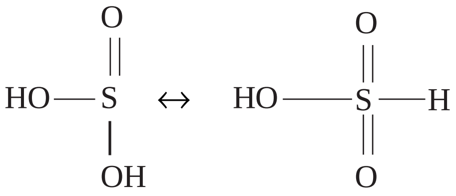
iii. Thionic acid series

iv. Peroxo acid series

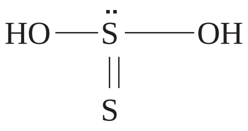
Each of these acids may have more than one structure. The structures of these acids which is possible resonating or fantomeric form are given.

i) Sulphurous acid series:

a) sulphurous acid – H_2SO_3 Oxidation state of S + 4.

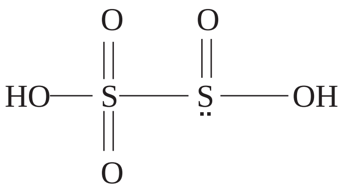


b) thio sulphurous acid. $H_2S_2O_2$, Oxidation state of S + 4.



c) Di sulphurous acid or

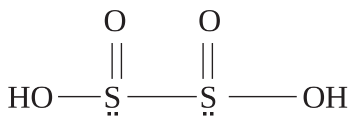
Pyro sulphurous $H_2S_2O_5$, Oxidation state of S +3, & +5



d) Dithionous acid

or

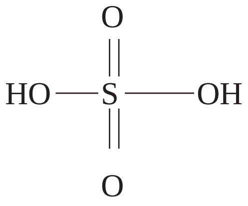
Sulphurous acid $H_2S_2O_4$, Oxidation state of S +3



$$\mathrm{HO-\overset{\overset{O}{||}}{\underset{\cdot\cdot}{S}}-\overset{\overset{O}{||}}{\underset{\cdot\cdot}{S}}-OH}$$

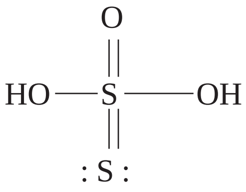
ii) Sulphuric acid series:

a) sulphuric acid H_2SO_4, Oxidation state of S +6



$$\mathrm{HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH}$$

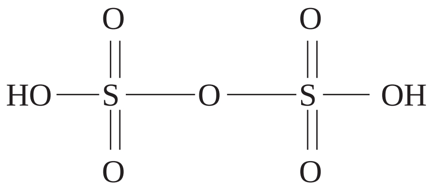
b) thio sulphuric acid. $H_2S_2O_3$, Oxidation state of S -2, +6



$$\mathrm{HO-\overset{\overset{O}{||}}{\underset{\underset{:S:}{||}}{S}}-OH}$$

c) Di sulphuric acid or

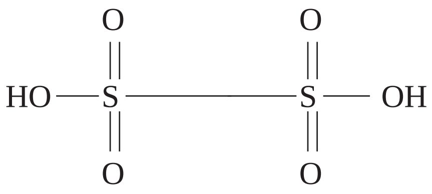
Pyro sulphuric acid $H_2S_2O_7$, Oxidation state of S +8, +6



$$\mathrm{HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-O-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH}$$

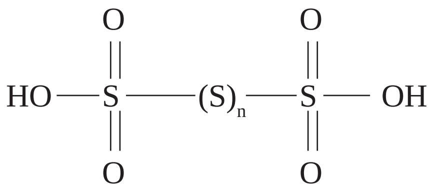
iii) Thionic acid series:

a) Dithionic acid $H_2S_2O_6$, Oxidation state of S +5



$$\mathrm{HO-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{S}}-OH}$$

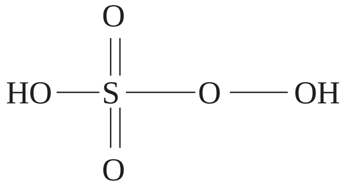
b) Poly thionic acid $H_2S_{(n+2)}O_6$, Oxidation state of S +5



$$\mathrm{HO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-(S)_n-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH}$$

iv) Peroxo acid series or peroxy acid series:

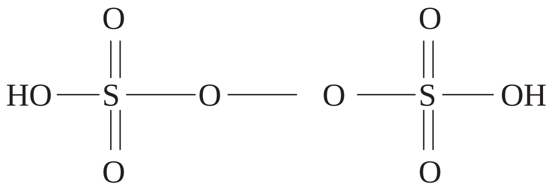
a) Peroxo mo sulphuric acid or caro's acid H_2SO_5, Oxidation state of S +6



$$\mathrm{HO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O-OH}$$

b) Peroxo di sulphuric acid or per sulphuric acid or Marshall's acid

$H_2S_2O_8$, Oxidation state of S +6



$$\mathrm{HO-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-O-\quad O-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH}$$

22.1.c Intext questions:

1. Write the structures of
   i) Dithionous acid ($H_2S_2O_4$)
   ii) Disulphurous acid $H_2S_2O_5$.

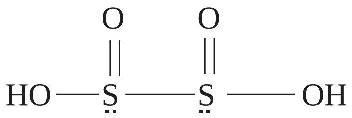
....

2. Write the structure of Dithionic acid $H_2S_2O_6$. What are the oxidation states of S atoms in it?

....

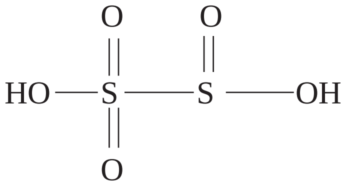
22.1.c Answers of intext questions:

1. a) Dithionous acid $H_2S_2O_4$



$$\mathrm{HO-\underset{\cdot\cdot}{\overset{\overset{\displaystyle O}{\|}}{S}}-\underset{\cdot\cdot}{\overset{\overset{\displaystyle O}{\|}}{S}}-OH}$$

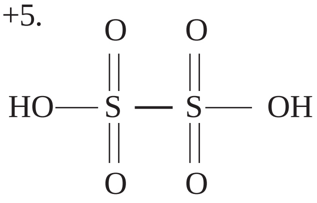
b) Disulphurous acid $H_2S_2O_5$



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{S}-OH$$

2. Dithionic acid $H_2S_2O_6$

   Oxidation state +5.



$$HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$

22.4a Fluorine & Chlorine

Preparation of Fluorine:

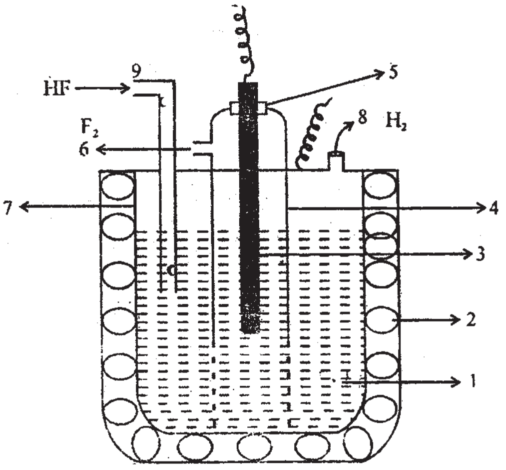
The isolation of fluorine from its minerals was a huge challenge in chemistry. Many unsuccessful attempts were made to isolate fluorine for over six decades. Commercially several types of electrolytic cells are used for the preparation of fluorine. All these methods utilize the same Moisasan's principle in fluorine isolation. The commonly used methods is **Whytlaw Gray's method.**

Whytlaw Gray Method:

In this method electrolysis is carried out in an electrically heated copper cell. The electrolysis fused potassium hydrogen fluoride (1:2; KF HF) the following reactions occur.

$$KHF_2 \xrightarrow[(700\text{–}1000^{o}C)]{\text{Fused}} K^+ + H^+ + 2F^- \text{ at anode } 2H^+ + 2e^- \rightarrow H_2 \rightarrow \text{ at anode } 2F^- \rightarrow F_2 + 2e^-$$

The copper vessel serves as cathode also. Anode is made of graphite. The anode is surrounded by a copper diaphragm at the bottom. This diaphragm prevents the mixing of H_2 and F_2 which react explosively if they come into contact.



1. Fused KHF2
2. Heating coil
3. Graphite (Anode)
4. Copper diaphram
5. Flourospar lid
6. Flourine
7. Copper cell (Cathode)
8. H_2
9. Way to HF

Fig. 22.4.a Witlaw Grey Method

Liberated at the anode is passed through the U – tube containing sodium fluoride. Hydrogen fluoride vapours accompanying fluorine as impurity are removed by NaF.

$$NaF + HF \longrightarrow NaHF_2$$

H_2 is liberated at the cathode. The corrosion of the cell by the action of F_2 is prevented by Teflon coating given to various parts of the cell. The Fluorine obtained in this method is almost pure with traces of the HF present in it.

Other methods of preparation of fluorine are also known.

Preparation of Chlorine:

Nelson's process:

Brine solution is electrolyzed. The following reactions take place

Ionization : $2\ NaCl \longrightarrow 2\ Na^{+} + 2\ Cl^{-}$

At the anode chloride ions are oxidized to chlorine.

$$2\ Cl \longrightarrow Cl_2 + 2\ e^{-} \text{ (de electronation or oxidation)}$$

Reduction of Na^+ to Na does not occur. But H_2O is reduced at the cathode.

At the cathode $2\ H_2O + 2\ e^{-} \longrightarrow H_2 - + 2\ OH^{-}$ (electronation or reduction)

$$2\ Na^{+} + 2\ OH^{-} \longrightarrow 2\ Na^{+}\ OH^{-}_{(aq)}$$

In the **electrolytic cell,** if the products come into contact with one another, other side reactions are likely to take place.

Eg : $2\ NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$

Or $2\ OH^{-} + Cl_2 \longrightarrow Cl^{-} + OCl^{-} + H_2O$

Therefore **Nelson's cell** arrangements are such that NaOH and Cl_2 do not come together

Nelson's Method:

In this process, a perforated steel U-tube lined inside with asbestos is used as cathode. The U-tube is suspended in outer iron tank. Brine solution is taken inside U-tube. A carbon rod is suspended

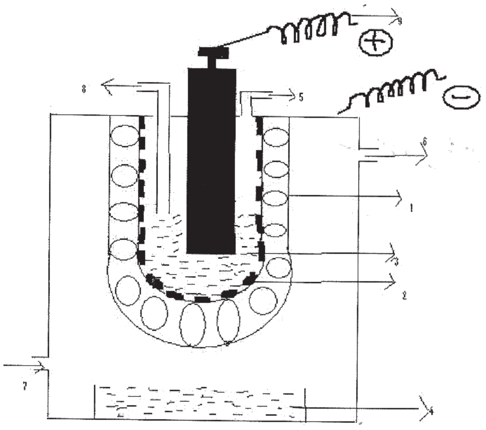


Fig. 22.4b Nelson's Cell

1. Perforated steel U-tube and cathode
2. Asbestos lining
3. Brine solution
4. NaOH solution collected
5. Cl_2 outlet
6. H_2 outlet
7. Steam inlet
8. Brine inlet
9. Graphite anode

into brine solution from the roof of the tank. The cathode and The anode are separated by the asbestos lining present inside U-tube. Chlorine liberated during the electrolysis is led out from the anode.

Na^+ ions diffuse through the asbestos lining. They combine with OH^- ions and form Na^+OH^-. H_2 escapes from the cathode compartment. H_2 and NaOH are the by products in this process. Sodium Hydroxide gets collected at the bottom. Steam is sent from the bottom of the tank while electrolysis is carried out. This passage keeps the solution hot and clears the perforations of the U-tube and of the asbestos lining.

22.4.a Intext questions:

1. Name the electrolyte used in the preparation of Cl_2 by Nelson cell method.

   ....

2. What is the product obtained at anode in Whytlaw grey's method

   ....

What you have learnt:

1. Preparation of Fluorine by Whytlaw grey's method.
2. Preparation of Chlorine by Nelson cell method.

Terminal Exercise:

1. Explain the Nelson Cell method of preparation of Cl_2
2. How do you prepare F_2 by Whytlaw grey method.

22.4.a Answer to Intext questions:

1. Sodium Chloride solution.
2. Fluorine.

22.5.a Physical–chemical method of isolations of inert gases

Noble gases are present in air though very rarely. They are separated from the other components like O_2, N_2 etc. two principle methods are employed for separating the noble gas. They are

1) physico – chemical methods
2) physical methods based on fractional distillation

The inert gases are separated from air in two steps A and B.

Step A:

This step involves the separation of a mixture of noble gases from air by adopting chemical methods.

1) **Ramsay – Rayleigh First method.**

Pure and dry air is passed over soda line (NaOH+ CaO intimate mixture) and potash solution. This removes CO_2 from air. The gases are passed through a long tube containing red hot copper. This removes O_2 from the gases. O_2 combines with Cu

$$2\,Cu + O_2 \longrightarrow 2\,CuO$$

Then the resulting gases are passed over hot mg metal. N_2 of the air is removed by the following reaction

$$N_2 + 3\,Mg \longrightarrow \underset{\text{Magnesium nitride.}}{Mg_3N_2}$$

The above process is repeated alternately several times till all the N_2 and O_2 are completely eliminated. A mixture of noble gases is obtained.

2) **Ramsey – Rayleigh second method:**

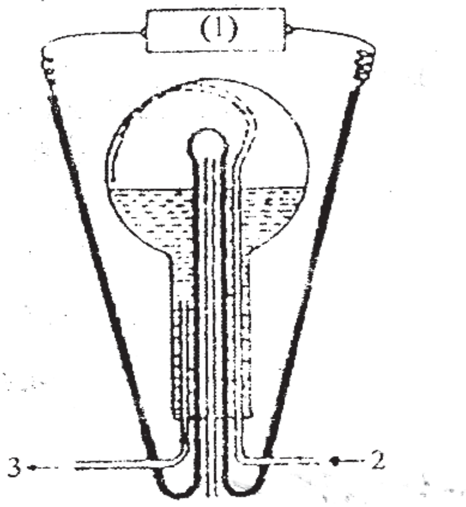


Fig. 22.5.a Remsey - Rayleight second method

1. Coil 2. NaOH Solution 3. NaOH Solution

N_2 and O_2 present in air combine under the influence of an electric discharge and form oxides of N_2 – the details of the process are given below.

A large flask of 50-60 liter capacity is fitted with five hoked rubber cork. Through the cork two stout pt electrodes are introduced. Two long tube are introduced into the flask through these tubes

NaoH is circulated. Through another hole in the cork long tube in passed through which a mixture of dry air and O_2 is sent in the air and O_2 in the ratio of 9:11.

An electric discharge at 6000-8000 volts is passed through the gas mixture. Nitrogen combine with O_2 to oxide of N_2

$$N_2 + O_2 \longrightarrow 2\,NO$$

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

$$2\,NO_2 + 2\,NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

Step B:

separation of the individual gases this step is based on adsorption of gases on activated charcoal. This was developed by "Dewar" principle involved in Dewar method.

1) Activated coconut charcoal adsorbs all the noble gases except Helium.
2) The adsorption depends on temperature lower the atomic weight of the Noble gas the lower is the temperature needed to adsorb it.

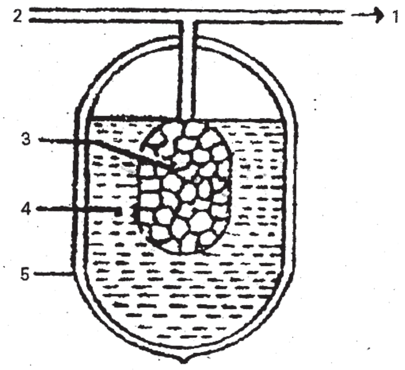


Fig. 22.5.a Dewar's flask

1. He and Ne 2. Mixture of noble gases 3. Coconut Charcoal
4. Liquid air 5. Dewar's flask

The mixture of inert gases is sent into a flask called Dewar's flask. It is a double walled flask-containing activated coconut charcoal

At 173 K_2Ar Kr and Xe gases are adsorbed by charcoal. While He and Ne remain un adsorbed.

The mixture of He and Ne is passed into another Dewer's flask at 93K only Ne gets adsorbed leaving behind Helium.

The charcoal with Ar, Kr, Xe is cooled to 77K. Argon comes out.

The temperature of the charcoal raised to 183K at this temperature Kr comes out Xe remains on the first charcoal is released by warning.

22.5.a Intext questions:

1. Draw the diagram Dewar flask and label it.

....

2. How O_2, N_2 removed from air in Ramsay Rayleigh method.

....

3. On what basis Dewar method for separating of Noble gas as developed.

....

22.5.a Answers to Intext Questions

1. See the diagram
2. By subjecting the O_2, N_2 to electric discharge. O_2 and N_2 will be removed in the form of NO

$$N_2 + O_2 \rightarrow 2\ NO$$

$$2NO + O_2 + 2NO_2$$

$$2NO_2 + 2NaOH \qquad NaNO_3 + NaNO_2 + H_2O$$

3. Noble gases adsorbs on activate charcoal.

Terminal Exercise:

1. Draw the neat labeled diagram of Dewar Flask.
2. Write the names of physical methods by which inert gases separated from the mixture.

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 4*s* subshell followed by 3*d* and 4*p* subshells. For the first time, we come across a group of elements in which a subshell of the previous principal quantum number (3*d*) starts getting filled instead of the expected subshell 4*p*. This group of elements that occurs in between the 4**s** and 4*p* elements is referred to as 3*d* elements or elements of first transition series (see periodic table). 4 *f* Series consist of 14 members from Ce to Lu (At. No. 58-71), where the penultimate subshell, 4 *f* 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 $KMnO_4$ 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 lanthanoides (4f-elements) and
- explain lanthanoide 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. (*n*–l) *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) whereas 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 3*d*, 4*d*, 5*d* and 6*d* 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 Questions 23.1

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 $(n-1)\,d^{1-10}\,ns^{1-2}$. The (n – 1) stands for inner shell and the *d*-orbitals may have one to ten electrons and the *s*-orbital of the outermost 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 3*d* 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 3*d* orbitals decreases with further increase of nuclear charge and becomes lower than 4*s*, and 4*p*, (in case of scandium At. No.21). Thus after filling of 4*s* orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to 3*d* orbital instead of 4*p*, 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 outermost 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 stabler than the one in which one electron is short, an electron gets transferred from 4*s* to 3*d* in case of the elements with atomic number 24 and 29. Consequently, configuration of chromium and copper have only one 4*s* electron (Table 23.1).

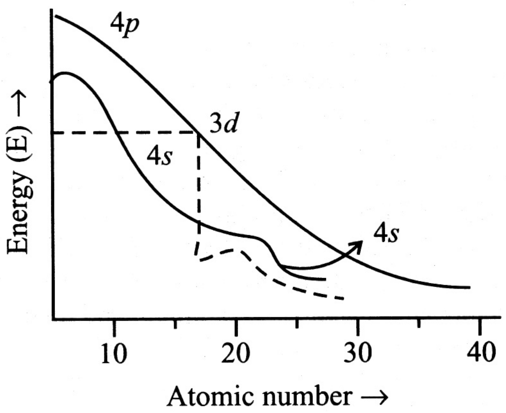


Fig. 23.1 : *Variation of energy of orbitals vs atomic number*

Table 23.1: 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	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$
Manganese	Mn	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

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 3*d* 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 3*d*, 4*d* and 5*d* 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 3*d* 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 3*d* orbitals are of higher energy than 4*s* orbitals (as is evident from the order of filling) the difference is so little that these are considered almost of same energy.

Intext Questions 23.2

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 Mn^{2+} 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	$3d^1\,4s^2$	$3d^24s^2$	$3d^3\,4s^2$	$3d^44s^2$	$3d^5\,4s^2$	$3d^64s^2$	$3d^7\,4s^2$	$3d^84s^2$	$3d^94s^2$	$3d^{10}4s^2$
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, 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 4 *f*- subshell (causing lanthanide contraction which you will study later in this lesson).

Intext Questions 23.3

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 $(n-1)d$ 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 3*d* 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_4^-, bonds formed between manganese and oxygen are 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.

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 whereas, 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, Ni^{2+} 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 3*d* metals ions are listed/in Table 23.3 which shows that greater the number of unpaired electrons, greater is the magnetic moment.

Table 23.3 : Magnetic moments of some ions of the transition elements:

Ion	Electronic configuration	Number of unpaired electrons	Calculated magnetic 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. 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 (A. = 4000 to 8000 A).

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	Pale green
Co^{2+}	7	Pink
Ni^{2+}	8	Green
Cu^{2+}	9	Blue

23.4.4 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%)

23.4.5 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

23.4.6 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 peroxodisulphate ions:

$$2I^{-}(aq) + S_2O_8^{2-}(aq) \xrightarrow{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

An oversimplified, 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 ($K_2Cr_2O_7$)

Mineral chromite ($FeO.Cr_2O_3$) is the starting material for the manufacture of all chromates and dichromates. Soluble chromates are prepared using alkali metal oxides, hydroxides or carbonates whereas 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 quick lime is heated in a reverberatory furnace in free supply of air. Carbon dioxide is evolved and sodium chromate is formed. The function of quick lime is to keep the mass porous and prevent fusion.

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

Chromite

The mass after roasting is extracted with water, which dissolves soluble sodium chromate leaving behind insoluble ferric oxide. After concentrating the solution containing sodium chromate, concentrated sulphuric acid is added.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium sulphate produced, crystallizes out and is removed. On further concentrating the solution, deliquescent red 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 triclinic crystals of potassium dichromate.

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Since potassium dichromate is moderately soluble in cold water (100 gL^{-1} at 298 K) but easily soluble in hot water (1000 g L^{-1}) at 373 K, 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 696 K. 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:

   $$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O$$

   The available oxygen then oxidizes ferrous, iodide ions and sulphur dioxide as follows:

   $$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$$

   $$2HI + [O] \rightarrow H_2O + I_2$$

   $$SO_2 + [O] + H_2O \rightarrow H_2SO_4$$

   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:

   $$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

   The ionic equation for the reducing action of Fe(II) can be represented as:

   $$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

   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 sulphur dioxide 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 an ionic chloride (such as NaCl, KCl etc.) forms red vapours of chromyl chloride, (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 whereas in alkaline medium, only monomeric chromate ions exist.

Uses:

1. Potassium dichromate is used as an important volumetric reagent for the estimation of Fe^{2+}, I^-, SO_3^{2-} etc.

2. It is used in the manufacture of chrome alum, 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 into 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 chrome alum. 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 ($KMnO_4$)

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 a trace 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 into 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 100 mL 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 S and SO_4^{2-} as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

$$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$$

(ii) 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 mouthwash, 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 Questions 23.6

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)

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 Electronic Configuration

Lanthanum is the first member of the third transition series, and it has one 5*d* and two 6*s* electrons. The next element is cerium, which while still retaining two 6*s* electrons, has two electrons in the 4*f* orbitals and none in the 5*d* orbitals. There are 7 separate 4*f* 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 4*f*- orbitals, respectively. These elements constitute the first inner transition series known as lanthanides and, although lanthanum itself does not possess any 4*f* electrons, it is customary to include this element in this series.

The filling up of the 4*f* 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 5*d* orbital. The element ytterbium has a full compliment of 4*f* electrons ($4f^{14} 5s^2 5p^6 5d^0 6s^2$) and the extra electron in the lutetium atom enters the 5*d* orbitals ($4f^{14} 5s^2 5p^6 5d^1 6s^2$). Except for lanthanum, gadolinium and lutetium, which have a single 5*d* electron, the lanthanoides do not have electrons in the 5*d* orbitals.

Table 23.6: Electronic configuration of lanthanides

Element	Symbol	Z	Electronic configuration
Lanthanum	La	57	$[Xe]4f^{o}5d^{1}6s^{2}$
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	$[Xe\ ]4f^{14}5d^{1}6s^{2}$

23.6.2 The lanthanoide contraction

Each succeeding lanthanoide differs from its immediate predecessor in having one more electron in the 4*f* 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).

Intext Questions 23.7

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 ground state: Gd, Lu, Ho,Er.

   ....

4. Write down the electronic configuration of the following ions: Eu^{3+}, Yb^{3+}, Ce^{4+}.

   ....

What You Have Learnt

- Transition elements have partially filled *d*-orbitals either in atomic or ionic state.
- They show general electronic configuration $(n-1)d^{1-10}ns^{1,2}$.
- 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.

Terminal Exercises

1. What distinguishes a transition metal from a representative metal?
2. Why is zinc 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 the irregularities.

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:

    (a) melting and boiling points.

    (b) atomic radius in the first transition series.

17. A solution of $KMnO_4$ 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.

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: $(n-1)d^{1-10}\,ns^{1\text{ or }2}$.
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 4*s* instead of 3*d* orbital. It is due to the fact that after Sc, 3*d,* becomes lower in energy than 4*s*.

23.3

1. due to strong interatomic 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., $Ni^{3+} 3d^7 n = 3$, $\sqrt{3(3+2)} = \sqrt{15} = 3.87$ 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 $Ce^{4+} = [Xe]4f^0$

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 photosynthesis in plants, is a magnesium complex and heamoglobin, 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, anionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

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 ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valance bond theory;
- apply VB theory to explain hybridization, shape and magnetic behavior of the following complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Cr(NH_3)_6]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ and
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.

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 are 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:

1. Metals exhibit two types of valence:

   (a) Primary valence (ionizable)

   (b) Secondary valence (non-ionizable).

   Primary or ionizable valence 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.

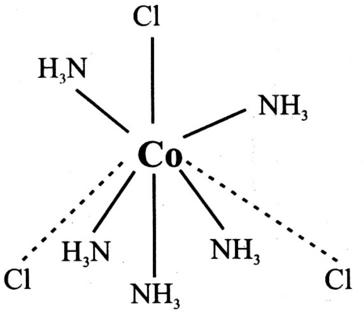
   Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence 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:



Primary valance (ionizable) (--------)
Secondary valance (non-ionizable) (———)

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 Questions 24.1

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?

   ....

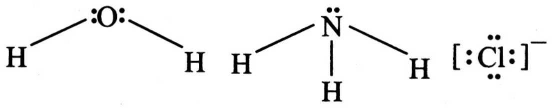
5. How many types of shapes are possible for four-coordinate complexes?

   ....

24.2 Definition of Some Important Terms

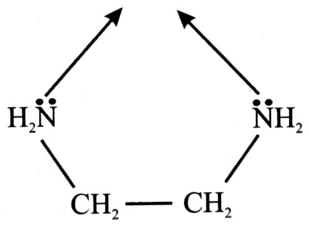
There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

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:



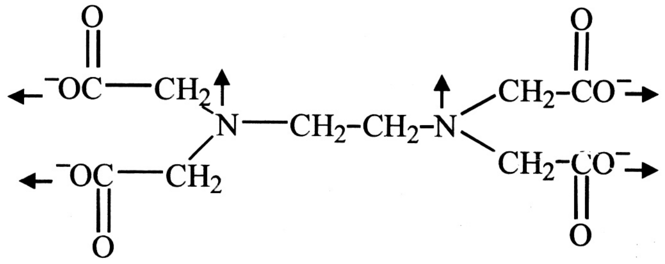
The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu^{2}+ is the acceptor atom in the $[Cu(NH_3)_4]^{2+}$ complex ion.

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 ethylenediarninetetraacetate 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 the central metal atom. The net charge on a complex ion is the 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.

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 polydenatate 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 hexaamminecobalt(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:

$[Co(H_2O)_6]C1_3$	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:

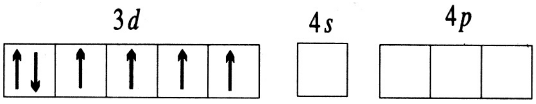
(a) Hybridization of valance orbitals of the central metal/ ion

(b) Bonding between ligand and the metal ion/atom.

(c) Relation between the type of bond and the observed magnetic behaviour.

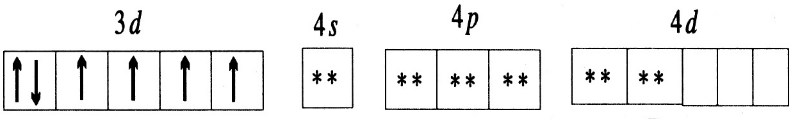
Six Coordinate Complexes

Let us explain by taking simple examples such as $[CoF_6]^{3-}$ and $[CO(NH_3)_6]^{3+}$, Although in both the 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 $3d^6$ 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.

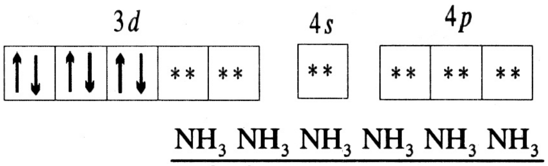
As CO^{3+} ion combines with six fluoride ligands in $[CoF_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one 4*s*, three 4*p* and two 4*d*. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. 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.

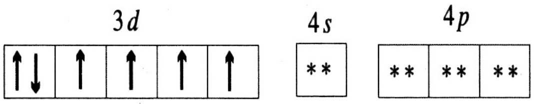
An alternative octahedral arrangement in $[Co(NH_3)_6]^{3+}$ is possible when the electrons on metal ion are rearranged as shown below:



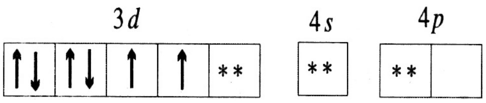
d^2sp^3, inner orbital complex

Since inner *d*-orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin 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*

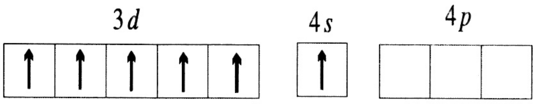
About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:

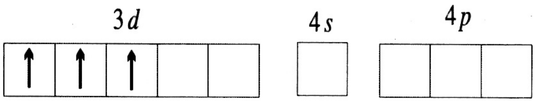
1. $Crr(NH_3)_6]^{3+}$

   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:

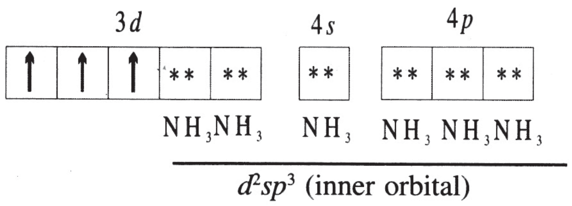
(i) Cr ground state:



(ii) Cr^{3+}



(iii) $[Cr(NH_3)_6]^{3+}$

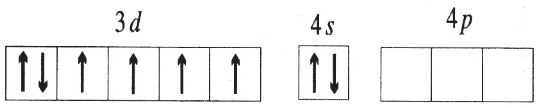


The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

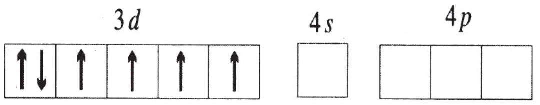
$$. \quad \sqrt{n}(n+2) = \sqrt{3}(\sqrt{3+2}) = \sqrt{15} = 3.87\text{B.M}$$

2. $[Fe(CN)_6]^{4-}$

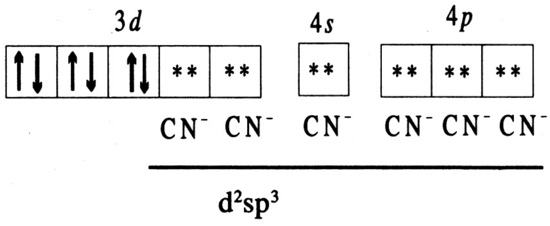
(i) Fe



(ii) Fe^{2+}



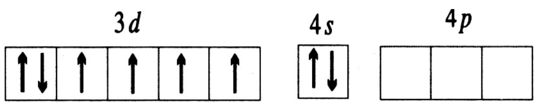
(iii) $[Fe(CN)_6]^{4-}$



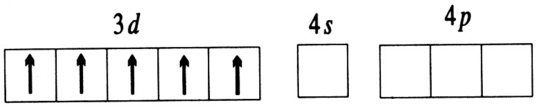
The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diagmagnetic.

3. $[Fe(CN)_6]^{3-}$

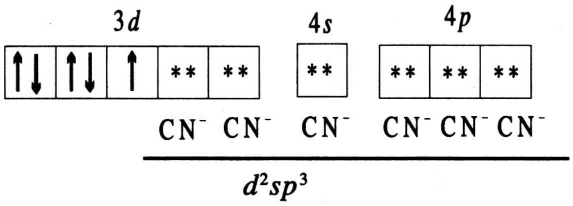
(i) Fe



(ii) Fe^3+



(iii) $[Fe(CN)_6]^{2-}$

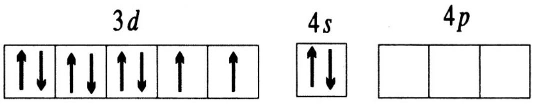


The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

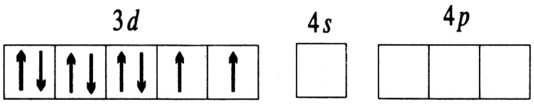
Four coordinate complexes:

1. $[NiCl_4]^{2-}$

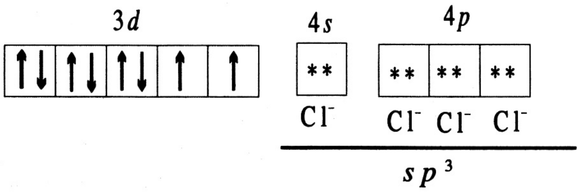
(i) Ni



(ii) Ni^{2+}



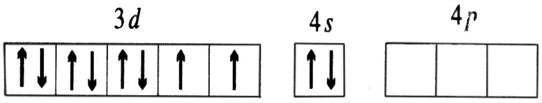
(iii) $[NiCl_4]^{2-}$



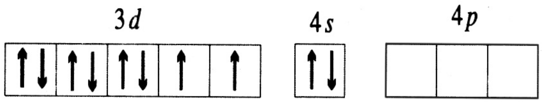
The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.

2. $Ni(CO)_4$

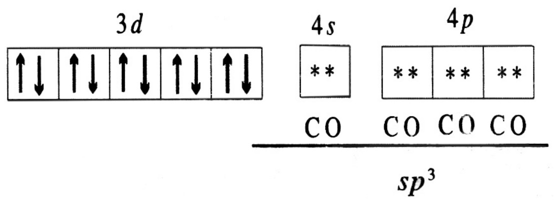
(i) Ni



(ii) Ni(O)



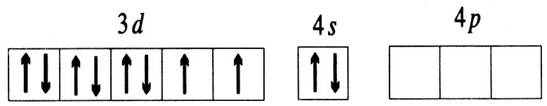
(iii) $Ni(CO)_4$



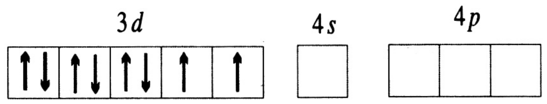
The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.

3. $[Ni(CN)_4]^{2-}$

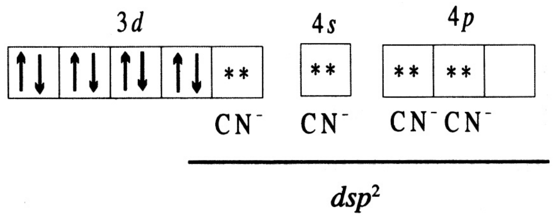
(i) Ni



(ii) Ni^{2+}



(iii) $[Ni(CN)_4]^{2-}$



The resulting complex is square planar and diamagnetic.

Intext Questions 24.4

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^3 or dsp^2 hybridization?

....

4. Which one is diamagnetic: $[Ni(CN)_4]^{2-}$ or $[NiCl_4]^{2-}$?

....

5. What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?

....

24.5 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 $[Au(CN)_2]^-$.

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

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

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+}

$$Ag^+ + 2NH_3(aq) \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]^+}$$

(b) Separation of IIA and IIB groups: 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. $K\,Fe^{II}[Fe^{III}(CN)_6]$.

(t) Cobalt (II) gives color with HCl due to the formation of complex $[CoCl_4]^{2-}$.

(g) Nickel forms a red complex $[Ni(DMG)_2]$ with dimethylglyoxime (H_2DMG).

Intext Questions 24.5

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 anticancer 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 (tetrahedral and square planar), and 6 (octahedral).
- Systematic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.
- Valance 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 (square planar) and d^2sp^3 or sp^3d^2 (octahedral).
- Complexes are very useful in qualitative analyses and in medicine.

Terminal Exercises

1. Define the following:
   - (i) Coordination number
   - (ii) Coordination sphere
   - (iii) Oxidation number
2. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.
3. Write the postulates of Werner's theory of coordination compounds.
4. 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) $[Fe(CN)_6]^{4-}$
5. Write down the formulae of the following complexes:
   - (i) Tris (ethylenediamine) platinum (IV)
   - (ii) Tetraaquadibromocobalt (III) ion
   - (iii) Sodium tetraiodozincate(II)
   - (iv) Tetracyanonickelate (II) ion
   - (v) Dichlorotetrathiocyanatochromium (III) ion
6. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?
7. $[NiCl_4]^-$ and $Ni(CO)_4$ are tetrahedral but differ in magnetic behaviour, explain.
8. $Nl(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic but have different geometry, explain.
9. $[NiCl_4]^{2-}$ is paramagnetic whereas $[Ni(CN)_4]^{2-}$ is diamagnetic, explain.

10. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:

    (i) $[Fe(CN)_6]^{4-}$

    (ii) $[Cr(NH_3)_6]^{2+}$

    (iii) $[Fe(CN)_6]^{3-}$

    (iv) $[NiCl_4]^{2-}$

    (v) $Ni(CO)_4$

11. Explain the application of complexes in extraction of elements, medicines and qualitative analyses.

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 valance 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, ethylenediammine and EDTA
5. +3, 6, Ethylenediammine.

24.3

1. (i) Tetraarnminedichlorocobalt(III) ion
   (ii) Ammonium-hexaisothiocyanatochromate(III)
   (iii) Tetracarbonylnickel(0)
   (iv) Potassium-hexacyanoferrate(II)
   (v) Tris(ethylenediamine)chromium(III) chloride
2. (i) $[NiCI_4]^{2-}$: (ii) $[Co(NH_3)_5NO_2]^{2+}$
   (ill) $K_3[Fe(CN)_6]^-$ (iv) $[Cr(en)_2Cl_2]^+$

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. $[Ni(CN_4]^{2-}$ 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. 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 electrovalency 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 phenomenon is known as isomerism.

The isomerism in complexes is broadly divided into two types. They are

1) Structural isomerism and

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 three types.

a) Ionization isomerism: Compounds which have the same stoichio metric composition but yield different ions in solution are called ionization isomers and this phenomenon as ionization isomerism.

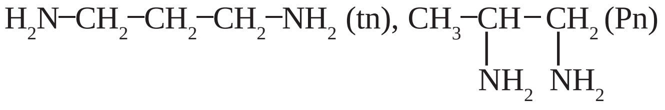
Eg:- $[Co(NH_3)_5Br]SO_4$; $[Co(NH_3)_5SO_4]$ Br

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:- $[Co(H_2O)_6]Cl_3$; $[Cr(H_2O)_5Cl]\ Cl_2 . H_2O$

c) Ligand isomerism: When the ligands in different complexes are themselves isomers then this isomerism is called Ligand isomerism.

Tri methylene diamine (tn) and propylene diamine (Pn) are ligand isomers.



$$H_2N-CH_2-CH_2-CH_2-NH_2 \text{ (tn)}, \quad CH_3-\underset{\underset{NH_2}{|}}{CH}-\underset{\underset{NH_2}{|}}{CH_2} \text{ (Pn)}$$

Eg:- $[Co(tn)_2Cl_2]$ Cl ; $[Co(Pn)_2Cl_2]Cl$

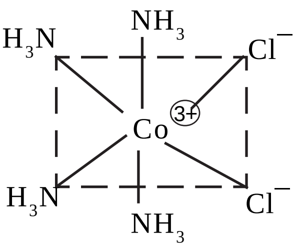
2) Stereo isomerism: Complexes having identical composition of coordination sphere but differ in the relative positions of co-ordination groups are called stereo isomers and this phenomenon as stereo isomerism.

It is sub divided into two types.

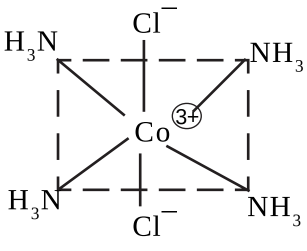
a) Geometrical isomerism: This is known as cis-trans isomerism. The isomers having same geometrical shapes but may differ in the position of the ligands around metal ion is called geometrical isomerism.

If the same ligands are arranged on one side of the metal ion, they are called cis and if they are arranged in opposite direction, they are called trans isomers.

Eg:- $[Co(NH_3)_4Cl_2]^+$



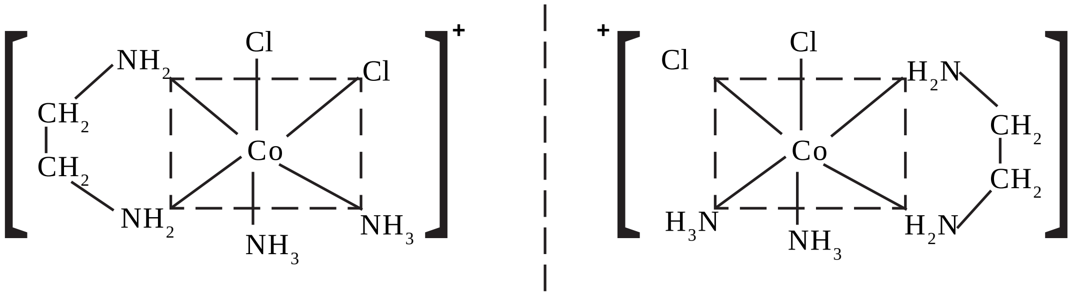
Cis form



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 super imposable. 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 dextrorotatory (or) d-form and if the light is rotated to left it is called Laevorotatory (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. Three types of structural isomerism are shown co-ordinate complexes these are
1. Ionization Isomerism, 2. Hydrate isomerism, 3. Ligand isomerism.

25

NOMENCLATURE AND GENERAL PRINCIPLES

Organic compounds are all 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 organism 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. The *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 also explained. Various types of reactions and electronic effects are discussed with examples. This lesson also covers different types of isomerism.

Objectives

After reading this lesson, you will be able to:

- name various types of organic compounds according to IUPAC system;
- distinguish between 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, hyperconjugation and steric hindrance, and
- explain structural isomerism and stereoisomerism.

25.1 Classification of Hydrocarbons

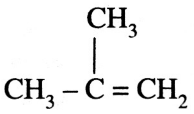
All organic compounds may be divided into two broad classes based upon the pattern of chain of carbon atoms. Let us now understand these classes of compounds.

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 and $CH_3-CH_2-CH_3$

   On the other hand, unsaturated compounds contain a double ($-C=C-$) or a triple ($-C\equiv C-$) bond between two carbon atoms.

   For example:



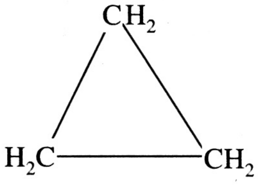
$$CH_3-\overset{\overset{\large CH_3}{|}}{C}=CH_2$$

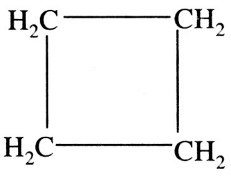
$CH_3-CH=CH_2$ $CH_3-C\equiv CH$

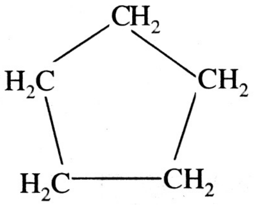
2. **Closed-chain or cyclic compounds:** These compounds have atleast one ring (cyclic) system. These are further divided into two sub-classes: **homocyclic and heterocyclic** based on the atoms present in the ring. They are called **homocyclic or carbocyclic** when the ring is formed by carbon atoms only.

   Homocyclic (carbocyclic) compounds may again be divided into two groups namely **alicyclic and aromatic** compounds.

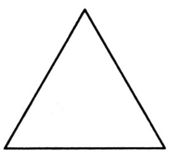
(i) **Alicyclic compounds:** This group includes saturated and unsaturated cyclic hydrocarbons which resemble with the aliphatic hydrocarbons in properties. Some examples are given below:

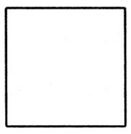


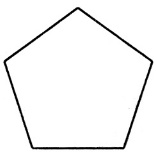




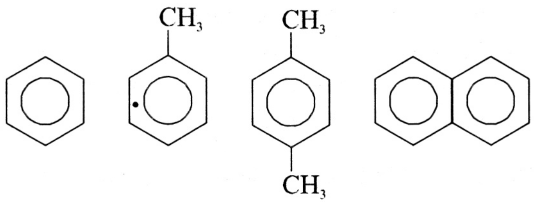
The above compounds can be represented in the form of condensed structures as shown below where each corner represents a $-CH_2-$group.



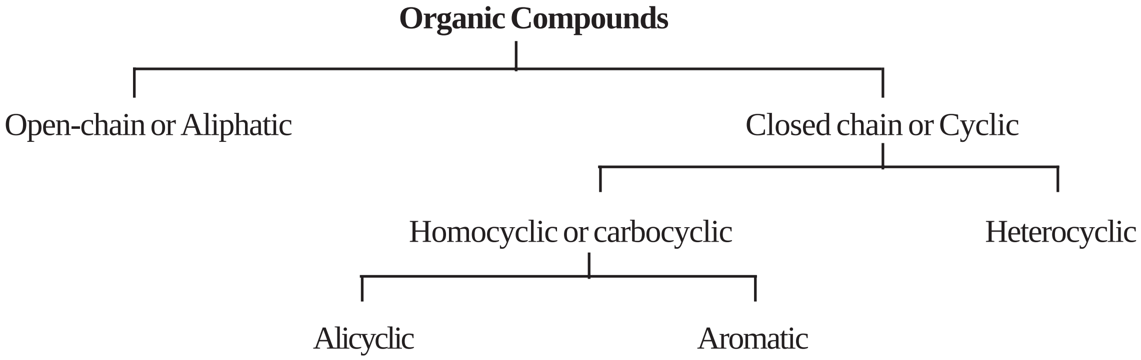




(ii) **Aromatic compounds:** The group of homocyclic compounds having special set of properties are called aromatic compounds which will be discussed in Lesson 26. They also have characteristic smell or *aroma* and hence called *aromatic*. These include aromatic hydrocarbons and their derivatives are examples of such compounds are as follows:

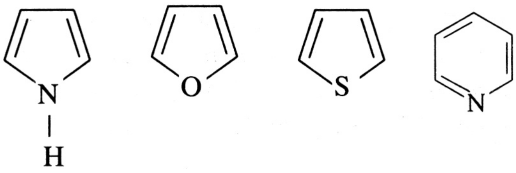


The above classification of the organic compounds can be summarised as below:



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 *nameformica).* 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 s 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 neighbouring compounds by the CH_2 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

Satuarated		**Unsaturated**			
General Name : Alkanes **General Formula :** C_nH_{2n+2}		**Alkenes** C_nH_{2n}		**Alkynes** 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 the in 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	Alkane
Unsaturated (>C=C<)	-ene	Alkene
Unsaturated (–C≡C–)	-yne	Alkyne

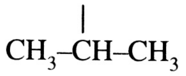
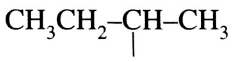
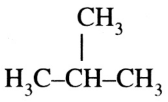
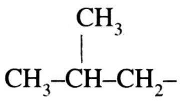
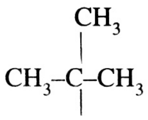
Let us consider some examples:

Compound	IUPACName	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.

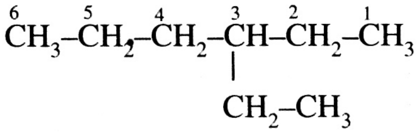
Table 25.4 : Some alkyl groups

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
		 $CH_3-\overset{\vert}{C}H-CH_3$	Isopropyl
Butane	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2$–	Butyl
		 $CH_3CH_2-\underset{\vert}{C}H-CH_3$	*sec*-Butyl
Isobutane	 $H_3C-\overset{\overset{CH_3}{\vert}}{C}H-CH_3$	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}H-CH_2-$	Isobutyl
		 $CH_3-\underset{\vert}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$	*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 *word root* and the saturation or unsaturation will determine the *suffix.*

Let us consider the following example:

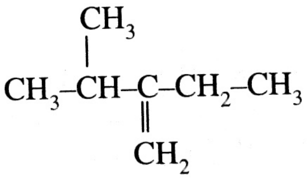


$$\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{4}{CH_2}-\underset{\underset{CH_2-CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

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,

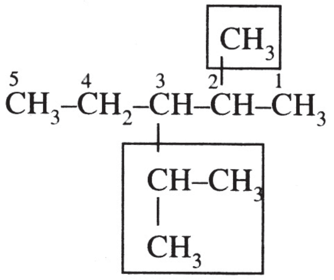


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_3$$

Wordroot -**But** + Suffix -**ene**

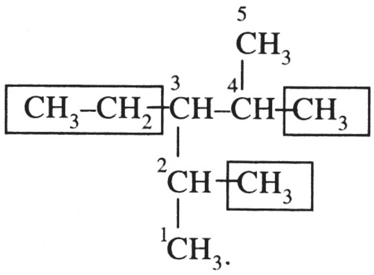
The main chain of carbon atoms containing double bond consists of *four* carbon atoms. Therefore, the compound will be a derivative of butene.

If two equally Long chains are possible, the chain with maximum number of side chains is selected as the main chain.



$$\overset{5}{CH_3}-\overset{4}{CH_2}-\underset{\underset{\boxed{\underset{\underset{CH_3}{|}}{CH}-CH_3}}{|}}{\overset{3}{CH}}-\overset{\overset{\boxed{CH_3}}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$$

***Main chain has* 2 *branches* (Wrong)**

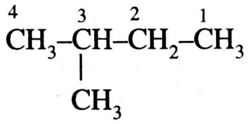


$$\boxed{CH_3-CH_2}-\underset{\underset{\underset{\underset{^{1}CH_3.}{|}}{^{2}CH-\boxed{CH_3}}}{|}}{\overset{3}{CH}}-\overset{\overset{\overset{5}{CH_3}}{|}}{\overset{4}{CH}}-\boxed{CH_3}$$

***Main chain has* 3 *branches* (Correct)**

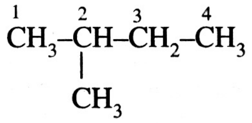
Rule 2: Lowest number or lowest sum rule: The longest carbon chain is numbered from one end to another and the positions of the side chain are indicated by the number of carbon atoms to which these are attached. The numbering is done in such a way that:

a) The substituted carbon atoms have the lowest possible numbers.



$\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$

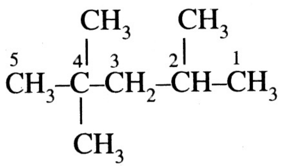
wrong numbering



$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$

Correct numbering

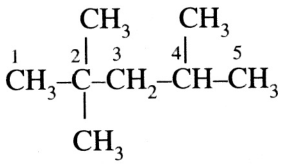
b) The sum of numbers used to indicate the positions of various alkyl groups must be the lowest.



$\overset{5}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{4}{C}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_3}$

Sum of positions* = 2+4+4 = *10

(Wrong)

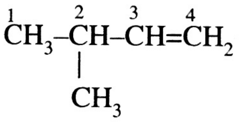


$\overset{1}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{4}{CH}}-\overset{5}{CH_3}$

***Sum of positions* = 2+ 2+4 = 8**

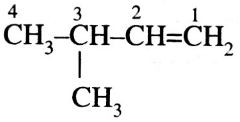
(Correct)

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:



$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{CH}=\overset{4}{CH_2}$

Wrong numbering



$\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\overset{2}{CH}=\overset{1}{CH_2}$

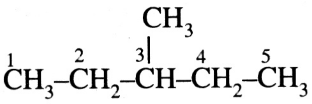
Correct numbering

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:

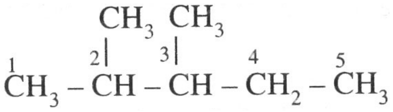


$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

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.



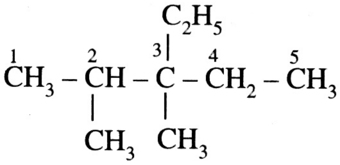
$$\overset{1}{C}H_3 - \underset{}{\overset{\overset{CH_3}{|}\,2}{C}}H - \overset{\overset{CH_3}{|}\,3}{C}H - \overset{4}{C}H_2 - \overset{5}{C}H_3$$

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



$$\overset{1}{C}H_3 - \underset{CH_3}{\underset{|}{\overset{2}{C}H}} - \underset{CH_3}{\underset{|}{\overset{\overset{C_2H_5}{|}\,3}{C}}} - \overset{4}{C}H_2 - \overset{5}{C}H_3$$

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.

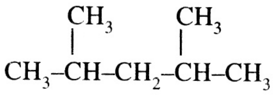
Intext Questions 25.1

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)



$$CH_3\text{–}\overset{\overset{CH_3}{|}}{C}H\text{–}CH_2\text{–}\overset{\overset{CH_3}{|}}{C}H\text{–}CH_3$$

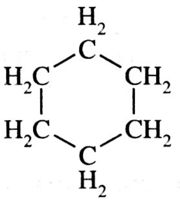
....

25.2.2 Nomenclature of Cyclic Hydrocarbons

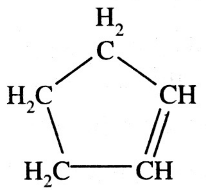
We already know that cyclic hydrocarbons can be divided into alicyclic and aromatic compounds. Now let us learn the nomenclature of these compounds.

a) **Alicyclic Compounds**

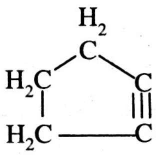
As we have already discussed (in Section 25.3) that alicyclic compounds have closed chain i.e. cyclic structures, hence their names are derived by putting *prefix* **'cyclo'** before the *word root.* The suffix **ane, ene or yne** are written according to the saturation or un saturation in the ring structure. Given below are some examples of alicyclic compounds.



Cyclohexane

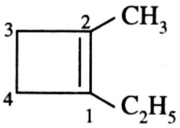


Cyclopentene

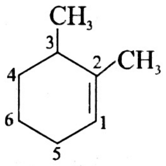


Cyclopentyne

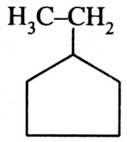
If an alkyl substituent is present, it is indicated by the appropriate *prefix* and its position is indicated by numbering the carbon atoms of the ring in such a way so as to assign the least possible number to the substituent. For example:



l-Ethyl-2-methylcyclobutene



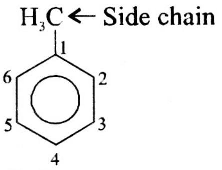
2,3-Dimethylcyclohexene



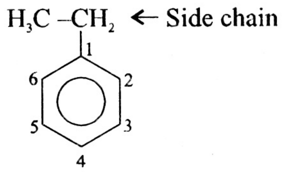
Ethylcyclopentane

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.

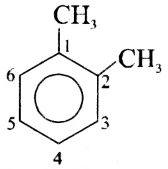


Methylbenzene (Toluene)

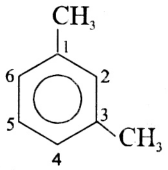


Ethylbenzene

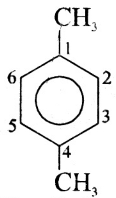
Benzene forms only one monosubstituted derivatives like methylbenzene or ethylbenzene. However, it can form three disubstituted compounds namely 1, 2; 1, 3 and 1, 4 derivatives. These are also known as *ortho-* (or *o-), meta-* (or *m-)* and *para-* (or *p-)* substituted compounds, respectively.



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**

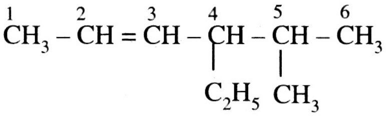
Step 1 The skeleton of parent hydrocarbon chain of six carbon atoms with C=C at C_2 is drawn.

$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\overset{6}{C}$$

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:



$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{C_2H_5}{\overset{4}{CH}}-\underset{CH_3}{\overset{5}{CH}}-\overset{6}{CH_3}$$

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.

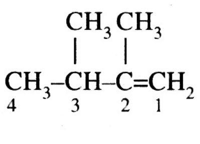
Step 3 Attach hydrogen atoms to the carbon atoms of main chain to satisfy tetravalency of all the carbon atoms,

The correct structure of the compound is as follows :

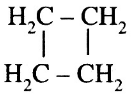
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH}=\overset{6}{CH}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

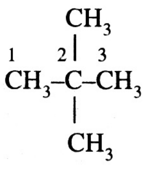
The following compounds illustrate some more examples:

(i) 2,3-Dimethylbut-1-ene (ii) Cyclobutane (iii) 2,2-Dimethylpropane



$$\underset{4}{CH_3}-\underset{3}{\overset{CH_3}{CH}}-\underset{2}{\overset{CH_3}{C}}=\underset{1}{CH_2}$$



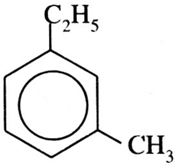


$$\overset{1}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{CH_3}$$

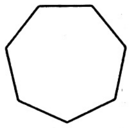
After this reverse exercise, you would have definitely gained confidence in naming and writing structures of various hydrocarbons.

Intext Questions 25.2

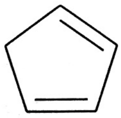
1. Write IUPAC names for the following compounds:

(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 :

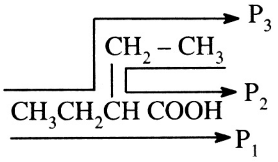
–Cl, –Br, –I, –COOH, –OH, $–NH_2$ etc.

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 :



$$CH_3CH_2\overset{\overset{\displaystyle CH_2-CH_3}{|}}{C}H\,COOH$$

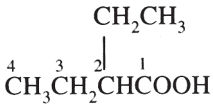
(Structure –I)

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.

Rule 3: There is a specific suffix for each functional group that replaces the ending -e in the name of the corresponding parent alkane.

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.



$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{\overset{CH_2CH_3}{|}}{\overset{2}{C}}H\overset{1}{C}OOH$$

(Structure I)

Rule 5 : While writing the name of the compound, place the substituents in the alphabetical order.

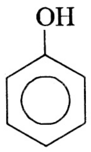
Table 25.5 list of some examples of the functional groups present in the organic compounds together with the names of the class of compounds they belong to.

Table 25.5. Some Common Functional Groups and their Aliphatic Derivatives

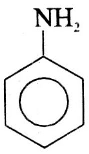
Functional Group	**Suffix/ Prefix**	**General name**	**Example (IUPAC name)**
–OH (Hydroxy)	–ol	Alkanol(Alcohols)	CH_3CH_2OH(Ethanol)
– COOH (Carboxyl)	–oic acid	Alkanoic acid	CH_3COOH (Ethanoic acid)
$-SO_3H$ (Sulphonic)	-	Alkysulphonic acid	$CH_3CH_2SO_2H$ (Ethyl sulphonic acid)
–CHO (Aldehydic)	-al	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	$CH_3C \equiv CCH_3$ (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**.

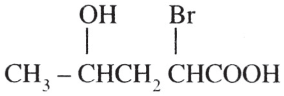


Phenol



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.



$$CH_3-\underset{}{\overset{OH}{\overset{|}{C}}}HCH_2\overset{Br}{\overset{|}{C}}HCOOH$$

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 is defined as 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 haring 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: $A - B \rightarrow A^{\bullet} + B^{\bullet}$

   (Free radicals)

   Now consider the following C - C bond fission:

   $$H_3C - CH_3 \xrightarrow[\text{Light}]{\text{Heat}} \bullet CH_3 + \bullet CH_3$$

   (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.

   $A : B \rightarrow A^{+} \quad + \quad B^{-}$

   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,

   $CH_3\overset{+}{C}H_2$ (Ethyl carbocation) and $CH_3\overset{+}{C}HCH_3$ (Isopropyl carbocation)

   On the other hand, an ion with a *negative charge* on the carbon atom is known as the carbanion.

For example,

   CH_3CH_2 (Ethyl carbanion), CH_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_2^{+}; Br^{+}, Cl^{+}, Ag^{+}, $CH_3\overset{+}{C}O$, 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, $:NH_3$ etc. Nucleophiles attacks a position of low electron density.

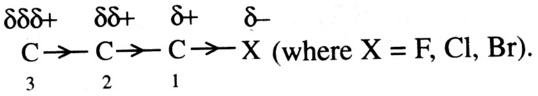
25.3.2 Electron Displacements in a Covalent Bond

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 C–X bond. Thus, the C-X bond is polarised as shown below.

$$C^{\delta+} \rightarrowtail C^{\delta-}$$

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)



$$\underset{3}{\overset{\delta\delta\delta+}{C}} \rightarrowtail \underset{2}{\overset{\delta\delta+}{C}} \rightarrowtail \underset{1}{\overset{\delta+}{C}} \rightarrowtail \overset{\delta-}{X} \text{ (where X = F, Cl, Br).}$$

This transmission of induced charges along a chain of (*σ 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.

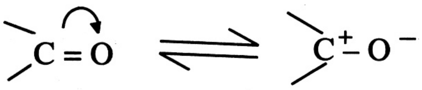
$$(CH_3)_3\,N^+ > -NO_2 > -CN > -F > -Cl > -Br > -I > -OH > -OCH_3 > -C_6H_s > -H$$

Groups with + I Effect (Electron Releasing Groups) :

Any atom or group of atoms that repels electrons more strongly than hydrogen, is said to have +1 effect. Following are the various groups in the decreasing order of +I effect.

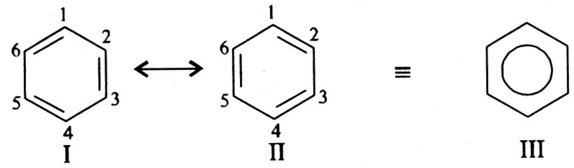
$$(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > -CH_3 > -H$$

(b) Electromeric effect : This type of temporary electron displacement takes place in compounds containing multiple covalent bonds (e.g $>C=C<$, $>C=O$, $>C=N$ 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.

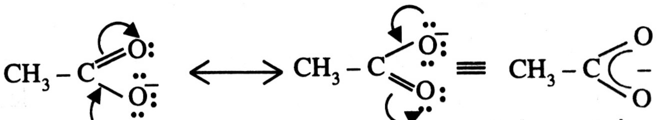
(c) Resonance : This phenomenon is exhibited by a number of organic molecules, which can be represented by two or more structures which are called resonating or canonical structures. However, none of those structures explains all the properties of the compound. All the possible structures of a compound are arrived at by the redistribution of valence electrons. The true structure of the compound is an intermediate of 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.



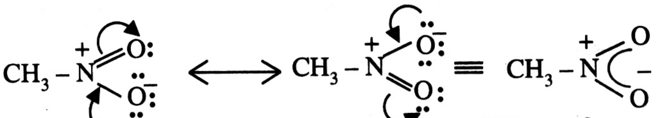
Resonating or canonical structures Resonance hybrid

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:

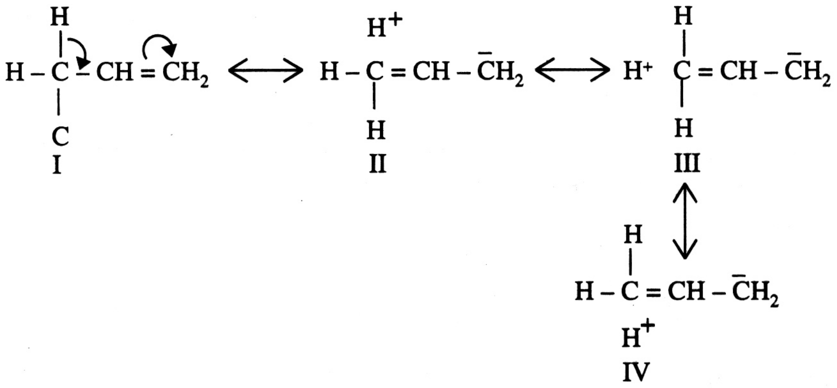


Ethanoate ion



Nitromethane

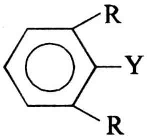
d) Hyperconjugation : Hyperconjugation is also known as *no-bond resonance.* It involves the conjugation of σ (sigma) bond with π(pi) bond. For example, hyperconjugation in propene can be represented as follows.



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.

$$\xrightarrow[\text{decreasing order of reactivity with alcohols}]{CH_3COOH>RCH_2COOH>R_2CHCOOH>R_3CCOOH}$$

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:

   $-NO_2$, $-CH_3$, $-CN$, $-C_2H_5$, $-C_6H_5$ and $CH_3\ \underset{|}{CH}-CH_3$

   ....

3. What is the difference between electromeric and inductive effects?

   ....

4. Classify the following species as electrophiles or nucleophiles :

   (i) H_3O^+ (ii) NO_2^+ (iii) Br^- (iv) $C_2H_5O^-$

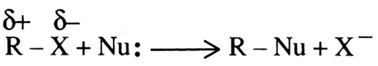
   (v) CH_3COO- (vi) SO_3 (vii) CN^- (viii) $^+CH_3$ (ix) $:NH_3$

   ....

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.

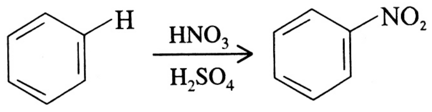


$$\overset{\delta+}{R} - \overset{\delta-}{X} + Nu: \longrightarrow R - Nu + X^-$$

Haloalkane

(where R- is an alkyl group and Nu: = –OH, $-NH_2$, –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.

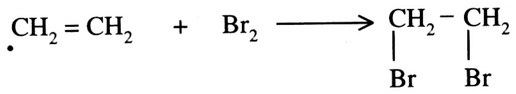


Nitrobenzene

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.



$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{Br}{CH_2} - \underset{Br}{CH_2}$$

1, 2-Dibromoethane (Colourless)

Similarly, hydrogen, halogen acids and chlorine add on to a –C=C– double bond, as shown below.

$$CH_3 - CH = CH_2 + H_2 \xrightarrow{\text{(Ni/Pt as catalyst)}} CH_3\,CH_2\,CH_3$$

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.

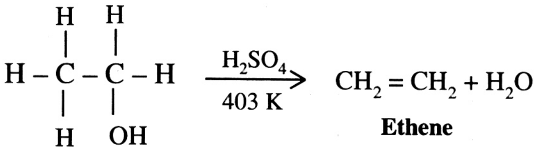
In alkynes (–C≡C–), two molecules of hydrogen add; first to give an alkene and finally the corresponding alkane, as shown below:

$$CH_3C \equiv CH \xrightarrow{+H_2/Ni-Pt} CH_2CH = CH_2 \xrightarrow{+H_2/Ni-Pt} CH_3CH_2CH_3$$

Propyne **propene** **Propane**

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.

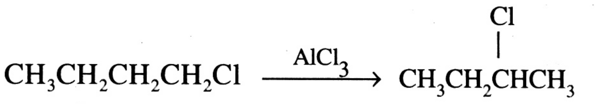


$$CH_3CH_2OH \xrightarrow[403\,K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethanol **Ethene**

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 ($AlCl_3$) rearranges to 2-chlorobutane.



$$CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3} CH_3CH_2CH(Cl)CH_3$$

1- Chlorobutane **2 - Chlorobutane**

Intext Questions 25.4

1. Write the products of each of the following reactions:

   (i) $CH_3CH_2Br + CN^- \longrightarrow$

   (ii) $CH_3Cl + RNH_2 \longrightarrow$

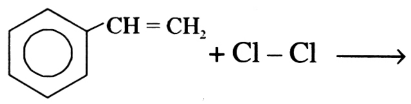
2. Write the conditions for nitration of benzene.

……

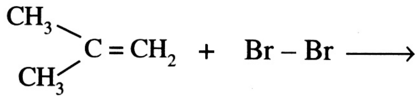
3. Predict the products of the following reactions :

   (i) $CH_2 = CH_2 \xrightarrow{+HBr}$

   (ii)

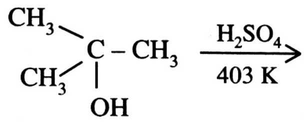


   (iii)



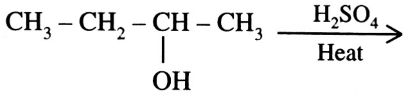
$$(CH_3)_2C = CH_2 + Br - Br \longrightarrow$$

   (iv)



$$(CH_3)_2C(OH) - CH_3 \xrightarrow[403\ K]{H_2SO_4}$$

   (v)

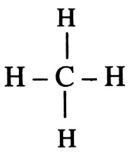


$$CH_3 - CH_2 - \underset{\substack{|\\ OH}}{CH} - CH_3 \xrightarrow[Heat]{H_2SO_4}$$

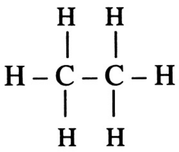
……

25.4 Isomerism

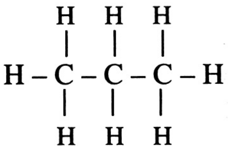
The simple alkanes containing upto three carbon atoms, i.e. methane, ethane and propane have only one possible structure. There is only one way in which the carbon atoms can be linked together as shown below :



Methane

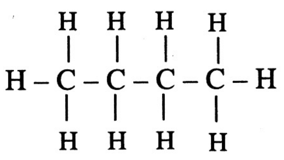


Ethane



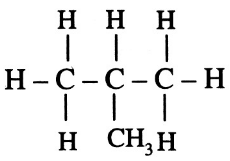
Propane

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.**



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

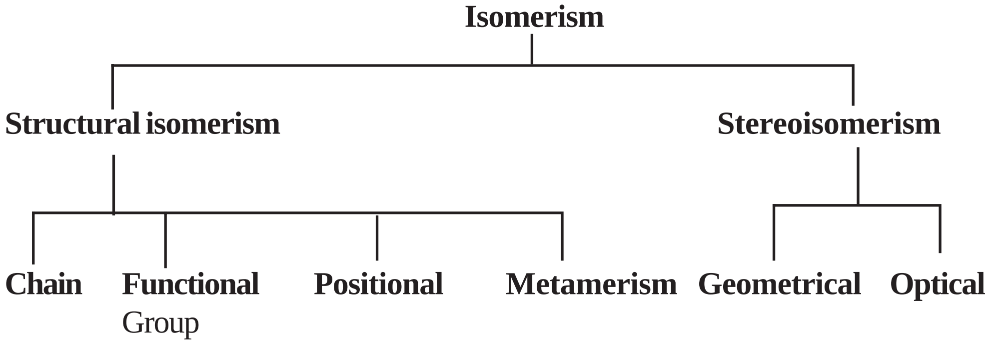
Butane (b.p.- –5 °C) 268 K



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array}$$

(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 :

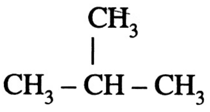


1. Structural Isomerism : Compounds which have the same molecular formula but differ in their structure are called structural isomers and the phenomenon is called structural isomerism. This is further subdivided into four types; chain, functional, positional isomerism, and metamerism.

(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**



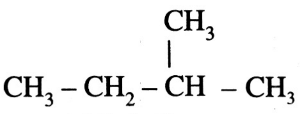
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & CH & - & CH_3 \end{array}$$

Isobutane

Similarly, pentane (C_5H_{12}) has the following three isomers:

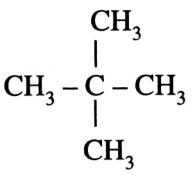
$CH_3-CH_2-CH_2-CH_2-CH_3$

***n*-Pentane**



$$\begin{array}{ccccccc} & & & & CH_3 & & \\ & & & & | & & \\ CH_3 & - & CH_2 & - & CH & - & CH_3 \end{array}$$

2-Methylbutane
(*Iso*pentane)



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

2,2- Dimethylpropane
(*Neo*pentane)

Similarily, 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 and CH_3-O-CH_3

Ethanol (alcohol) **Methoxymethane (ether)**

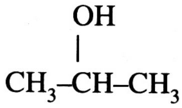
(Molecular Formula : $C_3H_6O_2$) CH_3CH_2COOH and $CH_3-COOCH_3$

Propanoic acid **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

Propan-1-ol

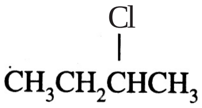


$$CH_3-\underset{}{\overset{OH}{CH}}-CH_3$$

Propan-2-ol

$CH_3CH_2CH_2CH_2Cl$ and

1-Chlorobutane



$$CH_3CH_2\overset{Cl}{C}HCH_3$$

2-Chlorobutane

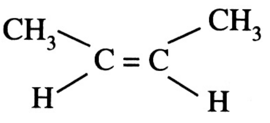
(iv) Metamerism is exhibited by those compounds in which functional group comes in between the carbon chain and breaks the continuity of the chain. This breaking occurs at different positions and different isomers are formed which are called Metamers. For example, 1-methoxypropane and ethoxyethane are two metamers differing in chain length (size of alkyl groups) on the two sides of oxygen atom as shown below.

$CH_3-O-CH_2CH_2CH_3$ and $CH_3\ CH_2-O-CH_2\ CH_3$

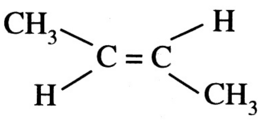
1-Methoxypropane **Ethoxyethane**

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.



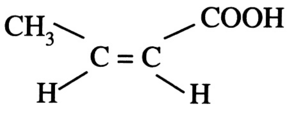
cis– **But-2-ene**



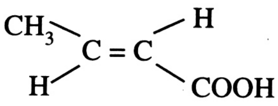
trans– **But-2-ene**

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**



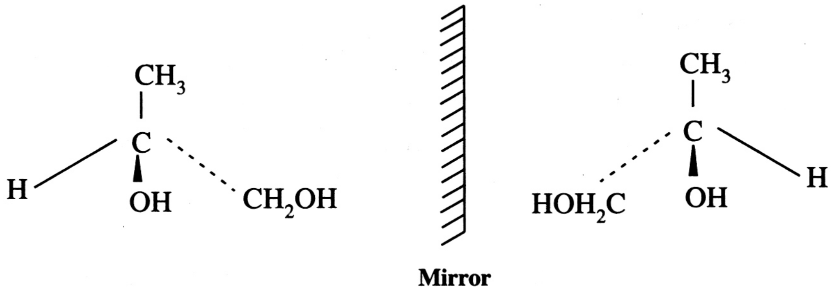
trans-**But-2-enoic acid**

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).

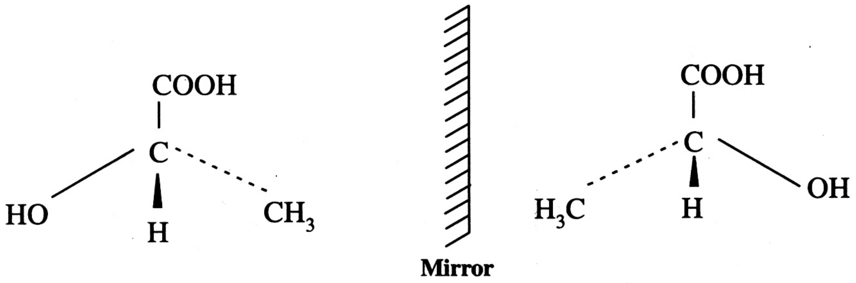
Geometrical isomerisms is also shown by cyclic compounds and compounds containing –C=N– bond, about which you will study at higher level.

(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 Lactic acid

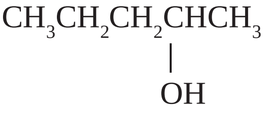
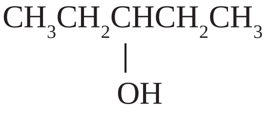
The optical isomers have identical physical properties except optical activity. They rotate the plane of plain polarized light in opposite directions. The plain polarized light is defined as the light that vibrates in one plane only. The rotation of the plane of polarized light is called optical activity. 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

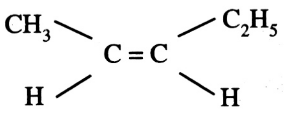
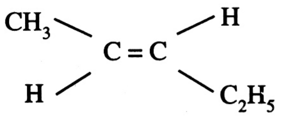
1. Is 1-butene a structural isomer of cis- or trans-2-butene?

....

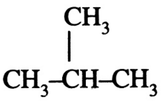
2. Identify the type of isomerism exhibited by the following pairs of compounds:

(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 
$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$

....

(iv) $CH_3CH_2CH_2OH$ 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) $CHF=CHF$ (iii) $CH_2=CHCH_2CH_3$

....

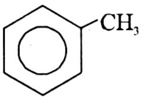
What You Have Learnt

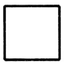
- Organic compounds are classified into aliphatic (open-chain), homocyclic (closed ring) or carbocyclic (alicyclic and aromatic) hydrocarbons and their derivatives, and heterocyclic compounds (contain at least one heteroatom i.e., N,S,O in the ring).
- **Homologous series** of organic compounds and IUPAC naming of different classes.
- 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.

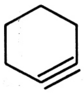
Terminal Exercise

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) $CH_3\ C \equiv CCH_3$
(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.

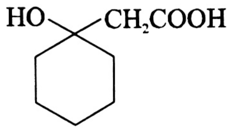
9. What is a nucleophilic aliphatic substitution reaction? Give one example.

10. Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.

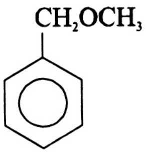
11. Write a short note on the following; (i) Structural isomerism (ii) Stereoisomerism

12. Define a functional group. Identify the functional group(s) present in following compounds:

(i)



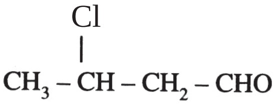
(ii)



(iii) $CH_3COCH_2C \equiv CH$

(iv) $CH_3 - CH_2 - CH_2 - O - CH_3$

(v)



$CH_3 - \underset{|}{\overset{Cl}{CH}} - CH_2 - CHO$

(vi) CH_3CONH_2

15. Describe hyperconjugation in terms of resonance.

Answersto Intext Questions

25.1

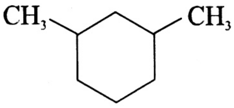
1. **Word root Suffix**

Word root	Suffix
(i) Hex	ane
(ii) Pent	2-ene
(iii) Prop	yne

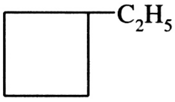
2. (i) Oct-2-ene (ii) 2, 4-Dimethylpentane

25.2

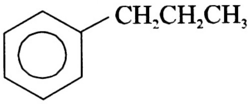
1. (i) l-ethyl-3-methylbenzene
   (ii) Cycloheptane
   (iii) Cyclopenta-l ,3-diene
2. (i)



(ii)



(iii)

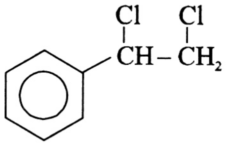


25.3

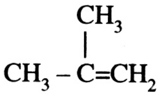
1. Covalent bond between two different atoms having large difference in their electronegativities.
2. -I effect groups $-NO_2$, $-CN$, $-C_6H_5$ +
   I effect groups $-CH_3$, $-C_2H_s$’ CH_3CHCH_3
   |
3. Electromeric effect is temporary polarization, whereas inductive effect is permanent polarisation 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) 
   $CH_3 - \overset{\overset{\large CH_3}{|}}{C}{=}CH_2$

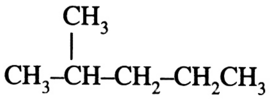
   (v) $CH_3 - CH = CHCH_3$(major product)

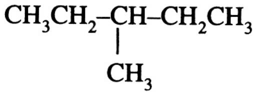
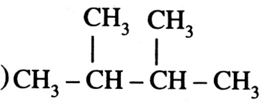
25.5

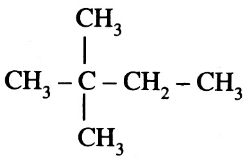
1. Yes
2. (i) Positional isomerism

   (ii) Geometrical isomerism

   (iii) Chain isomerism

   (iv) Functional group isomerism
3. (i) $CH_3CH_2CH_2CH_2CH_2CH_3$ (ii) 
   $CH_3{-}\overset{\overset{\large CH_3}{|}}{CH}{-}CH_2{-}CH_2CH_3$

   (iii) 
   $CH_3CH_2{-}\underset{\underset{\large CH_3}{|}}{CH}{-}CH_2CH_3$ (iv) 
   $CH_3 - \overset{\overset{\large CH_3}{|}}{CH} - \overset{\overset{\large CH_3}{|}}{CH} - CH_3$

   (v) 
   $CH_3 - \overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - CH_2 - CH_3$
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.

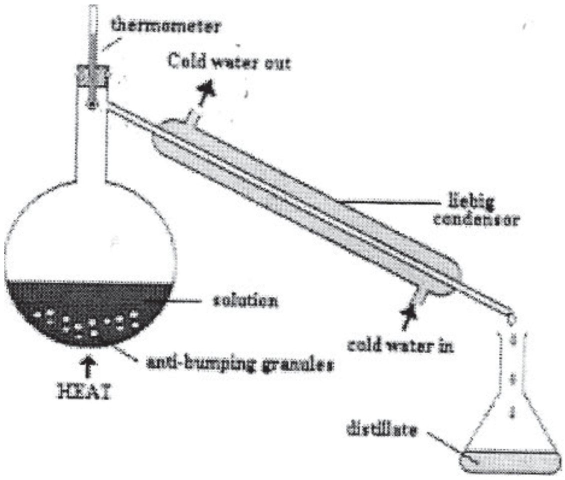


Fig. 25.a Distillation

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 lipids 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.

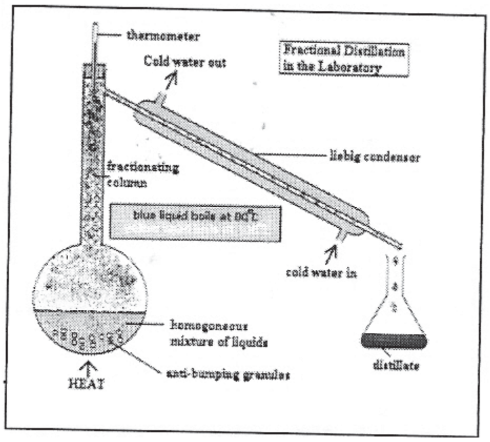


Fig. 25.b Fractional Distillation

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.

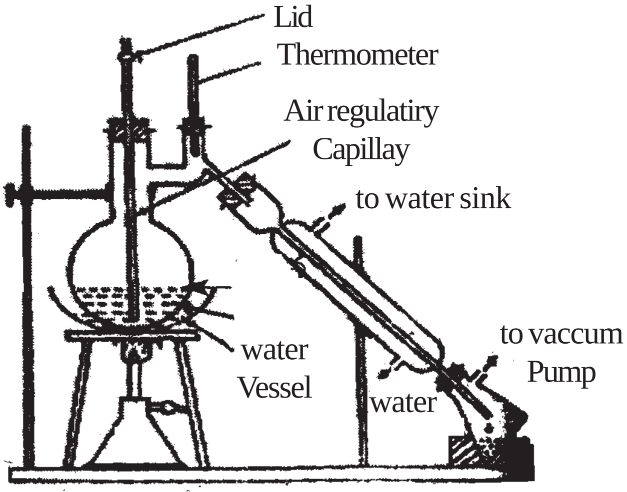


Fig. 25.c Distillation under reduced pressure

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

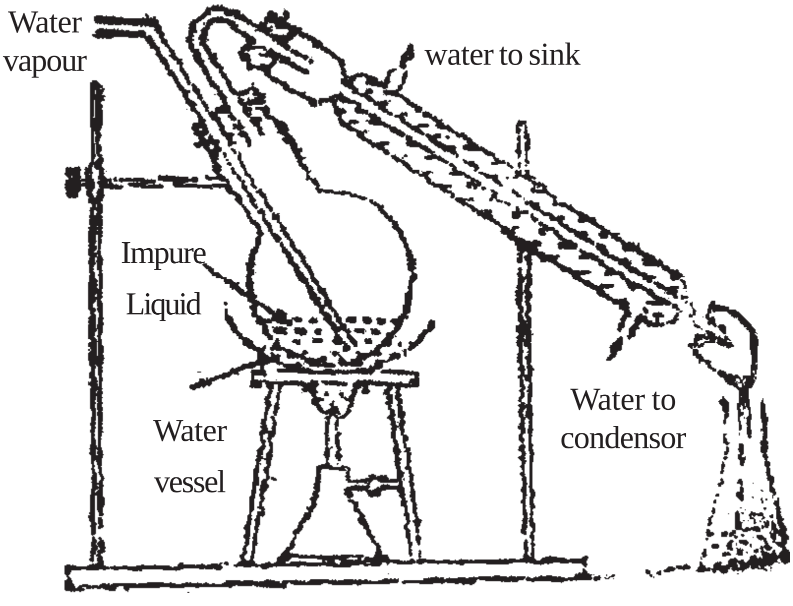


Fig. 25.d. Steam distillation

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 ie., 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.

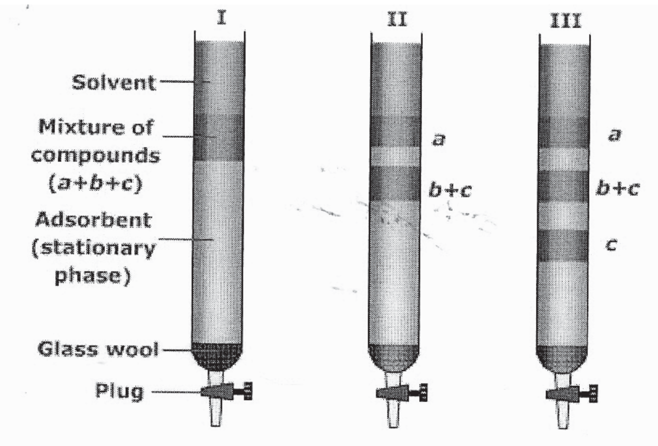


Fig. 25.e Column Chromatography

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.

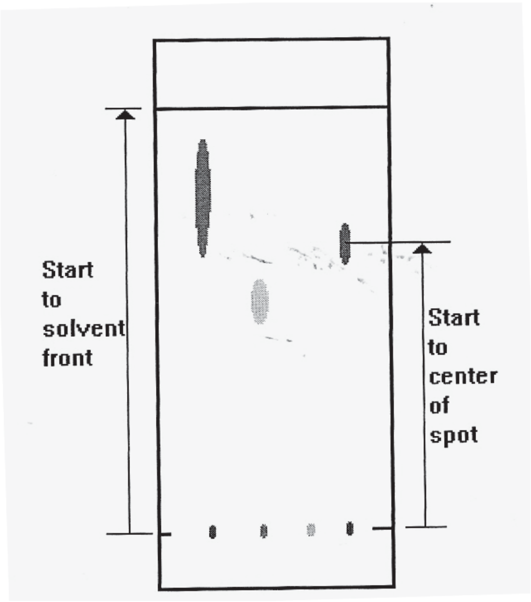


Fig. 25.f Thin layer chromatography

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.

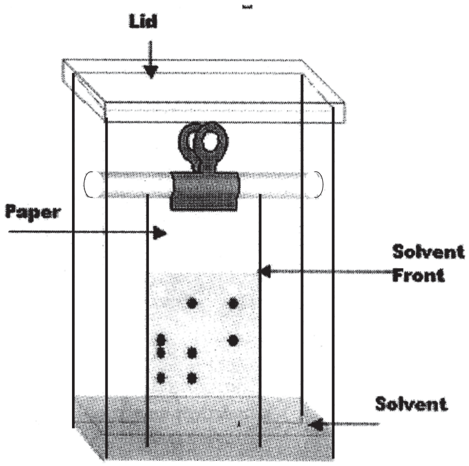


Fig. 25.g. Partition Chromatography

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.

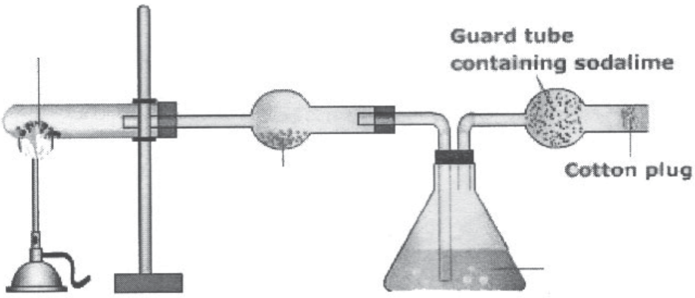


Fig. 25.h.a Detection of Carbon and Hydrogen

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

in the compound

$$2H + CuO \longrightarrow H_2O + Cu$$

In the compound

$$\underset{\text{Lime water}}{CO_2 + Ca(OH)_2} \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

$$\underset{\text{(anhydrous)}}{5H_2O + CuSO_4} \longrightarrow CuSO_4 . 5H_2O$$

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.

$$\underset{\text{present in organic compound}}{C + N +} \quad Na \xrightarrow{\text{fusion}} \underset{\text{sodium cyanide}}{NaCN}$$

$$\underset{\text{from organic compound}}{S +} \quad 2\,Na \xrightarrow{\text{fusion}} \underset{\text{sodium sulphide}}{Na_2S}$$

$$\underset{\text{from organic compound}}{X\,(Cl, Br, I) + Na} \xrightarrow{\text{fusion}} \underset{\text{sodium halide}}{NaX\,(X{=}Cl, Br, I)}$$

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.

$$6NaCN + FeSO_4 \longrightarrow \underset{\text{Sod. Ferrocyanide}}{Na_4[Fe(CN)_6]} + Na_2SO_4$$

$$2Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow \underset{\text{prussianblue}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

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.

$$Na_2S + \underset{\text{Sod. nitroprusside}}{Na_2\,[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet colour}}{Na_4\,[Fe(CN)_5NOS]}$$

When nitrogen and sulphur both are present in any organic compound, sodium thiocyanate is formed during fusion. It gives ‘blood red coloration’ when $FeCl_3$ is added due to the formation of ferric thiocyanate.

$$Na + \underset{\substack{\text{From organic}\\\text{compound}}}{C + N + S} \longrightarrow \underset{\text{Sod. thiocyanate}}{NaCNS}$$

$$3Na\,CNS + Fe^{3+} \longrightarrow \underset{\text{blood red colour}}{Fe(CNS)_3} + 3\,Na^{+}$$

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.

$$\underset{\text{lead acetate}}{(CH_3COO)_2\,Pb} + \underset{\substack{\text{in sodium}\\ \text{extract}}}{Na_2S} \longrightarrow \underset{\text{black ppt}}{PbS} + 2CH_3COONa$$

iii. Tests for halogens:

The sodium fusion extract is acidified with nitric acid and treated with $AgNO_3$. Different coloured precipitates are formed which confirm halogens.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt}}{AgCl} + NaNO_3$$

$$NaBr + AgNO_3 \longrightarrow \underset{\text{pale yellow ppt}}{AgBr} + NaNO_3$$

$$Nal + AgNO_3 \longrightarrow \underset{\text{yellow ppt}}{Agl} + NaNO_3$$

c) Detection of Phosphorous:

The compound is heated with an oxidizing agent (Na2O2) the ‘P’ in the organic compound is oxidized to Phosphate. The solution is boiled with conc. HNO3 and treated with ammonium Molybdate. Formation of canery yellow precipice indicates the presence of phosphorous.

$$2P + 3Na_2O_2 + \underset{\text{air}}{O_2} \longrightarrow 2\,Na_3PO_4$$

$$Na_3PO_4 + 3\,HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_3 + 21\,HNO_3 \longrightarrow (NH_4)_3\,PO_4\,12MoO_3 + 21NH_4NO_3 + 12H_2O$$

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 tube containing Potash and H_2O in the U 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.

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{W_2}{W} \times 100$$

Where W_2 is the weight of CO_2 formed, W is the weight of organic compound

$$\text{Percentage of carbon} = \frac{2}{18} \times \frac{W_1}{W} \times 100$$

Where W_1 is the weight of H_2O formed, W is the weight of organic compound

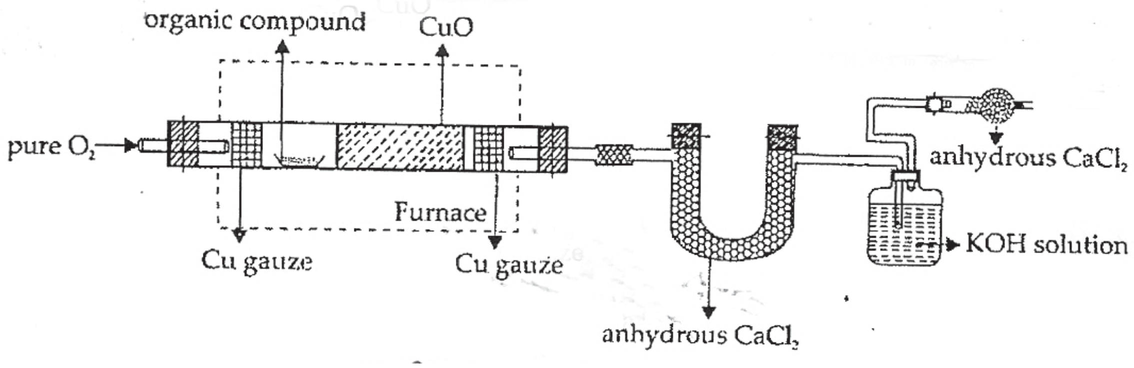


Fig. 25.i.a Estimation of Carbon and hydrogen

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.

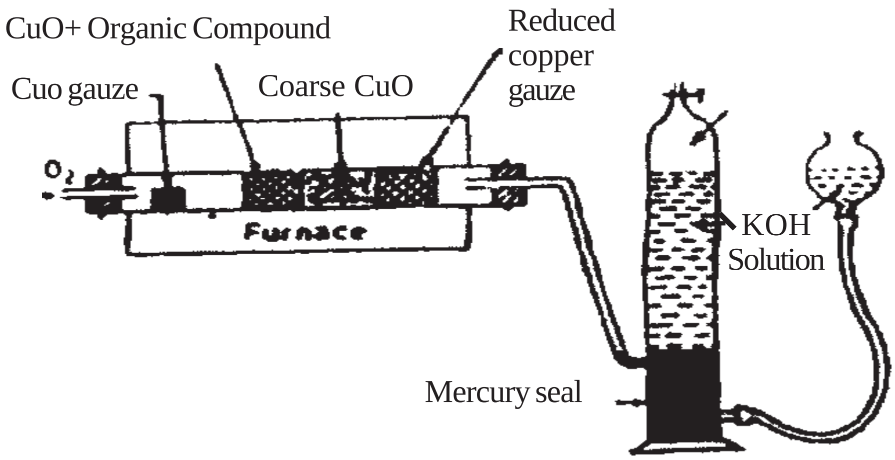


Fig. 25.j. Duma's method for the estimation of nitrogen

Calculations

Let, the mass of the organic compound taken b e = W g

Volume of nitrogen collected = V_1 ml; Atmospheric pressure = 760 mm Hg

Temperature at which gas is collected = T_1K

Therefore, Pressure of the N_2 gas, $P_1 = (P - p)$ mm of Hg

Volume of nitrogen at STP = $\frac{P_1V_1 \times 273}{760 \times T_1} = \text{VmL}$

(using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$)

28g of nitrogen at STP occupies 22400ml 1 mol of N_2 = 28g = 22400 mL

Mass of V mL of nitrogen at STP = $\frac{28V}{22400}$ g

Therefore,

Percentage of nitrogen in the compound = $\frac{28V}{22400} \times \frac{100}{W}$

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 **<u>digestion.</u>**

2. The ammonium sulphate is distilled in presence of excess base so that it decomposes into ammonia gas. This is called **<u>distillation.</u>**
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 **<u>estimation.</u>**

   The quantity of ammonia produced is thus determined and from this the percentage of nitrogen in the organic compound is calculated. Fig. 25.k.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

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

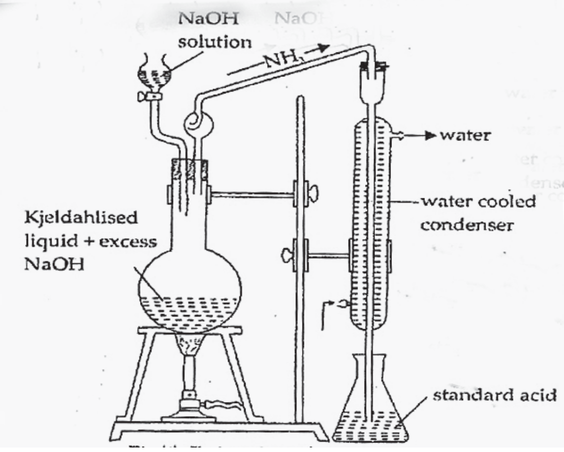


Fig. 25.k Estimation of Nitrogen

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 ie 14 g Nitrogen

So $(V_1 – V_2)$ ml (N) NH_3 has [14 × $(V_1 – V_2)$ ml × 1/w × 1/1000 gram

So the % of N in the w gm organic compound is

$$14 \text{ x } (V_1 – V_2) \times 1/w \times 1/1000 \times 100$$

$$\text{ie } 1.4 \times (V_1 – V_2)/w \ \%N$$

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 200^{0}C 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.

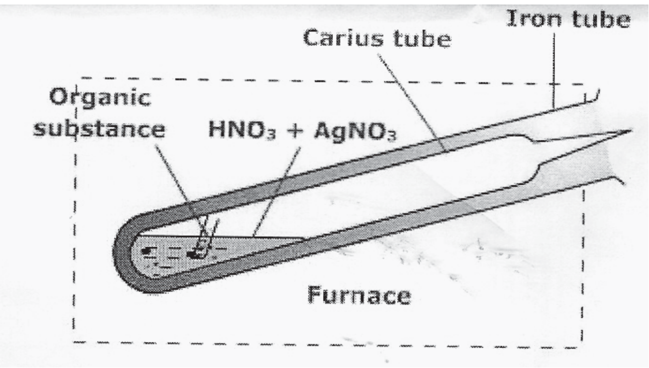


Fig. 25.l. Carius method for the estimation of halogens.

Calculations

Let, the mass of the organic compound taken be = W g

Mass of AgX formed = W_1 g

From stoichiometry, 1 mole of AgX contains 1 mole of X

Therefore,

$$\text{Mass of halogen in } W_1 \text{ of AgX} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times W_1$$

$$\text{Percentage of halogen} = \frac{\text{Mass of halogen in } W_1 \text{ of AgX}}{\text{Mass of organic compound taken}} \times 100$$

$$= \frac{\text{Atomic mass of } X \times W_1}{\text{Molecular mass of AgX}}$$

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_4^{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_1 g of $BaSO_4$ precipitate = $W_1 \times \frac{32}{233}$ g

If Wg of organic compound has $W_1 \times \frac{32g}{233}$

Percentage of sulphur in the compound = $\frac{W_1 \times 32}{233} \times \frac{100}{W}$

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 W_1 g of $Mg_2P_2O_7$ = $W_1 \times \frac{62}{222}$ g

Percentage of phosphorus in the compound = $W_1 \times \frac{62}{222} \times \frac{100}{W}$

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 calsorplim 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_2 & H_2O respectively.
8. Lassaigne's test.
9. By Duma's method, Kjeldahl's method
10. Carius method.

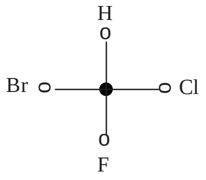
25.4.a Configuration and Fisher Projections

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.

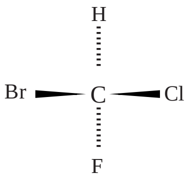
If chain contains more than one carbon, the chain is written vertically.

The carbon atoms of the chain are at the centre of crosses and not shown through symbols.

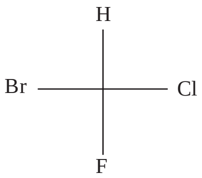
Eg:



Ball - and - stick model

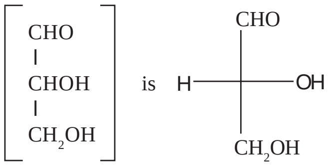


Wedge - and - das model



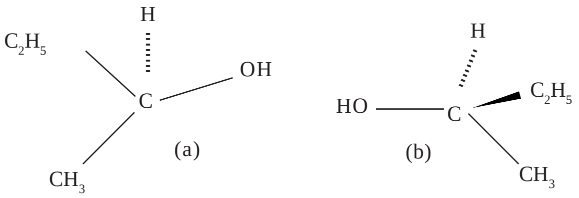
Fisher Projection formula

Fisher Projection formula for glyceraldehyde



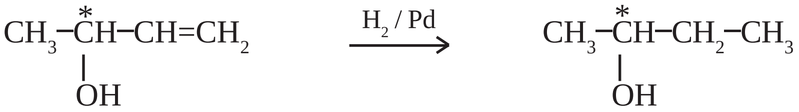
Absolute and Relative configuration

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.



a and b represent absolute configuration of 2-butanol. Without any additional information it is difficult to say which is (+) 2-butenol 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.

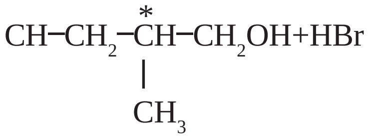
Eg: When (+) -3- butane -2-ol is hydrogenated the product is (+)-2-butanol.



$$CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}}H-CH=CH_2 \xrightarrow{H_2 / Pd} CH_3-\underset{\underset{OH}{|}}{\overset{*}{C}}H-CH_2-CH_3$$

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.

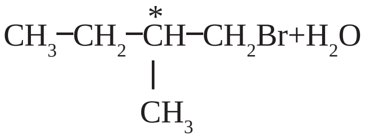
Eg:



$$CH-CH_2-\underset{\underset{CH_3}{|}}{\overset{*}{C}}H-CH_2OH+HBr$$

2-methyl -1- butanol

$(\propto)^{25}_{D} = +5.8^{O}$



$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{*}{C}}H-CH_2Br+H_2O$$

1-bromo 2-methyl butane

$(\propto)^{25}_{D} = +4.0^{O}$

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:

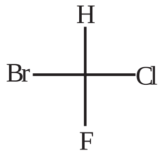
- To draw the fisher projection formula of stereo isomers.
- Different methods of notation of stereo isomers.
- Absolute and relative configuration of stereo isomer.

Terminal Questions:

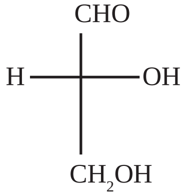
1. How do you represent fisher projection formula of a stereo isomers?
2. What is meant by relative and absolute configuration?

25.4.a Answers for intext questions:

1.



2.



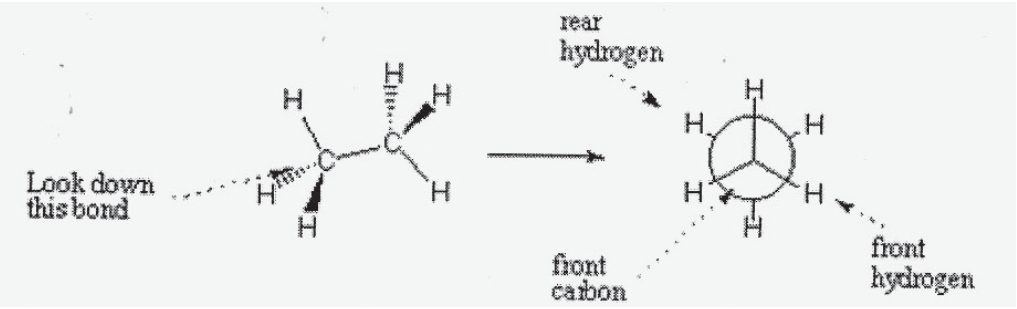
25.4(b) Asymmetric carbon and elements of symmetry

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.

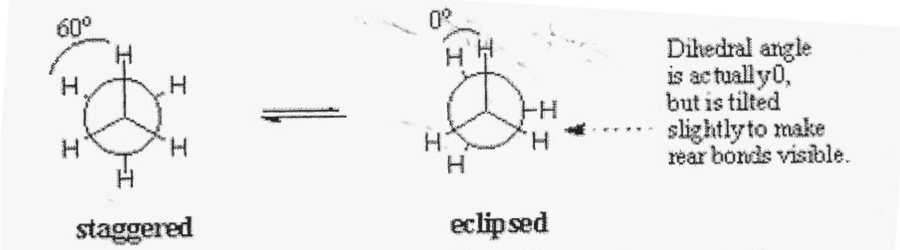
Several methods are used by organic chemists to visualize the conformations of molecules. One of these methods uses **wedges** to denote bonds that are extending out from the plane of the page toward the reader and **dashes** to indicate bonds that are going into the plane of the page away from the reader. This notation is frequently used to represent the tetrahedral geometry of sp^3 hydrilized 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.



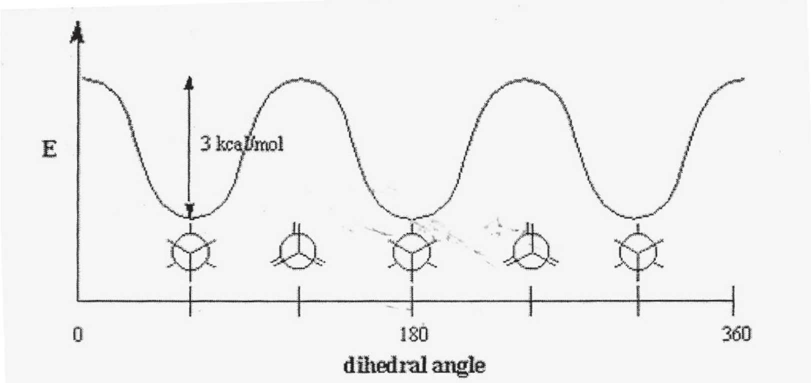
Line wedge representation **Newman projection**

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.



The eclipsed and staggered conformations 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 the 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.

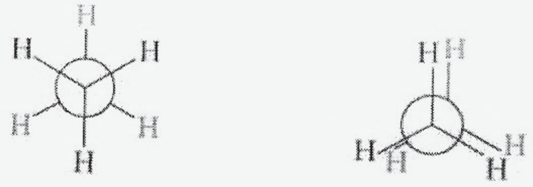


Energy diagram for rotation about the C-C bond in ethane

The staggered and eclipsed conformation are interconvertable by rotation. They are three important ways to represent the conformers. They are Wedge-and-ash, sawhorse and Newman projection formulae. They are represented as

(a) Wedge-and-dash

(b) Sawhorse



(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 ?

   ....

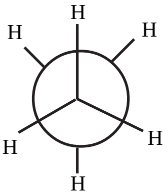
What you have learnt:

- 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?

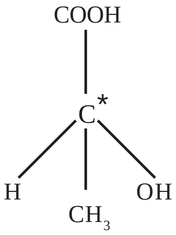
25.4.b Answers to Intext questions:

1. 

2. Staggered form, eclipsed form
3. 3k. 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.

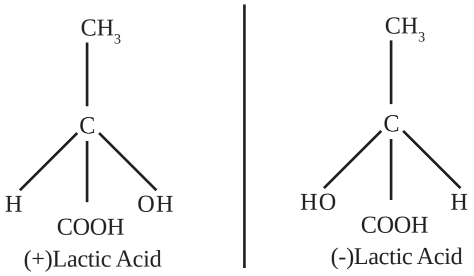


Lactic Acid

The four valencies of C* are satisfied by H,OH, CH_3, 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:



(+)Lactic Acid (-)Lactic Acid

These two are non super imposable mirro images. Hence called enantiomers.

Enanti omers 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.

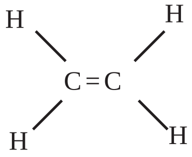
Elements of symmetry:

There are three types of elements of symmetry. They are centre of symmetry, plane of symmetry, axis of symmetry.

1. **Centre of symmetry:**

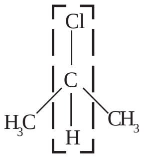
A molecule is said to have centre of symmetry if it has same groups on either side from the centre.

Eg:

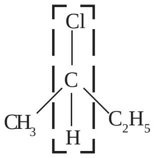


2. **Plane of Symmetry:**

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

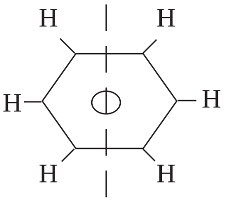


2 - chloro butane
has no plane of symmetry

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 thro '360^{0}' 6 time cdentiacal configuration is obtained. Hence it is said to have Six fold axis of symmetry.

If benzene is rotated thro’ 360^0 6 time 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:

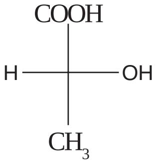
- Asymmetric carbon is one whose four valencies are satisfied by different atoms or groups.
- Enantiomers are a pair of optical isomers which have object mirror image relationship is non super imposable.
- Chirality is molecules which are dissymmetric.
- Three types of elements of symmetry. They are 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)



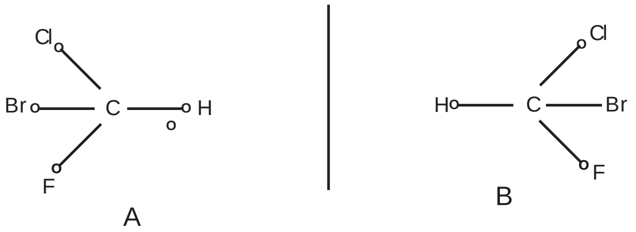
$$\begin{array}{c} COOH \\ H-\!\!\!-\!\!+\!\!-\!\!\!-OH \\ CH_3 \end{array}$$

2) The pair of optically active is omers which lane 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 a chiral. According to van't 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.

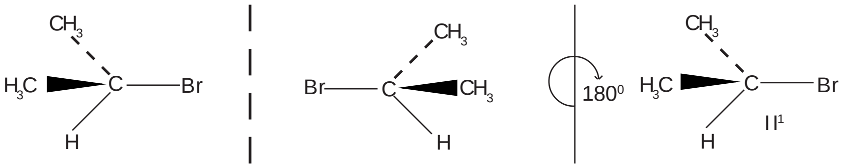
Eg: Bromo Floro chloro methane.



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.

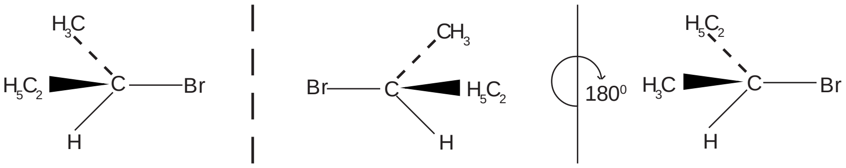
For Eg: 2 - bromo propane



A B B¹

I & II are mirror images. If II is rotated thro ‘180^0 II’ is super imposable on I. Hence these are not enantiomers.

Eg: 2 - bromo butane



1 2 2^1

The mirror image of 1 is 2. 2 when rotated thro 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 namenclature

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 diasteremer is broken down to give pare 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.

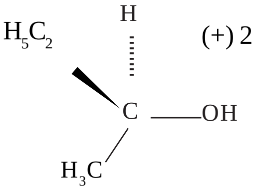
R.S. Notation :

The Cahn-Ingold – Prelog formulated rules to specify the absolute configuration ata stereogenic centre. The rules were developed as sequence rules.

Rules :

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:



(+) 2- butanol

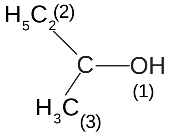
$-OH > CH_3CH_2- > CH_3 > H$

highest atomic number   lowest atomic number

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.

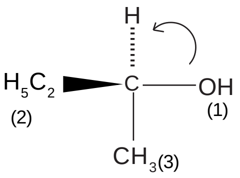
4. If the priority groups are arranged in clockwise manner (i.e., 1,2,3) then the configuration is assigned 'R' (R in latin means rectors which means right side) and if the priority groups are in anti clockwise direction, the configuration is assigned as 'S' (S in latin stands for simister means left 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, C_2H_5 (3) priority keeping away the least priority 'H' the molecule is viewed as



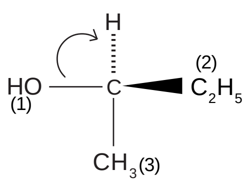
1→2→3 are in anticlockwise direct ion.

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

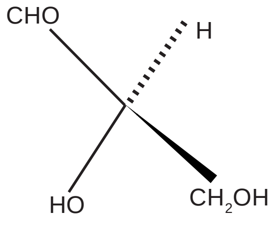


R (-) -2- butanol

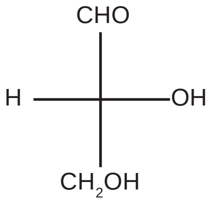
The racemic mixture is written as (R), (S). 2-butanol. While writing the three dimensional formulae to describe R,S configuration, Fisher projection formulae is written such that the groups having the viewer are on the horizontal line.

D,L notation of configuration :

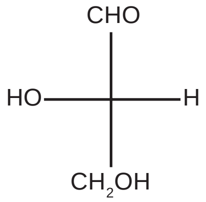
This method gives the relative configuration with respect to slyceraldehyde. D is assigned to the molecule whose configuration is Similar to D (+) slyseraldyhyde about the chiral carbon. In D(+) dylyceraldehyde, in Fisher projection formula –OH is written on the right side to the chiral carbon and for the enantiomer of 'L' configuration. –OH is written to the left.



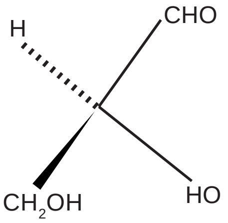
D(+) glyceraldehyde



Fisher projection formula for D(+) glyceraldehyde

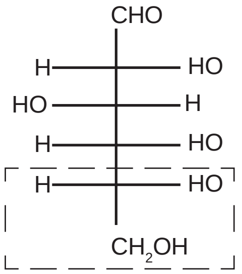


L(-) glyceraldehyde

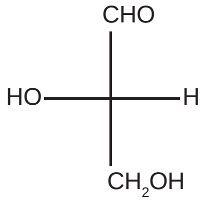


The substances which have similar configuration with that of D (+) glyceraldehydes belong to D-series, while which have similar configuration that of L(-) glyceraldyhyde belong to L series. It should be noted that there is no relation with D L configurationally relation to d,L or (+) – which represent optical activity generally D,L relation is used to represent the stereo chemical aspect of carbohydrates and amino acids.

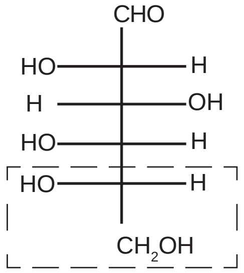
Eg :



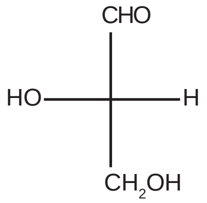
D (+) Glucose



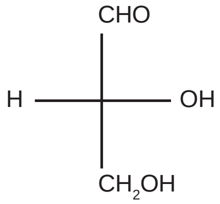
D (+) Glyceraldehyde



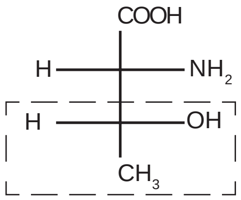
L (-) Glucose



L (-) Glyceraldehyde



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.

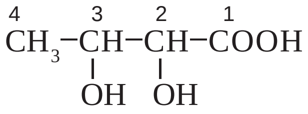
25.4.e Answers to Intext questions :

1. d or L
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.

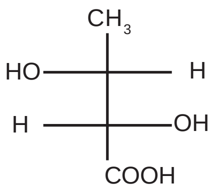
For a molecule with one chiral centre, two pairs of enantiomers are possible for molecule with two chiral centres i.e., four enantiomers are possible. For compounds with ‘n’ Chiral centres, generally 2^n Stereo isomers are possible and 2^{n-1} pairs of enantiomers.

For Example : 2,3 di-hydroxy butanoic acid.

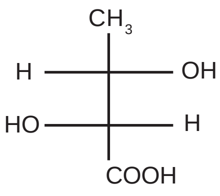


$$\overset{4}{CH_3}-\underset{OH}{\overset{3}{CH}}-\underset{OH}{\overset{2}{CH}}-\overset{1}{COOH}$$

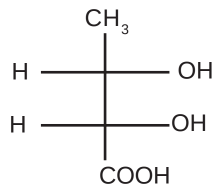
C-2, C-3 are chiral centres i.e., 2, 4 stereo isomers are possible i.e., at c-2 R, or S configuration and at c-3 R & S configuration.



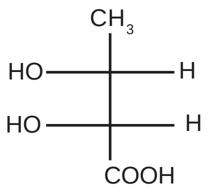
I $(\mu)_D = +9.5^0$



II $(\mu)_D = -9.5^0$



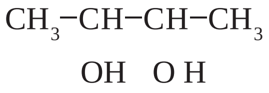
III $(\mu)_D = -17.8^0$



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. III for II also III & IV are not having object, mirror image relationship. Such molecules which do not have object mirror image relationship are called diastereomers.

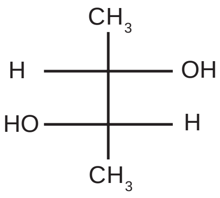
Example : 2,3 butanediol



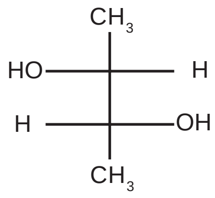
$$\underset{}{CH_3}-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$$

Four isomers can be written

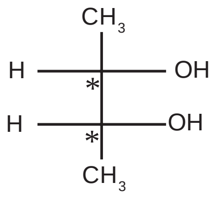
They are



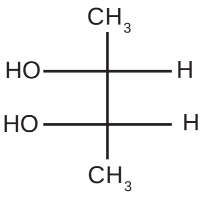
I



II



III



IV

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 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 (+) endrevaline is more reactive than (-) endrevaline.

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 2^n stereo isomers and 2^{n-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.

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 distillation 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:

From Haloalkanes (Alkyl Halides): Monohaloalkanes 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

$$CH_3Br + Zn + 2\,HCl \longrightarrow CH_4 + ZnCl_2 + HBr$$

Bromomethane Methane

(ii) HI in the presence of red phosphorus

$$C_2H_5I + HI \xrightarrow[423K]{\text{red phosphorus}} C_2H_6 + ZnCl_2 + HBr$$

Iodoethane Methane

(iii) Catalytic reduction

$$CH_3C1 \quad + \quad H_2 \xrightarrow{\text{Pt (catalyst)}} CH_4 + HCl$$

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.

$$C_2H_5Br \quad + \quad Mg \xrightarrow{\text{dry ether}} C_2H_5MgBr$$

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.

$$CH_3MgBr \quad + \quad C_2H_5OH \longrightarrow CH_4 \quad + \quad Mg(OC_2H_5)Br$$

$$C_2H_5MgBr \quad + \quad H_2O \longrightarrow C_2H_6 \quad + \quad Mg(OH)Br$$

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.

$$ROH + 2HI \xrightarrow{\text{redP / 423K}} RH + I_2 + H_2O$$

Alcohol Alkane

$$RCHO + 4HI \xrightarrow{\text{redP / 423K}} RCH_3 + 2I_2 + H_2O$$

Aldehyde Alkane

$$RCOR' + 4HI \xrightarrow{\text{redP / 423K}} RCH_2R' + 21_2 + H_2O$$

Ketone Alkane

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 :**

   $$RCOOH + 6\,HI \xrightarrow{\text{redP / 423K}} RCH_3 + 3I_2 + 2H_2O$$

   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.

   $$RCOONa \xrightarrow{\text{electrolysis}} RCOO^- + Na^+$$

   Sodium salt of carboxylic acid Anion Cation

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.

$$2\ CH_3COONa \longrightarrow CH_3 - CH_3$$

Sodium ethanote Ethane (at anode)

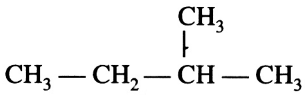
Note that the alkanes with even number of carbon atoms can easily be prepared by this method.

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}).

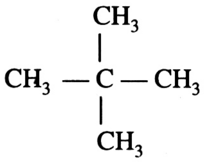
$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

n-Pentane



$$CH_3 - CH_2 - \overset{\displaystyle CH_3 \atop |}{CH} - CH_3$$

2-Methylbutane
(Isopentane)



$$CH_3 - \underset{\displaystyle | \atop CH_3}{\overset{\displaystyle CH_3 \atop |}{C}} - CH_3$$

2,2-Dimethylpropane
(Neopentane)

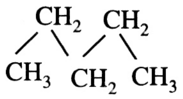
Amongst these three isomeric compounds, neopentane will have the weakest intermolecular forces of attraction due to the smallest surface area of its molecules.

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.

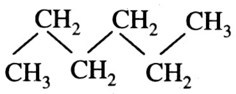
Boiling Point : *The boiling points of alkanes also increase with the increase in the molecular mass.* In straight chain alkanes, the increase in boiling points due to the increase in surface area of the molecules. Branching in a chain reduces the surface area and therefore, decreases the boiling point 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.

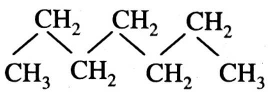
In alkanes, each carbon atom is sp^3 hybridized which results in a bond angle of 109°28'. In straight chain hydrocarbons the carbon atoms are arranged in a zig-zag way in the chain. If the molecule contains an odd number of carbon atoms, then the two terminal methyl groups lie on the same side. So the 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.



***n*-Pentane**



***n*-Hexane**



***n*-Heptane**

(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.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[-HCl]{\text{Diffused Sunlight}} \underset{\text{Chloromethane}}{CH_3CI}$$

$$CH_3Cl + Cl_2 \xrightarrow[-HCl]{} \underset{\text{Dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[-HCl]{} \underset{\text{Trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow[-HCl]{} \underset{\text{Tetrachloromethane}}{CCl_4}$$

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 ($\overset{*}{C}l$). The chlorine radicals then combine with methane and form methyl radial [$\overset{*}{C}H_3$]. 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.

$$Cl_2 \xrightarrow{h\nu} 2Cl^* \qquad (h\nu = \text{energy of light})$$

(ii) Chain Propagation Step: The free radicals give rise to the formation of more free radicals as is shown in the following reaction.

$$CH_4 + \overset{*}{C}I \longrightarrow \overset{*}{C}H_3 + HCI$$

$$C\overset{\bullet}{H}_3 + Cl_2 \longrightarrow CH_3CI + \overset{\bullet}{C}l$$

(iii) Chain Termination Step : In this step, free radicals combine with one another and the further reaction stops.

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}l \longrightarrow CH_3Cl$$

$$\overset{\bullet}{C}l + \overset{\bullet}{C}l \longrightarrow Cl_2$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 - CH_3$$

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.

$$2C_2H_6 + 5O_2 \xrightarrow{heat} 4CO + 6H_2O$$

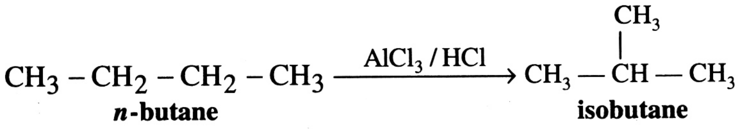
3. **Cracking or Pyrolysis :** At very high temperature and in the absence of air, the alkanes break apart into smaller fragments. For example,

$$CH_3 - CH_2 - CH_3 \xrightarrow{873\,K} CH_3CH = CH_2 + H_2$$

or

$$CH_2 = CH_2 + CH_4$$

4. **Isomerisation :** *n*-Alkanes, in the presence of aluminium halide and HCl, are converted to their branched isomers.



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3/HCl} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

n-butane **isobutane**

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).

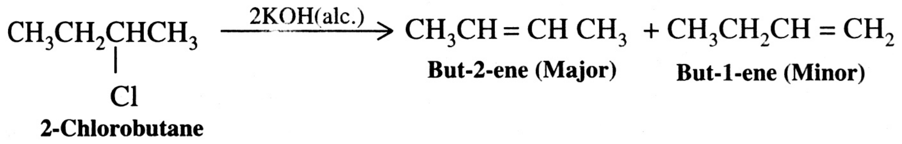
26.2.1 Methods of Preparation

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



$$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3 \xrightarrow{2KOH(alc.)} CH_3CH = CH\,CH_3 + CH_3CH_2CH = CH_2$$

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.

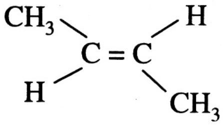
Table 26.1 : Boiling points of Alkenes

Alkene	Ethene	Propene	But-1-ene	Pent=1-ene	Hex-1-ene
b.p. (K)	169	226	267	303	337

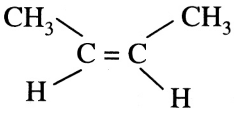
The increase in boiling point can be attributed to the van der Waals forces which increases with number of carbon atoms of the alkene. The branched chain alkenes have lower boiling points than those of straight chain isomers.

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

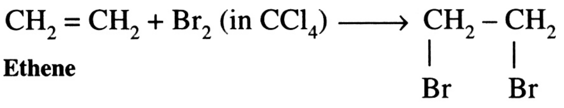
1. **Addition Reactions :** The chemical reactions in which a molecule adds to another molecule are called an *addition reaction.* These reactions are characteristic of unsaturated compounds like alkenes and alkynes. The following reactions illustrate the addition reactions of alkenes.

   (i) Addition of Hydrogen : Addition of hydrogen to unsaturated hydrocarbons takes place in the presence of a catalyst like Ni, Pt or Pd.

   $$CH_2 = CH_2 + H_2 \xrightarrow[573K]{Ni(Pt\ or\ Pd)} CH_3 - CH_3$$

   Ethene Ethane

   (ii) Addition of Halogens : Halogens on addition to alkenes, form 1,2-dihaloalkanes.

   $$\underset{\textbf{Ethene}}{CH_2 = CH_2} + Br_2\ (in\ CCl_4) \longrightarrow \underset{\textbf{1, 2-Dibromoethane}}{\underset{Br\qquad Br}{\underset{|\qquad\ |}{CH_2 - CH_2}}}$$

   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.

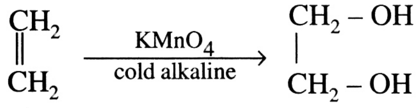
$$n(CH_2 = CH_2) \xrightarrow[\text{heat, pressure}]{} -\!\!\left(CH_2 - CH_2\right)_n\!\!-$$

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 $KMnO_4$

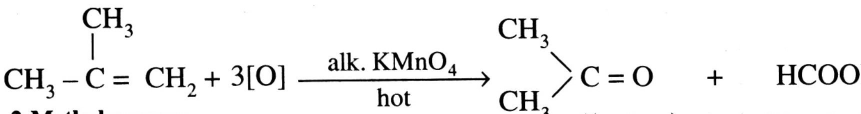
Alkenes are unsaturated hydrocarbons having Pi (π)-bond(s) between the carbon atoms, so they are easily oxidized by cold dilute alkaline solution of $KMnO_4$.



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow[\text{cold alkaline}]{KMnO_4} \begin{matrix} CH_2 - OH \\ | \\ CH_2 - OH \end{matrix}$$

Ethene **Ethanediol**

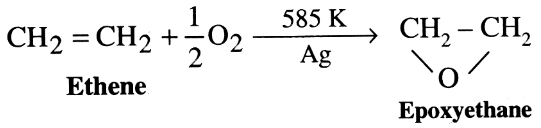
When an alkaline solution of $KMnO_4$ (Baeyer's Reagent) is added to an alkene, the purple colour of $KMnO_4$ gets discharged. This reaction is used to test unsaturation in hydrocarbons. On treatment with hot alkaline $KMnO_4$ the alkene gets oxidized to ketones or further to acids depending upon its structure. This happens due to the breaking of carbon-carbon double bond.



$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 + 3[O] \xrightarrow[\text{hot}]{\text{alk. } KMnO_4} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\Big\rangle C = O \quad + \quad HCOOH$$

2-Methylpropene **(Acetone) Propanone** **(Formic Acid) Methanoic acid**

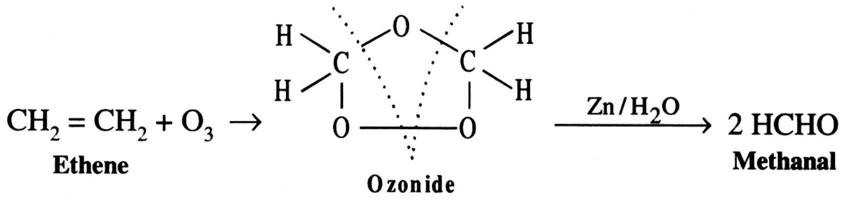
(ii) Oxidation with Oxygen : Ethene on oxidation with oxygen in the presence of silver (Ag) gives epoxyethane. The reaction is shown below:



(iii) Combustion : The oxidation reaction, in which carbon dioxide and water are formed along with the liberation of heat and light, is called combustion.

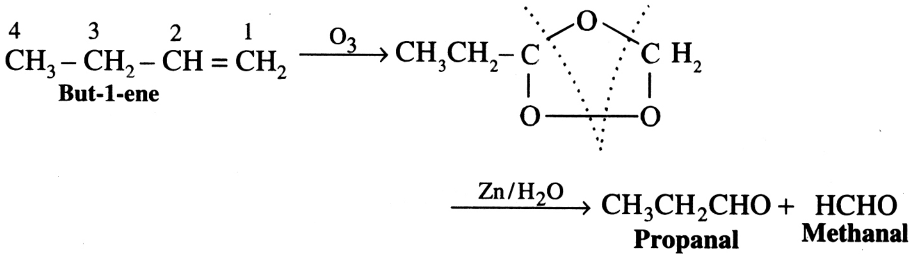
$$CH_2 = CH_2 + 3O_2 \xrightarrow{heat} 2CO_2 + 2H_2O \qquad \Delta H = -1411\ KJ\ mol^{-1}.$$

(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.

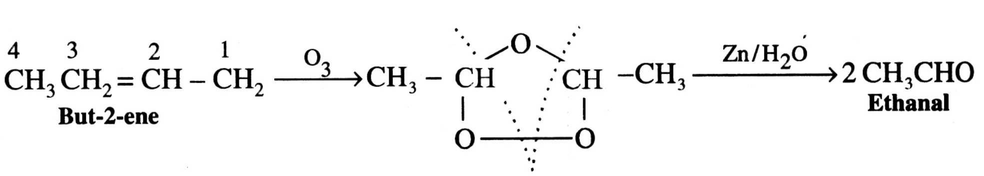


This process of addition of ozone to an unsaturated hydrocarbon followed by hydrolysis is called **ozonolysis.**

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.

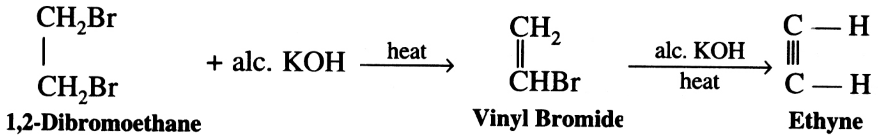
1. **From Calcium Carbide :** Ethyne can be prepared in the laboratory, as well as on a large scale, by the action of water on calcium carbide.

   $$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Water}}{2H_2O} \longrightarrow \underset{\text{Ethyne}}{H – C \equiv C – H} + Ca(OH)_2$$

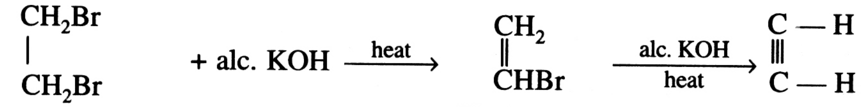
   Ethyne prepared by this method generally contains the impurities of hydrogen sulphide and phosphine due to the impurities of calcium sulphide and calcium phosphide in calcium carbide.

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.



$$\underset{\text{1,2-Dibromoethane}}{\begin{array}{c}CH_2Br\\|\\CH_2Br\end{array}} + \text{alc. KOH} \xrightarrow{\text{heat}} \underset{\text{Vinyl Bromide}}{\begin{array}{c}CH_2\\\|\\CHBr\end{array}} \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{\text{Ethyne}}{\begin{array}{c}C — H\\|||\\C — H\end{array}}$$



$$\begin{array}{c}CH_2Br\\ |\\ CH_2Br\end{array} + \text{alc. KOH} \xrightarrow{\text{heat}} \begin{array}{c}CH_2\\ \|\\ CHBr\end{array} \xrightarrow[\text{heat}]{\text{alc. KOH}} \begin{array}{c}C - H\\ |||\\ C - H\end{array}$$

1,2-Dibromoethane **Vinyl Bromide** **Ethyne**

3. **Preparation of higher alkynes :** Higher alkynes can be prepared by the reaction of alkynides of lower alkynes with primary alkyl halides.

$$R - C \equiv CH + Na \xrightarrow{liq.NH_3} R{-}C \equiv C^- Na^+$$

$$R - C \equiv C^- Na^+ + CH_3I \longrightarrow R{-}C \equiv C{-}CH_3 + NaI$$

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 l,l-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.

$$CH\equiv CH+H_2O \xrightarrow[1\%HgSO_4]{40\%H_2SO_4} [CH_2 = CHOH] \xrightleftharpoons{\text{Re arrangement}} CH_3CHO$$

Ethyne Vinyl Alcohol (Unstable) Ethanal

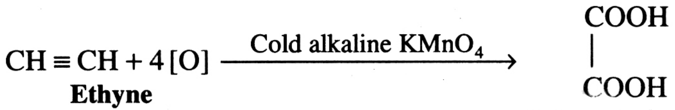
(v) Addition of H_2SO_4: Conc. H_2SO_4 adds to ethyne as shown below.

$$CH \equiv CH \xrightarrow{conc.H_2SO} CH_2 = CHHSO_4 \xrightarrow{H_2SO_4} CH_3 - CH\ (HSO_4)_2$$

Vinyl hydrogen sulphate Ethylidene hydrogen sulphate

2. **Oxidation:** Alkynes undergo oxidation with oxygen, $KMnO_4$ and ozone.

(i) Oxidation with $KMnO_4$



$$CH\equiv CH + 4\,[O] \xrightarrow{\text{Cold alkaline } KMnO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Ethyne **Ethanedioic acid**

The colour of alkaline solution of $KMnO_4$ is discharged on reaction with alkynes. Alkynes on heating with alkaline $KMnO_4$ give carboxylic acids.

$$R - C \equiv C - R' \xrightarrow[heat]{KMnO_4+KOH} RCOOH + R'COOH$$

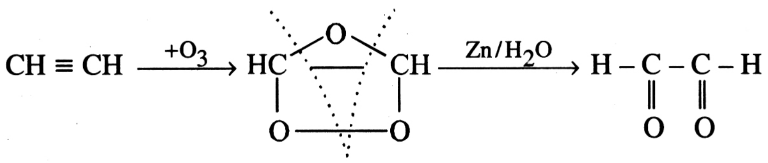
However, ethyne, on similar treatment, gives carbon dioxide and water.

$$CH\equiv CH + 4\,[O] \xrightarrow[heat]{KMnO_4+KOH} (COOH)_2 \xrightarrow[Heat]{[O]} 2\,CO_2 + H_2O$$

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

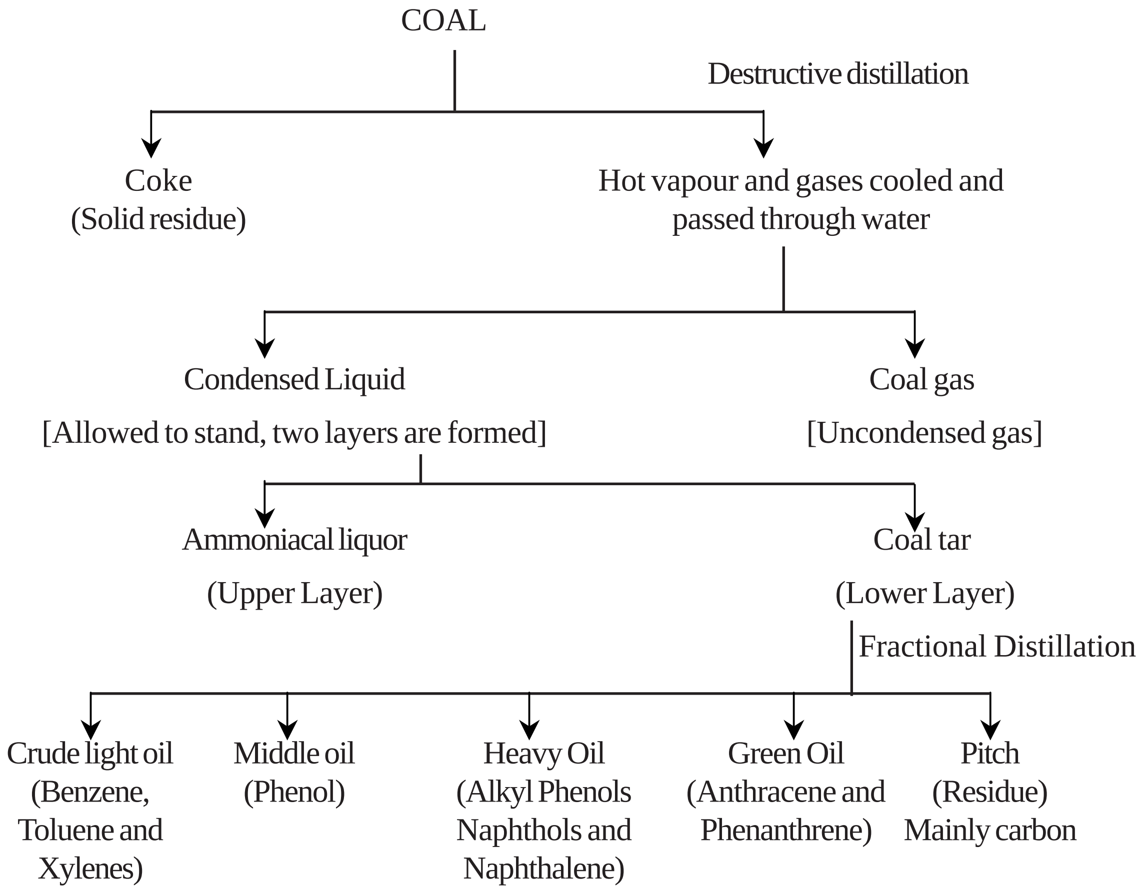


Fig. 26.1 : Destructive Distillation of coal

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.

$$C_6H_6 + 3H_2 \xrightarrow{\text{Ni or Pt}} C_6H_{12}$$

Benzene Cyclohexane

(ii) Benzene undergoes the addition of chlorine in the presence of sunlight.

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6$$

Benzene Benzene hexachloride (B.H.C.)

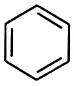
Benzene does not respond to the tests of unsaturation which are shown by alkenes and alkynes Le., both the alkenes and the alkynes decolourize bromine water and alkaline solution of potassium permanganate (Bayer's Reagent). However, benzene undergoes substitution reactions.

e.g. $$C_6H_6 + Br_2 \xrightarrow{\text{Fe or FeCl}_3} C_6H_5Br + HBr$$

Benzene Bromobenzene

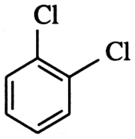
Kekule Structure : A ring structure for benzene was proposed by Kekule in 1865. According to him, six carbon atoms are joined to each other by alternate single and double bonds to form a hexagon ring. As the proposed structure of benzene has three double bonds, so its properties should resemble with the properties of alkenes. But the chemical properties of benzene are different from alkenes.

or

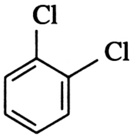


As Kekule's structure contains three single bonds and three double bonds, one may expect that in benzene there should be two different bond lengths i.e. 154 pm for C-C single bond and 134 pm for C=C double bond. But the experimental studies show that benzene is regular hexagon with an angle of 120^0 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).

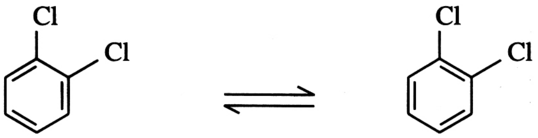


(a)



(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.

$$\text{Cyclohexene} \quad + H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 119.5 \text{ KJ mol}^{-1}$$

(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-I. But, the actual heat of hydrogenation of benzene is 208.2 KJ mol^{-1}.

$$\text{Benzene} + 3H_2 \xrightarrow[\text{Heat}]{\text{Catalyst}} \text{Cyclohexane} + 208.2\ \text{KJ mol}^{-1}$$

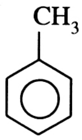
(Three - C = C- bond)

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.

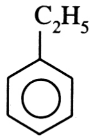
26.4.2 Physical Properties of Aromatic Hydrocarbons

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)

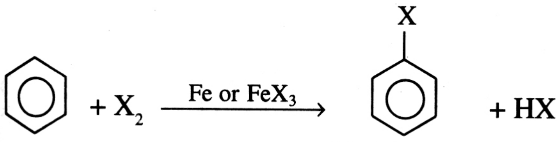


Ethylbenzane
(b.p. 409 K)

26.4.3 Chemical Properties of Aromatic Hydrocarbons

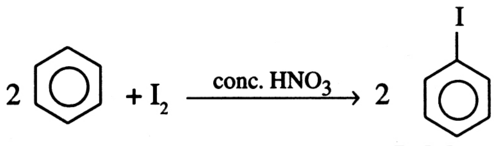
Aromatic hydrocarbons generally undergo electrophilic substitution reactions in which hydrogen atom of the aromatic ring is replaced by an electrophile. Such reactions are discussed below in detail taking benzene as an example.

(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 = CI or Br).



Halobenzene

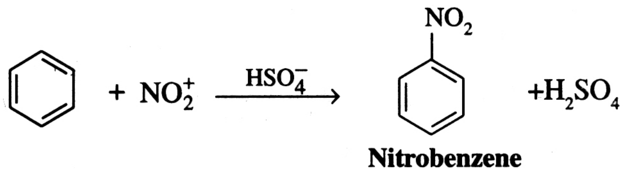
In case of iodination the m formed can reduce iodobenzene back to be benzene which is prevented by carrying out this reaction in the presence of HNO$_3$ or HIO$_3$. These acids react with HI as soon as it is formed.



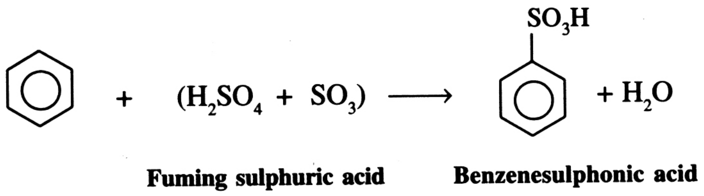
Iodobenzene

(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.

$$2\,H_2SO_4 + HNO_3 \longrightarrow 2\,HSO_4^- + NO_2^+ + H_3O^+$$

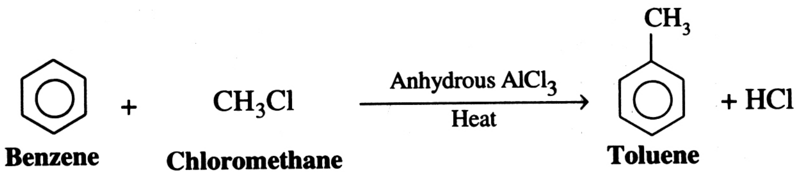


(iii) Sulphonation: The chemical reaction in which the hydrogen atom of benzene is replaced by $-SO_3H$ group when benzene is heated with fuming sulphuric acid (oleum), is called sulphonation.

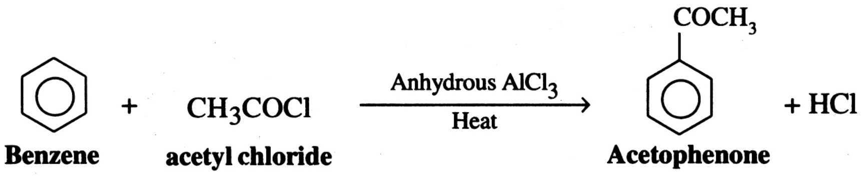


(iv) Friedel-Craft's Reactions: In Friedel-Craft's reaction, benzene is heated either with alkyl halide (alkylation) or acyl halide (acylation) in the presence of a catalyst (anhydrous AlCl3). The products formed are alkyl or acyl derivatives of benzene.

Alkylation

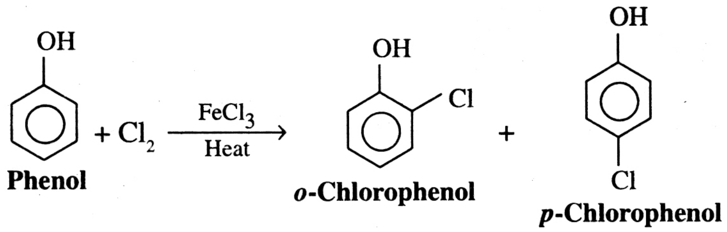


Acylation

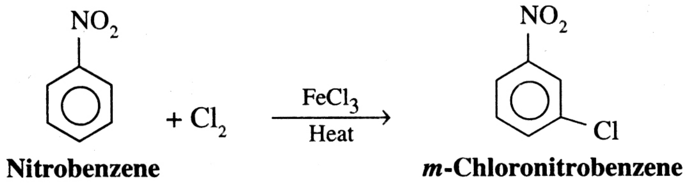


26.4.4 Directive Influence of Functional Groups

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.



In case of nitrobenzene, we find that -NO_2group 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.

   ....

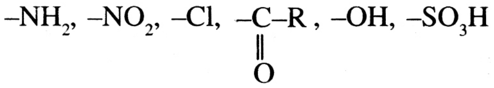
   (ii) phenol reacts with chlorine in the presence of $FeCl_3$.

   ....

   (iii) nitrobenzene reacts with chlorine in the presence of $FeCl_3$.

   ....

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, (ill) 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 sp^2 and sp^3, 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 ha 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.

   $H - C \equiv C - H + 2\,Na \longrightarrow Na - C \equiv C - Na + H_2$

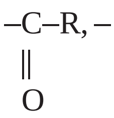
   Ethyne   Disodium acetylide
3. The s-character in : Ethane = 25%, Ethene = 33%, Ethyne = 50%

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

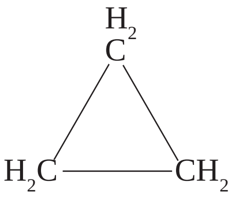
   

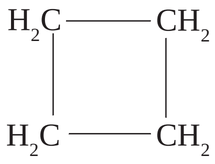
   m-directing groups: $NO_2, -\underset{\underset{O}{\|}}{C}-R, - SO_3H$

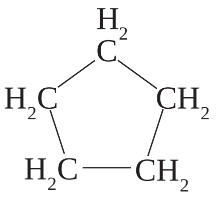
26.1.4.a Cycloalkenes

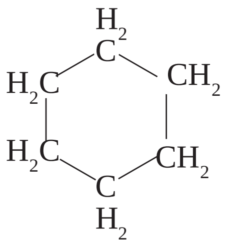
Alkenes are the simplest class of hydrocarbons with general molecular formula C_nH_{2n+2}. They are acyclic, saturated molecules. All the carbons are sp^3 hybridized. Cycloalkenes are hydrocarbons with carbon atoms joined in ring. Like alkenes, they also have C-C single bonds with sp^3 carbons and general 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

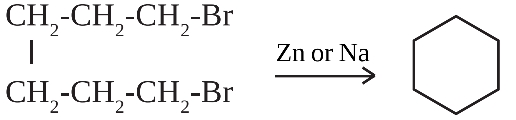

Cyclobutane


Cyclopentane


Cyclohexane

Cyclohexane: Methods of preparation:

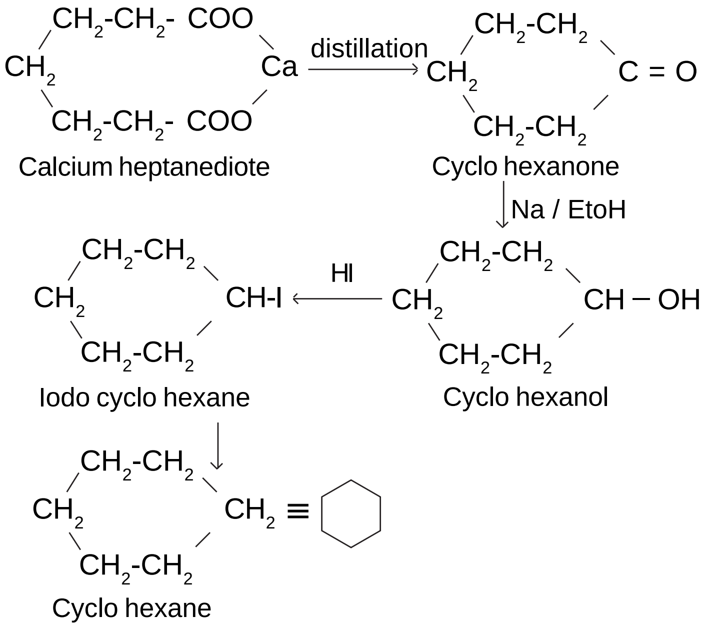
1. **Freund's method:** From (a, w) – dihalo alkenes. When 1:6 dibromo hexane is treated with metallic sodium or zinc, internal wurt$_3$ reaction takes place to form cyclo hexane.


1, 6 dibromo hexane

Cyclo hexane

2. **Wislicenus method:** Calcium or barium salts of dicarbonylic acids ondistillation 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.


Calcium heptanediote

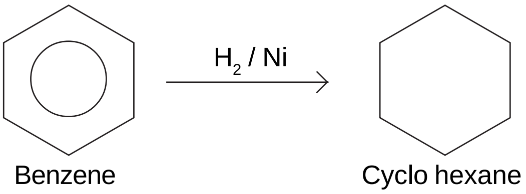
Cyclo hexanone

Cyclo hexanol

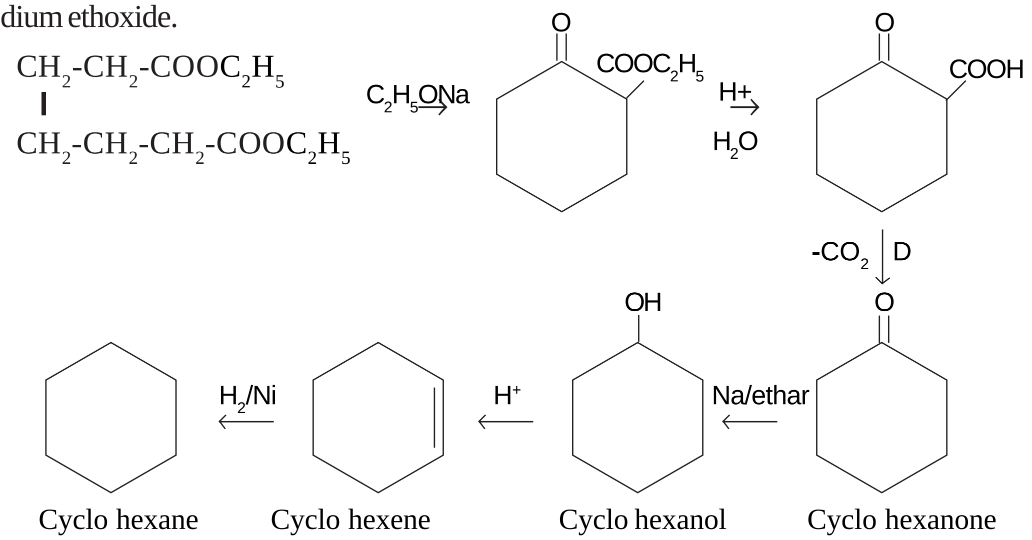
Iodo cyclo hexane

Cyclo hexane

3. **By reduction of benzene with Hydrogen / Nickel:** By catalytic reduction of benzene cyclo hexane is prepared.

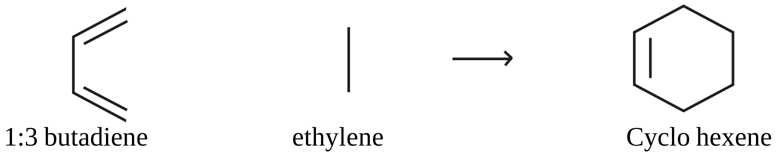


4. **Dieckmann Condensation:** It is intra molecular condensation esters of dicarboxylic acids using Sodium ethoxide.



5. **Diel's Alder reaction:** This reaction is addition of a mono ene called dienophile to a conjugated diels. Two new sigma bonds are formed at the cost of two IT 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_nH_{2n}.
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_2H_{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:

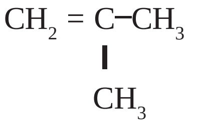
In the IUPAC nomenclature of these compounds suffix used is 'ene'. This class of compounds start from n=2. For the root word 'ene' is suffixed to name the compound.

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. for	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:	$CH_2 = CH-CH_2-CH_3$	$CH_3-CH=CH-CH_3$
C_4H_8:	1-Butene or But-1-ene	2-butene or But – 2 – ene
	I	II



$$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$$

2-methyl propene

Three isomers are possible for C_4H_8, I&III, II&III are chain isomers, I&II are position isomers. For C_5H_{10} 5 structures are possible.

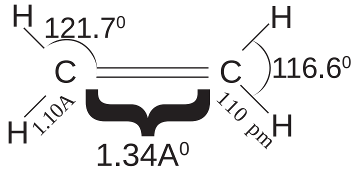
Activity:

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 p 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 alkenes and the characteristic reactions are electrophilic addition reactions.

The structure of ethylene can be represented as

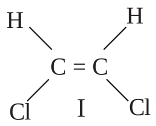


Geometrical Isomerism:

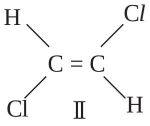
The phenomenon of existence of more than one compound with same structure but cliffering in spatial arrangements of atoms or groups due to restricted rotation about C=C is called geometrical isomerism. These are stereo isomers. The formula should be cab=cab.

Eg: 1) CHCl=CHCl

Two spatial arrangements are possible due to planar configuration.

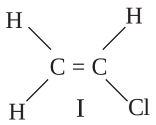


I

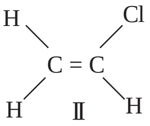


II

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

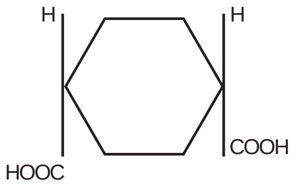


II

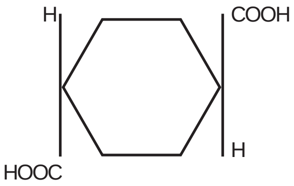
I & II are identiacal. So they are not isomers.

If there are 'n' number of conjugated or isdated 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?

....

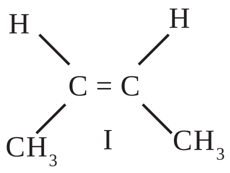
3 What is the hybridization of carbon in ethane?

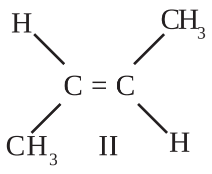
....

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_aH_{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. for	Root Word	IUPAC Name	Common Name
2	C_2H_2	eth	Ethene	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

$CH \quad C\text{-}CH_2\text{-}CH_3$ $\qquad$ $CH_3\text{-}C \quad C\text{ -}CH_3$

1- Butyne $\qquad$ 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_4-P_4, 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^0shorter than C-C (1.54 A^0) or C=C (1.34 A^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.

$H\text{-}C \equiv C\text{-}H$

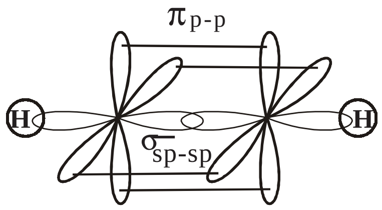


Fig. 26.3.a Orbital overlapping in Ethyne / Acetylene

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 $-C\equiv C-$ 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. $1.20A^0$

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.

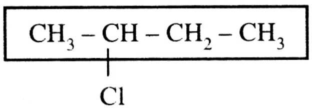
27.1 Nomenclature of Haloalkanes and Haloarenes

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.

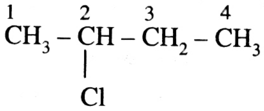


$\boxed{CH_3-\underset{}{C}H-CH_2-CH_3}$ with $\underset{Cl}{|}$ on C-2: $CH_3-\underset{\underset{Cl}{|}}{C}H-CH_2-CH_3$

The longest chain of carbon atoms in the above example is shown in the box.

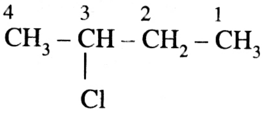
2. Numbering of the carbon atoms in the chain is done in such a way that the carbon atom bearing the halogen atom gets the lowest number.

For example.



$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{C}H}-\overset{3}{CH_2}-\overset{4}{CH_3}$

(Correct) I



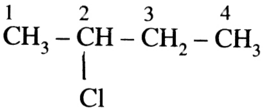
$\overset{4}{CH_3}-\underset{\underset{Cl}{|}}{\overset{3}{C}H}-\overset{2}{CH_2}-\overset{1}{CH_3}$

(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 halocompound is

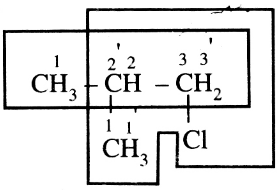


$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{C}H}-\overset{3}{CH_2}-\overset{4}{CH_3}$

2- Chlorobutane

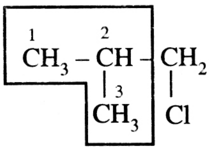
4. In case of alkyl substituted haloalkanes, the longest chain containing halogen atom is selected for numbering.

For example:



$\overset{1}{CH_3}-\underset{\underset{\overset{1\,1}{CH_3}}{|}}{\overset{2\,2}{C}H}-\underset{\underset{Cl}{|}}{\overset{3\,3}{CH_2}}$

I

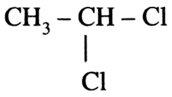


$\overset{1}{CH_3}-\underset{\underset{CH_3}{|\,3}}{\overset{2}{C}H}-\underset{\underset{Cl}{|}}{CH_2}$

II

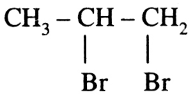
In structure I, the selection of chain is shown by two different ways. Both the ways of selection are correct since they include chloro group. In structure II numbering shown is not correct since it does not include chloro group.

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.



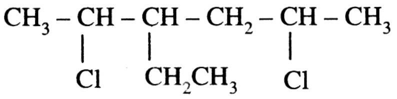
$CH_3-\underset{\underset{Cl}{|}}{CH}-Cl$

1, 1 - Dichloroethane



$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$

1, 2 - Dibromopropane

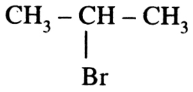
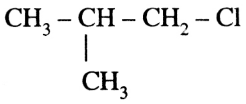
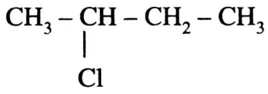
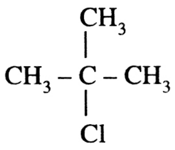


$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_2CH_3}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

2,5 - Dichloro - 3 - etylhexane

Some more examples are given in Table 27.1 to illustrate the above rules.

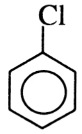
Table 27.1: Names of Some Haloalkanes

Compound	IUPAC name	Common name
CH_3CH_2Br	Bromoethane	Ethyl bromide
$CH_3CH_2CH_2Br$	l-Bromopropane	*n*-Propyl bromide
 $CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$	2-Bromopropane	iso-Propyl bromide
 $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl$	l-Chloro- 2- methylpropane	*iso-Butyl* chloride
 $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$	2-Chlorobutane	*sec*- Butyl chloride
 $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$	2-Chloro- 2-methylpropane	tert-Butyl chloride

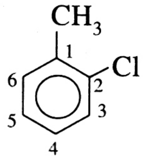
* All compounds essentially do not have common names.

Nomenclature of Haloarenes

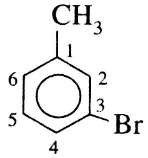
Haloarenes are those aromatic halogen compounds in which the halogen atom is directly linked to an aromatic ring. Their general formula is Ar-X where Ar- represents an aromatic ring and X denotes the halogen. In naming a haloarene, the prefix *chloro, bromo-or iodo-* etc. is are added to name of arene 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.



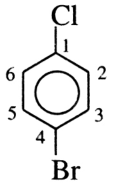
Chlorobenzene



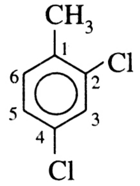
2-Chlorotoluene
(*o*-Chlorotoluene)



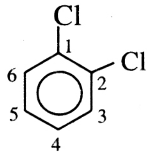
3-Bromotoluene
(*m*-Bromotoluene)



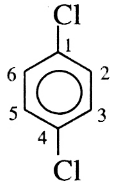
4-Bromochlorobenzene
(*p*-bromochlorobenzene)



2, 4-Dichlorotoluene



1, 2-Dichlorbenzene
(*o*-Dichlorobenzene)

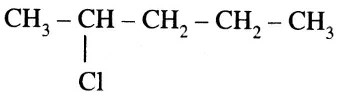


1, 4-Dichlorobenzene
(*p*-Dichlorobenzene)

Intext Questions 27.1

1. Write the IUPAC names of each of the following compounds:

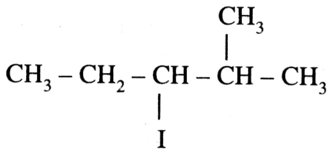
(i)



$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_2-CH_3$

....

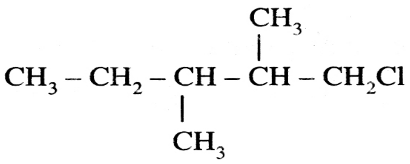
(ii)



$CH_3-CH_2-\underset{\underset{I}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

....

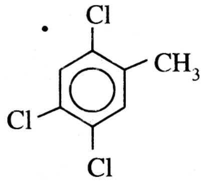
(iii)



$$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2Cl$$

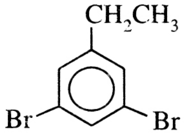
....

(iv)



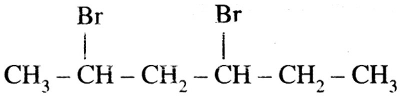
....

(v)



....

(vi)



$$CH_3-\overset{Br}{\overset{|}{CH}}-CH_2-\overset{Br}{\overset{|}{CH}}-CH_2-CH_3$$

....

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.

$$CH_3 - CH_3 + Cl_2 \xrightarrow{\text{Sunlight}} CH_3 - CH_2Cl + HCl$$

Ethane Chloroethane

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.

$$CH_3 - CH_3 + Br_2 \xrightarrow{\text{Sunlight}} CH_3 - CH_2 - Br + HBr$$

Ethane Bromoethane

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.

$$CH_3CH_2OH + HCI \xrightarrow{\text{anhy.}ZnCl_2} CH_3 - CH_2\,Cl + H_2O$$

Ethanol Chloroethane

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.

$$CH_3CH_2OH + HBr \xrightarrow[\Delta]{\text{conc.}H_2SO_4} CH_3CH_2Br + H_2O$$

Ethanol Bromoethane

(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.

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$3\,C_2H_5OH + PBr_3 \longrightarrow 3\,C_2H_5Br + H_3PO_3$$

(c) Reaction with Thionyl Chloride : Thionyl chloride ($SOCl_2$) is another reagent which reacts with an alcohol to yield a chloroalkane.

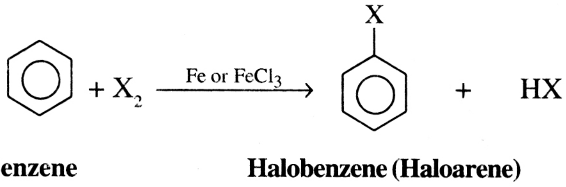
$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + SO_2\uparrow + HCI\uparrow$$

Ethanol Chloroethane

As both the byproducts, SO_2 and HCl are gases, the purification of final product is not required.

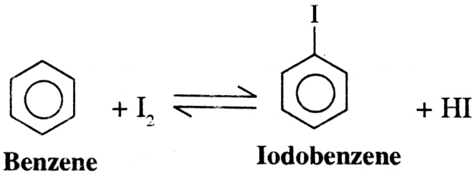
27.2.2 Preparation of Haloarenes

(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.

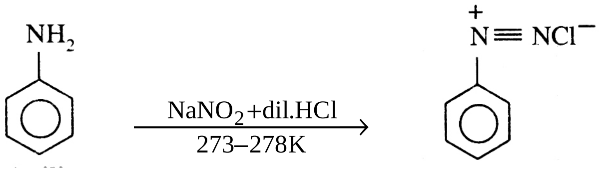


However, in the presence of an oxidizing agent such as nitric acid, iodic acid (HIO_3), mercury oxide, the HI produced is either oxidized to iodine or is eliminated as mercuric iodide and, thus, iodobenzene is obtained.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Fluorobenzene cannot be prepared by direct fluorination of aromatic hydrocarbons since the reaction is very violent and cannot be controlled.

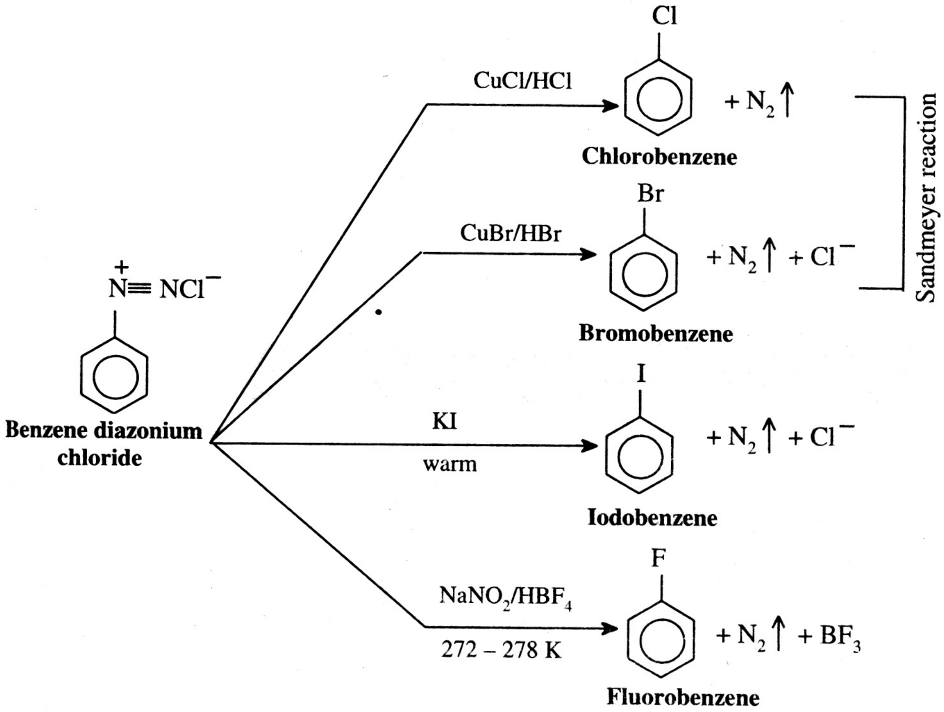
(ii) From Diazonium Salts: Benzene diazonium salt is formed by treating an aromatic primary amine with $NaNO_2$ and dil. HCI at low temperature. The process is known as diazotisation.



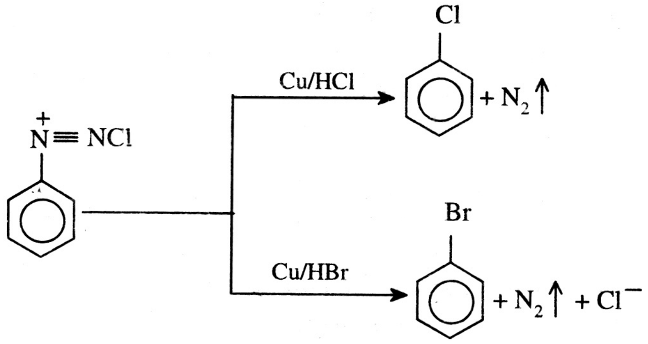
Aniline Benzene diazonium chloride

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?

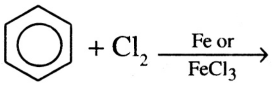
   ....

3. Give one example of preparation of chlorbenzene using Sandmeyer reaction?

   ....

4. Complete the following reaction:

....



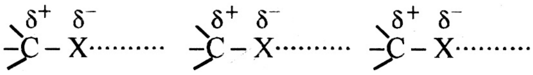
....

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 C_{18} 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:

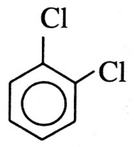


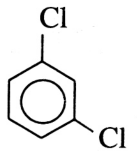
For a given alkyl or aryl group, the boiling points increase from fluoro to iodo compounds as the size of halogen atom increases. The boiling points of halomethanes, haloethanes and halobenzene given in the Table 27.2 to show this variation.

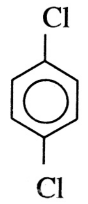
Table 27.2: Boiling Points of Haloalkanes and Haloarenes

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_s-X	184.3	241	285	311.4	345
C_6H_s-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.



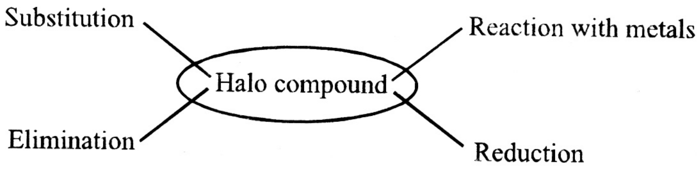




m.p. 256K 249K 325K

27.3.2 Chemical Properties

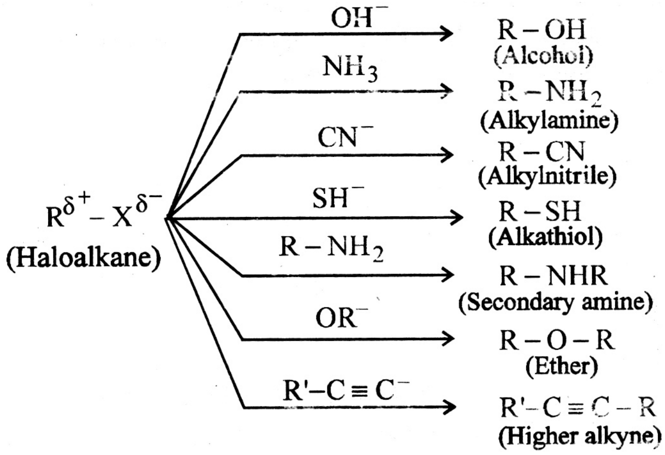
Halo compounds can undergo the following types of reactions:



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 chloroethane with sodium hydroxide, the chlorine atom of chloroethane is substituted by the hydroxyl group and ethanol is formed as the reaction product.

$$C_2H_5 - Cl + OH^- \longrightarrow C_2H_5OH + Cl^-$$

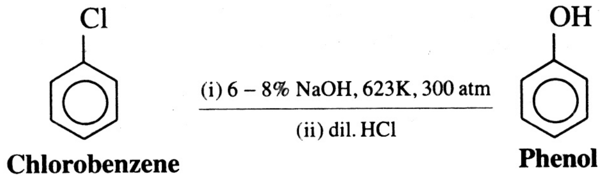
In this reaction, it is to be noted that the hydroxide ion (nucleophile) displaces the chlorine atom from C_2H_5Cl as chloride ion (another nucleophile). Such reaction which are initiated by the attack of a nucleophilic are known as nucleophilic reactions. In haloalkanes, the carbon atom carrying the 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.



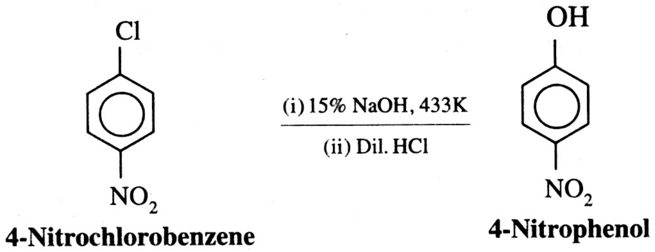
In all the above reactions, the stronger nucleophile (HO^-, $C_2H_5O^-$, CN^- or NH_3 etc.) displaces a weaker nucleophile X- as lunds

$$\underset{\substack{\textbf{Stronger}\\ \textbf{nucleophile}}}{Nu:} + R^{\delta+}-X^{\delta-} \longrightarrow \underset{\substack{\textbf{Weaker}\\ \textbf{nucleophile}}}{R-Nu + :X^{-}}$$

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.

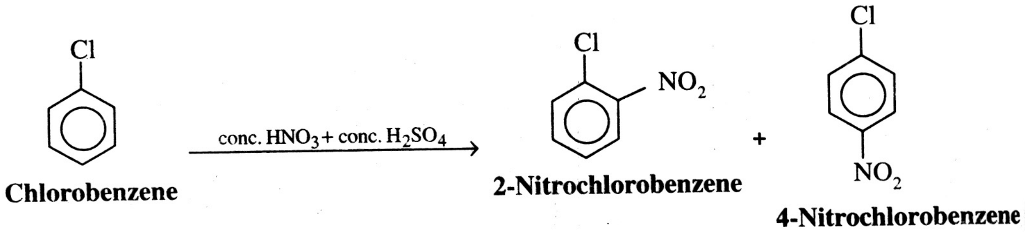


It is also observed that the presence of electron withdrawing groups such as NO_2^+ groups at o- and p-position (but not a m-position) with respect to halogen activates the halogens towards nucleophillic displacement. For example:



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_2^+. As *ortha* 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.



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	**Energy/KJ mol^{-1}**
C-F	485
C - Cl	339
C-Br	284
C-I	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 :

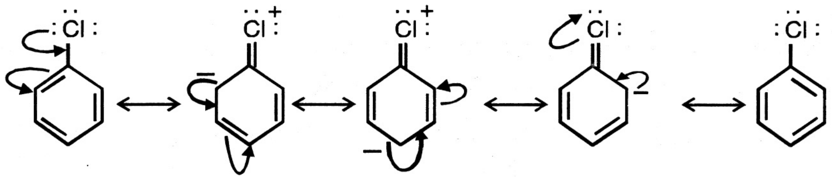


Fig. 27.1 : *Resonance Structures of Chlorobenzene*

2. **Elimination reactions :** When haloalkanes are 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

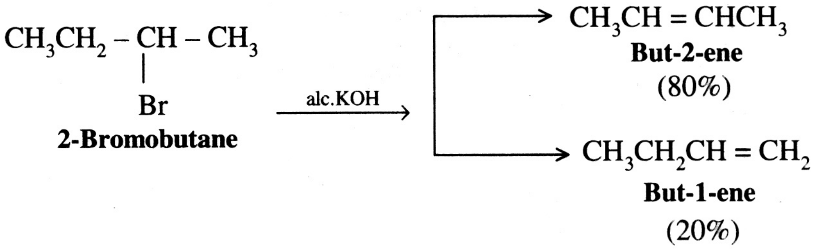
If a haloalkane is heated with concentrated alcoholic potassium hydroxide, the major product formed is an alkene due to the elimination of hydrogen halide. This is called β-elimination or dehydrohalogenation.

$$C_2H_5Cl \xrightarrow{aq.KOH} CH_2 = CH_2$$

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).



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**.

$$C_2H_5 - Cl + Mg \xrightarrow{\text{dry ether}} C_2H_5 - Mg - Cl$$

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**.

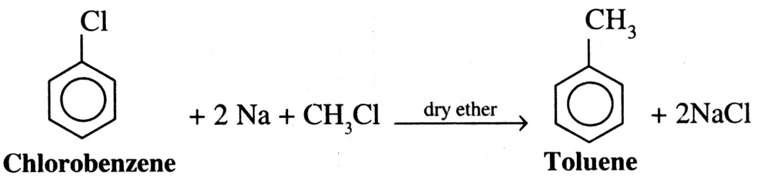
$$2\,R - X + 2\,Na \xrightarrow{\text{dry ether}} R - R + 2\,Na^+\,X^-$$

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 automobilies.

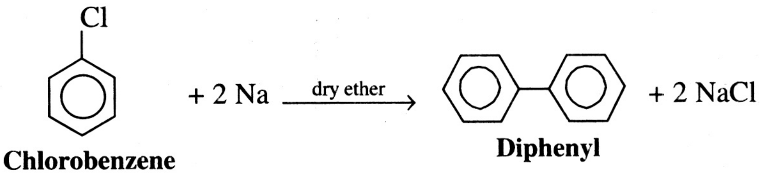
$$4CH_3CH_2Br + 4Pb \xrightarrow{\text{dry ether}} (CH_3CH_2)_4Pb$$

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). 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) ale. 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 1UPAC name is tricchloromethane. 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:

$$CH_3CH_2OH \xrightarrow[-2HCl]{Cl_2} CH_3CHO \xrightarrow[-3HCl]{3Cl_2} Cl_3CCHO$$

Ethanol Ethanal Trichloroethanal (Chloral)

$$Ca(OH)_2 + 2Cl_3C - CHO \longrightarrow (HCOO)_2Ca + 2CHCl_3$$

Calcium formate Chloroform

$$CH_3COCH_3 \xrightarrow[-3HCl]{3Cl_2} Cl_3C - CO - CH_3$$

Propanone

$$Ca\ (OH)_2 + 2\ CCI_3CO - CH_3 \longrightarrow (CH_3COO)_2\ Ca + 2\ CHCI_3$$

Calcium acetate chloroform

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.

$$CHCI_3 + O_2 \xrightarrow{light} COCl_2 + 2\ HCI$$

Phosgene

$$COCl_2 + 2C_2H_5OH \longrightarrow CO(OC_2H_5)_2 + 2HCI$$

Ethyl carbonate

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.

$$C_2H_5NH_2 + CHCI_3 + 3\ NaOH \longrightarrow C_2H_5NC + 3\ NaCl + 3\ H_2O$$

Ethylamine Ethyl isocynanide

27.4.2 Iodoform

Iodoform is a pale yellow solid with a distinct smell. Its IUPAC name is triiodomethane.

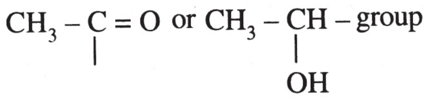
Preparation

Iodoform is prepared by heating ethanol or acetone with iodine in the presence of alkali.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3I_2 + 4\,NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3CONa + 3NaI + 3H_2O$$

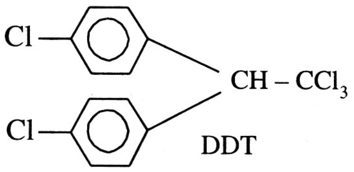
Yellow crystals of iodoform can easily be recognized by the characteristic smell. Formation of iodoform is used to test compounds containing



$CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group This test is known as **iodoform test**. Iodoform is used as an antiseptic.

27.4.3 Dichlorodiphenyltrichloroethane (DDT)

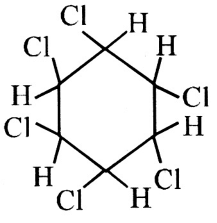
It is available in several different forms : powder, aerosols, granules, etc.



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?

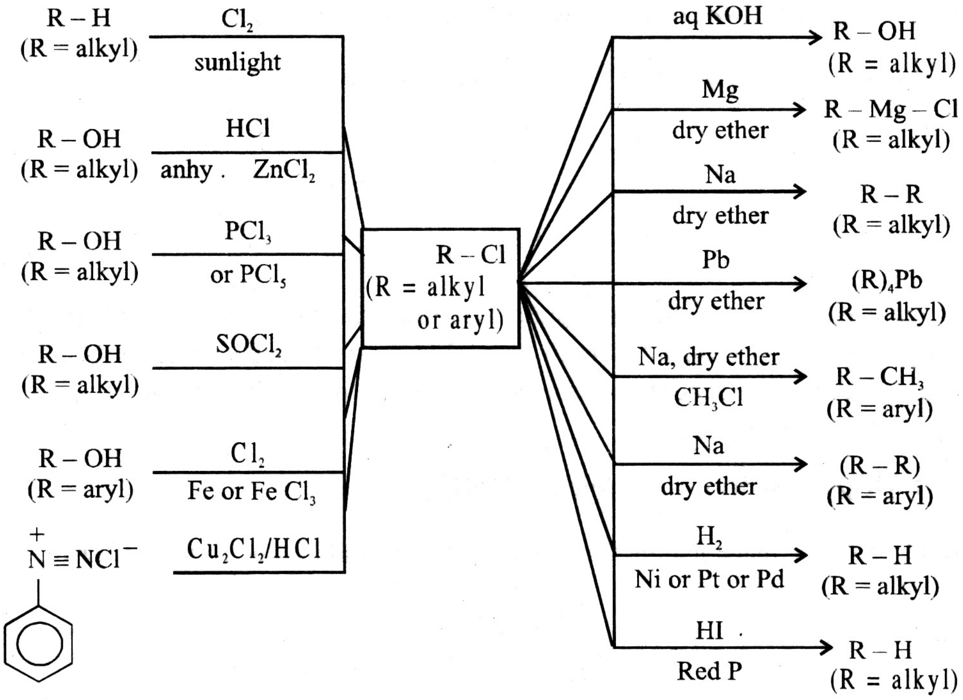
   ....

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.
- Methods of preparation and chemical properties of haloalkanes and haloarenes which are summarized below :



- Due to the polar nature, halo compounds have higher melting and boiling points than the corresponding hydrocarbons.

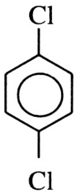
- Chemically, fluoro compounds are comparatively least reactive and iodo compounds are the most reactive. Also, haloalkanes are more reactive than haloarenes in reactions involving cleavage of C-X bond.
- Haloalkanes undergo nucleophilic substitution reactions. But in haloarenes, the substitution in 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 $CH_3-\overset{|}{C}=O$ or $CH_3-\overset{|}{C}H-OR$ group.

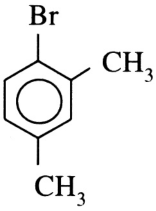
Terminal Exercise

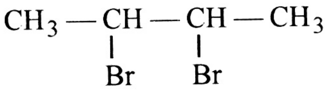
1. Give IUPAC names of the following compounds:

   (i) see-butyl chloride

   (ii) *iso*- propyl bromide

   (iii)


   (iv)


   (v)


$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

2. Name the product obtained by treating 2-propanol with hydrogen chloride in presence of anhydrous zinc chloride. Also write reaction involved.

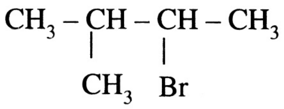
3. Alkyl halides are more reactive towards nucleophilic reagents than aryl halides. Discuss briefly.
4. Write chemical equations for the reactions of :
   (i) n-propanol with PCI_s.
   (ii) chlorine gas with benzene in presence of $FeCl_3$ as catalyst.
   (iii) bromoethane with aqueous KOH solution.
   (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?

   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.

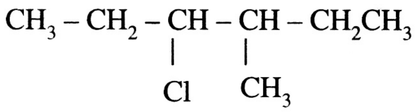
Answers to Intext Questions

27.1

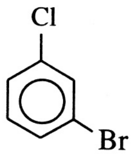
1. (i) 2-Chloropentane
   (ii) 3-Iodo-2-methylpentane
   (iii) I-Chloro-2,3-dimethylpentane
   (iv) 1,3,4- Trichloro-6-methylbenzene or 2,4,5 - Trichlorotoluene
   (v) 1,3-Dibromo-5-ethylbenzene
   (vi) 2,4-Dibromohexane

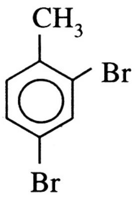
2. (i) 

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

(ii) 

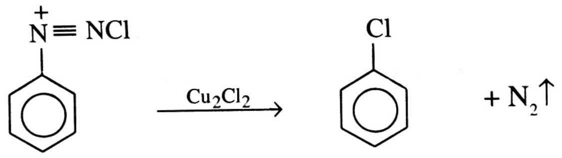
$$CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_3$$

(iii) 

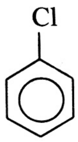
(iv) 

27.2

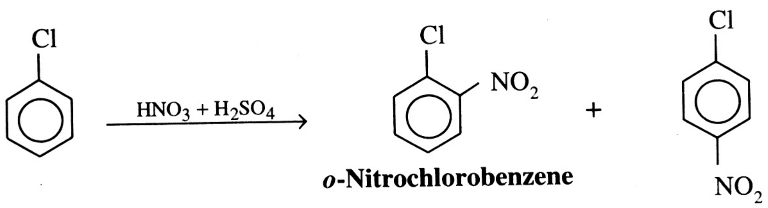
1. $CH_3CH_2CH_2CI$
2. l-chloropropane
3. The Diazonium salt on treatment with copper (I) chloride Cu2 Cl_2 gives chlorobenzene.



Chlorobenzene

4. 

27.3

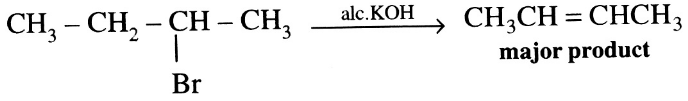
1. Due to their inability to form hydrogen bonds.
2. *Para* dichlorobenzene; due to greater symmetry and hence a better packing.
3. 

***o*-Nitrochlorobenzene**

***p*-Nitrochlorobenzene**

4. (i) $C_2H_5Cl \xrightarrow{aq.KOH} C_2H_5OH$

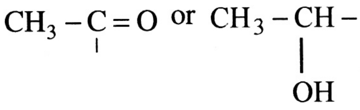
   (ii) $C_2H_5Cl \xrightarrow{aq.KOH} CH_2 = CH_2$

5. 

$$CH_3-CH_2-\underset{\displaystyle |\atop \displaystyle Br}{CH}-CH_3 \xrightarrow{alc.KOH} \underset{\textbf{major product}}{CH_3CH=CHCH_3}$$

27.4

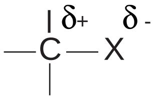
1. (i) Trichloromethane (ii) Triodomethane
2. Chloroform oxidises to phosgene in the presence of air and sunlight. Dark coloured bottles reduce formation of poisionous phosgene

   $CHCl_3 + O_2 \xrightarrow{sunlight} COCl_2 + HCI$
3. Compounds having  $CH_3-\underset{|}{C}=O$ or $CH_3-\underset{\displaystyle |\atop \displaystyle OH}{CH}-$ 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) SN^2 2) SN^1.

SN^2 (Nucleophilic substitution bi molecular reaction):

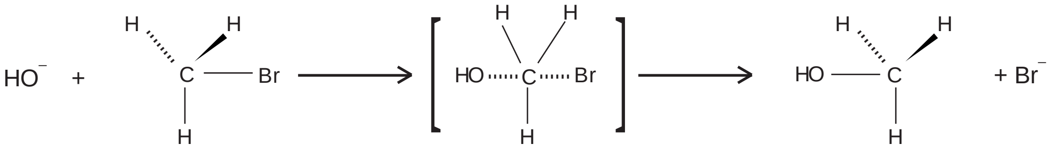
In this reaction the rate of the reaction depends on both the reactants concentration. So, it is a second order reaction. Here the rate depends on alkyl halide concentration and nucleophile concentration.

Rate α [Alkyl halide] [Nucleophile]

Eg:- $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

The above reaction takes place in two steps.

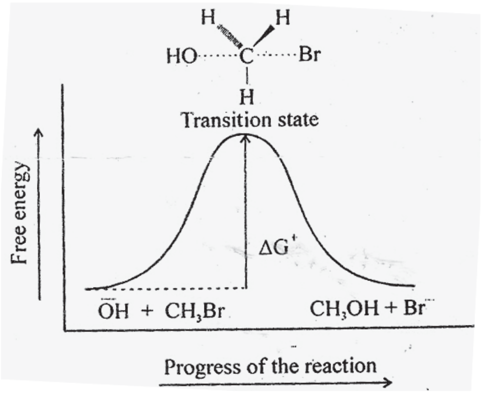
In the first step of SN^2 reaction the nucleophile attacks from back side of the carbon of alkyl halide forming a weak bond with the carbon and a transition state is formed.



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 SN^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

$$CH_3\,x > 1^0R\text{-}x > 2^0R\text{-}x > 3^0R\text{-}x.$$

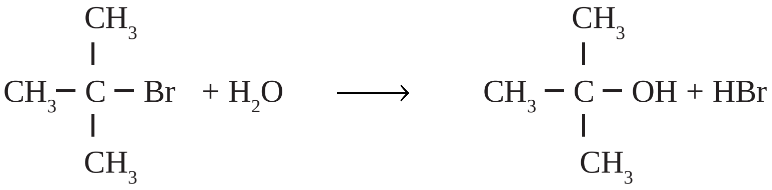
If the basicity difference between releasing group and nucleophile increases the rate of a reaction also increases in SN^2 reaction.

SN^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 SN^1 reaction.

Here the rate depends on the concentration of alkyl halide.

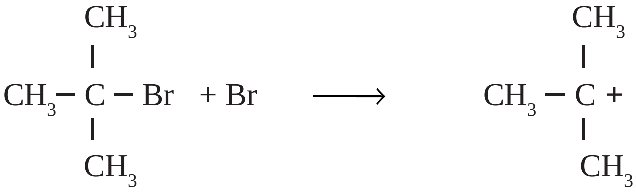
Rate of the reaction a [alkyl halide]



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br\ \ +H_2O \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH+HBr$$

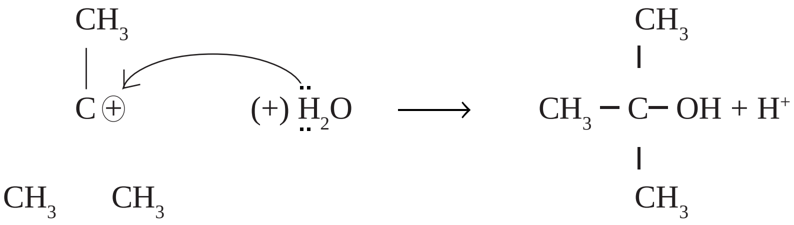
The above SN^1 reaction takes place in two steps.

In the first step of SN^1 reaction alkyl halide undergoes ionization and carbonium ion is formed.



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br\ \ +Br \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}+$$

In the second step nucleophile attacks on this carbonium ion and the products are formed.



$$\overset{\displaystyle CH_3}{\overset{|}{C}}\oplus \quad (+)\,\ddot{\underset{..}{H}}_2O \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH+H^+$$

$$CH_3 \quad CH_3$$

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 SN^1 reaction if asymmetric alkyl halide is involved raumic mixture is formed in the reaction.

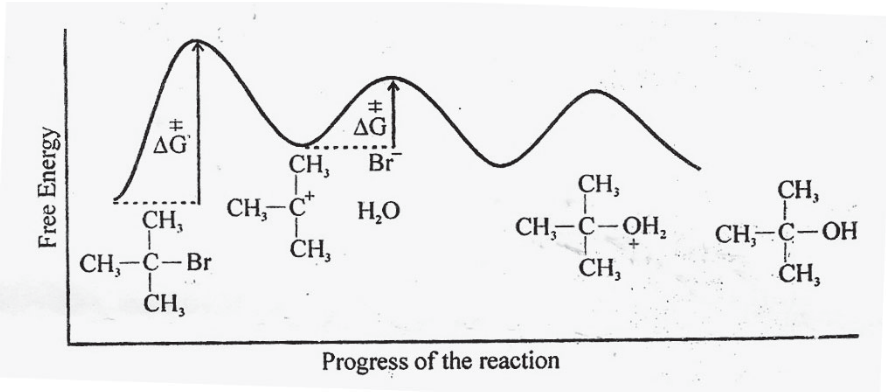
The reactivity order in alkyl halides is

3^0R- x > 2^0R-x > 1^0R-x > CH_3-x.

Due to the resonance in allyl and benzyl halides stabilized carbonium ion is formed. So in this halides SN^1 reaction takes place more i.e., they have higher reactivity towards SN^1 reaction.

$[CH_2{=}CH{-}CH_2 \leftrightarrow CH_2 - CH = CH_2]$

Allyl carbo cation.



27.2.1.a Intext questions:

1. Write the order of reactions. In SN^1 and SN^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.

28

ALCOHOLS, PHENOLS AND ETHERS

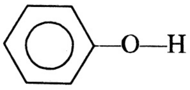
So far you have learnt the chemistry of hydrocarbons which serve as basic skeleton for the attachment of various functional groups to give a large number of their derivatives. In the last lesson, we discussed one such class of compounds *viz halogen derivatives of hydrocarbons*. Another very useful and 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 ($>C=O$).

Among the compounds with carbon-oxygen single bond are the classes of *alcohols*, *phenols* and *ethers* having the following general structures.

R—O—H

Alcohol



Phenol

R—O—R′

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.

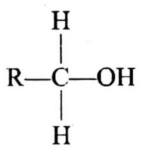
28.1 Alcohols

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.

$CH_3 - OH$	CH_3CH_2 -OH
Methanol	Ethanol
(Methyl alcohol)	(Ethyl alcohol)

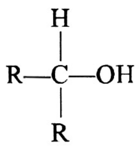
28.1.1 Classification and Nomenclature of Alcohols

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.



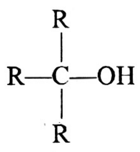
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH$$

primary alcohol



$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-OH$$

secondary alcohol



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-OH$$

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.

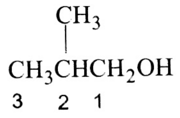
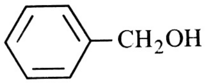
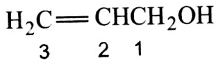
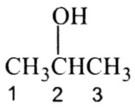
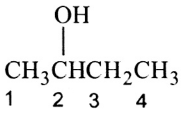
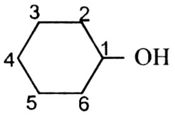
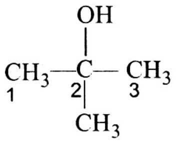
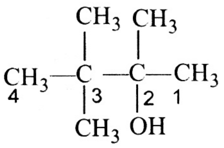
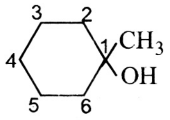
Step 3: Number the other substituents according to their position on the chain.

Step 4: Write the name of the alcohol by listing the substituents in the alphabetical order along with their position.

You may remember from Lesson 25 *that the hydroxyl group takes precedence over double and triple bonds.*

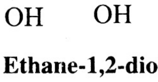
Table 28.1 illustrates some common alcohols and their IUPAC and common names. Go through them in light of the steps given above for nomenclature.

Table 28.1 : Some common Alcohols and their Names

Primary Alcohol	 $\underset{3\quad 2\quad 1}{CH_3\overset{\overset{CH_3}{\vert}}{C}HCH_2OH}$ **2-Methylpropan-1-ol** **(Isobutyl alcohol)***	 **Phenylmethanol** **(Benzyl alcohol)**	 $\underset{3\quad 2\quad 1}{CH_3CHCH_2OH}$ **1-Propanol** **(*n*-Propyl alcohol)**  $\underset{3\qquad 2\quad 1}{H_2C{=}CHCH_2OH}$ **Prop-2-en-1-ol**
Secondary Alcohol	 $\underset{1\quad 2\quad 3}{CH_3\overset{\overset{OH}{\vert}}{C}HCH_3}$ **Propan-2-ol** **(*Iso*propyl alcohol)**	 $\underset{1\quad 2\quad 3\quad 4}{CH_3\overset{\overset{OH}{\vert}}{C}HCH_2CH_3}$ **Butan-2-ol** **(*sec* Butyl alcohol)**	 **Cyclohexanol** **(Cyclohexyl alcohol)**
Tertiary Alcohol	 $\underset{1}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{\overset{OH}{\vert}}{\underset{2}{C}}}-\underset{3}{CH_3}$ **2-Methylpropan-2-ol** **(*tert*-Butyl alcohol)**	 $\underset{4}{CH_3}-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{\underset{3}{C}}}-\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{\underset{2}{C}}}-\underset{1}{CH_3}$ **2,3,3-Trimethylbutan-2-ol**	 **1-Methylcyclohex-1-ol**

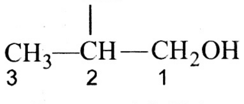
* The names given in the brackets are common names.

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:



$\underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH_2}$

Ethane-1,2-diol
(Ethylene glycol)

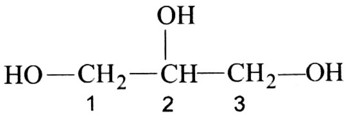


$\underset{3}{CH_3}-\underset{2}{\overset{\overset{OH}{\vert}}{CH}}-\underset{1}{CH_2OH}$

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.



$$\underset{1}{HO-CH_2}-\underset{2}{\overset{\overset{\displaystyle OH}{|}}{CH}}-\underset{3}{CH_2}-OH$$

1,2,3-Propanetriol
(Glycerol)

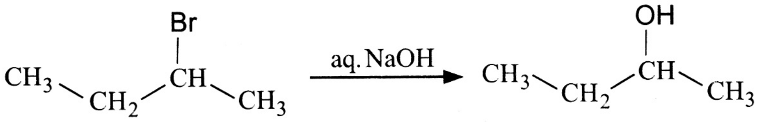
28.1.2 General Methods of Preparation

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.

$$\underset{\text{Chloroethane}}{CH_3CH_2Cl} + NaOH(aq.) \longrightarrow \underset{\text{Ethanol}}{CH_3CH_2OH} + NaCl$$



2-Bromobutane **Butan-2-ol (90%)**

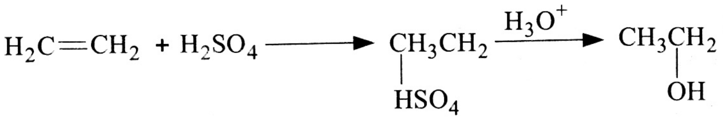
2. From hydration of Alkenes

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

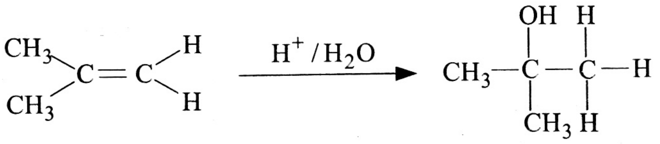
Alkenes can be hydrated to yield alcohols in the presence of acid catalysts.



$$\underset{\textbf{Ethene}}{H_2C{=}CH_2} + H_2SO_4 \longrightarrow \underset{\textbf{Ethyl hydrogen sulphate}}{\underset{\displaystyle HSO_4}{\underset{|}{CH_3CH_2}}} \xrightarrow{H_3O^+} \underset{\textbf{Ethanol}}{\underset{\displaystyle OH}{\underset{|}{CH_3CH_2}}}$$

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.

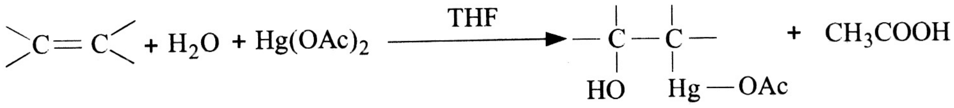


2-Methylpropene **2-Methyl-2-propanol**

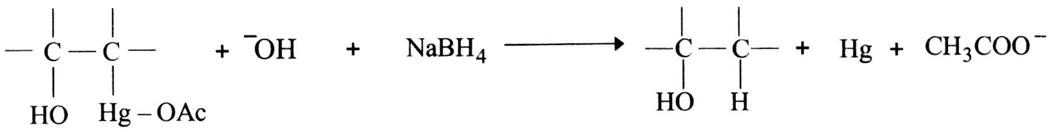
(ii) Oxymercuration demercuration

Alkenes react with mercury (II) acetate, i.e. mercuric acetate $[Hg(O\overset{\overset{O}{\|}}{C}CH_3)_2$ also represented as $Hg(OAc)_2]$ in aqueous tetrahydrofuran (THF) solvent to give hydroxyalkyl mercury compounds which are reduced to alcohols by sodium borohydride.

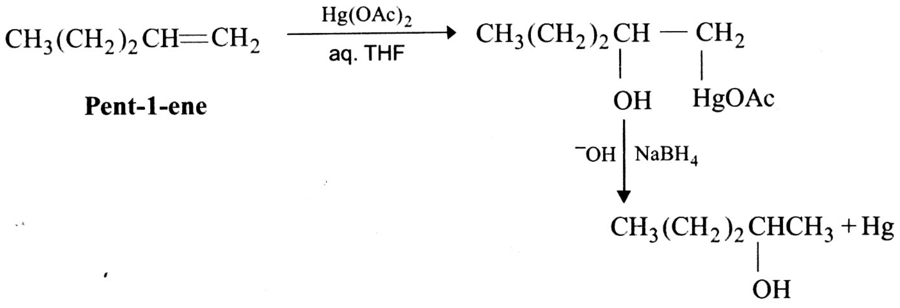
Step 1: Oxymercuration



Step 2: Demercuration



This method gives very good yield of alcohols and here also, the addition takes place in Markovnikov's fashion.

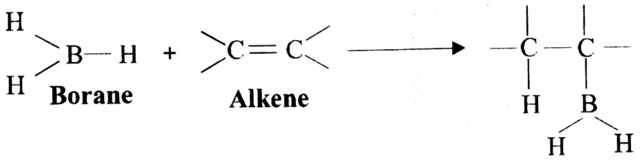


Pent-1-ene

Pentan-2-ol
(93%)

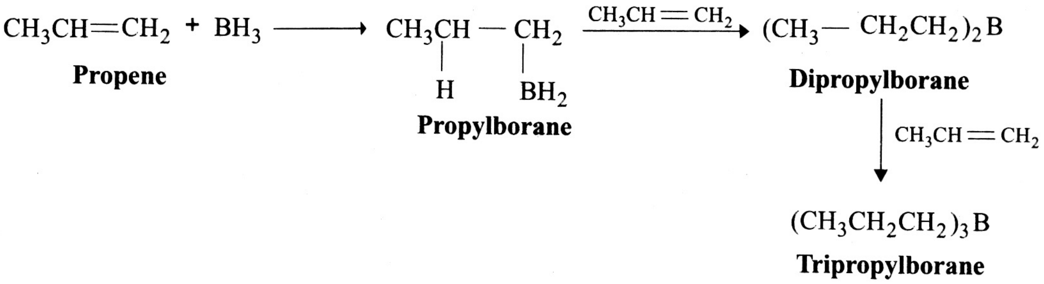
(iii) Hydroboration - Oxidation

When an alkene reacts with BH_3 (a boron hydride) in THF solution, an organoborane is obtained.



Organoborane

Since BH_3 has three hydrogens, above addition can occur three times to give trialkylborane (R_3B). This is shown below for propene.



$$\underset{\textbf{Propene}}{CH_3CH{=}CH_2} + BH_3 \longrightarrow \underset{\textbf{Propylborane}}{CH_3\underset{H}{\underset{|}{C}}H - \underset{BH_2}{\underset{|}{C}}H_2} \xrightarrow{CH_3CH{=}CH_2} \underset{\textbf{Dipropylborane}}{(CH_3-CH_2CH_2)_2B} \xrightarrow{CH_3CH{=}CH_2} \underset{\textbf{Tripropylborane}}{(CH_3CH_2CH_2)_3B}$$

The trialkylborane so obtained is oxidised using alkaline hydrogen peroxide solution to give three molecules of alcohols and boric acid.

$$(CH_3CH_2CH_2)_3\ B \xrightarrow[\text{Tripropylborane}]{H_2O_2\,/\,OH} 3CH_3CH_2CH_2OH + B(OH)_3$$

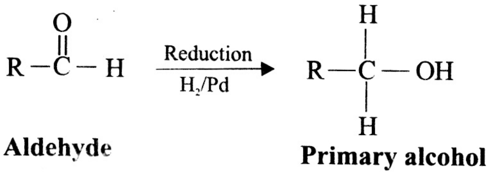
Propanol Boric acid

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

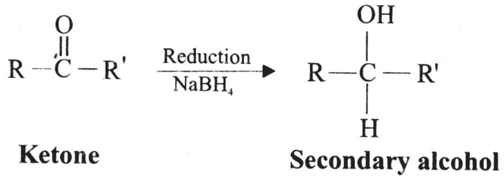
Carbonyl compounds (which contain $-\overset{O}{\overset{\|}{C}}-$ group) such as aldehydes, ketones, carboxylic acids and esters can be reduced to alcohols.

Aldehydes give primary alcohols while ketones yield secondary alcohols on reduction.



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2/Pd]{\text{Reduction}} R-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH$$

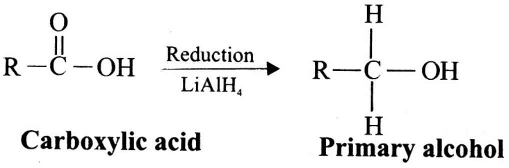
Aldehyde **Primary alcohol**



$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[NaBH_4]{\text{Reduction}} R-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-R'$$

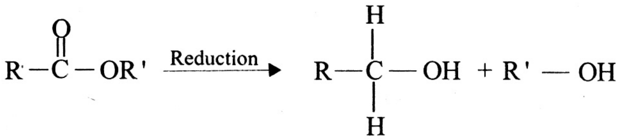
Ketone **Secondary alcohol**

Carboxylic acids and esters also give primary alcohols on reduction.



$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[LiAlH_4]{\text{Reduction}} R-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH$$

Carboxylic acid **Primary alcohol**

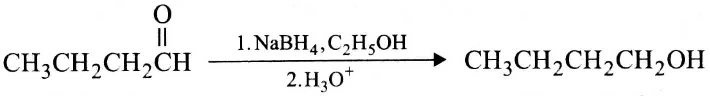


$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow{\text{Reduction}} R-\underset{H}{\overset{H}{|}}{C}-OH + R'-OH$$

Ester **Primary alcohol**

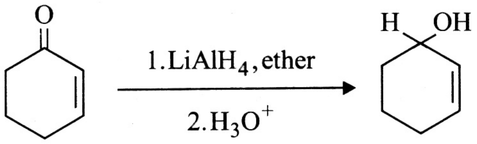
The reduction is carried out using hydride reagents such as lithium aluminium hydride ($LiAIH_4$) and sodium borohydride ($NaBH_4$). $LiAIH_4$ is stronger and reacts explosively with water while $NaBH_4$ is convenient to handle and reacts slowly.

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.



$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[2.H_3O^+]{1.NaBH_4, C_2H_5OH} CH_3CH_2CH_2CH_2OH$$

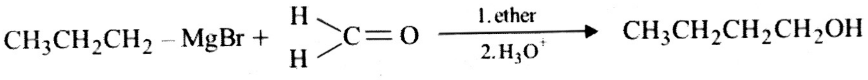
Butanol **Butan-1-ol**



Cyclohex-2-enone **Cyclohex-2-enol**

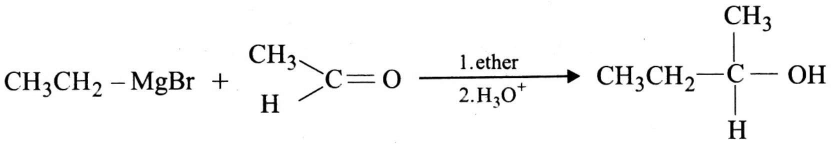
4. From Aldehydes and Ketones using Grignard Regents

Grignard reagents react with methanal (or formaldehyde) to give a *primary alcohol.*



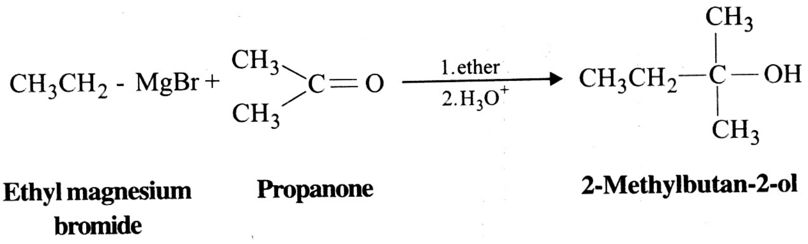
Propyl magnesium bromide **Methanal** **Butan-1-ol (Primary alcohol)**

All other aldehydes yield *secondary alcohols* on reaction with Grignard reagents.



Ethyl magnesium bromide **Ethanal (Acetaldehyde)** **Butan-2-ol (Secondary alcohol)**

With ketones, Grignard reagents give *tertiary alcohols.*



$$CH_3CH_2\text{-}MgBr + (CH_3)_2C{=}O \xrightarrow[2.H_3O^+]{1.\text{ether}} CH_3CH_2\text{—}C(CH_3)_2\text{—}OH$$

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 :

$$\begin{array}{ccc} \underset{\textbf{Sugar}}{C_{12}H_{22}O_{11}} + H_2O & \xrightarrow{\text{Investase}} & \underset{\textbf{Glucose}}{C_6H_{12}O_6} + \underset{\textbf{Fructose}}{C_6H_{12}O_6} \\ & & \Big\downarrow \textbf{Zymase} \\ & & \underset{\textbf{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2 \end{array}$$

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.

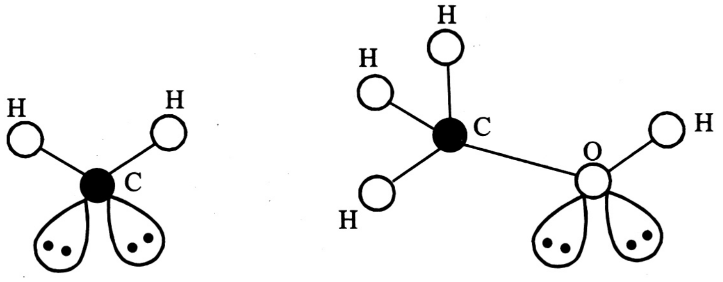


Fig. 28.1: *Water and Methanol molecule*

You know that the electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the O–H 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.

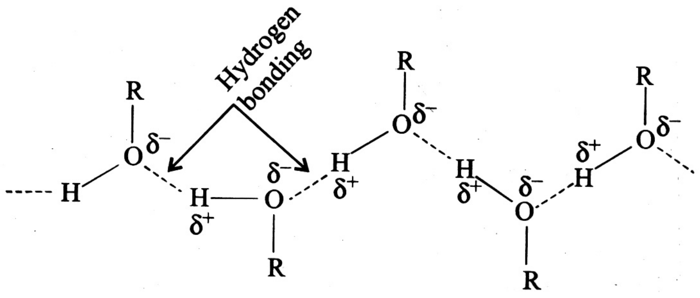
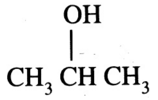
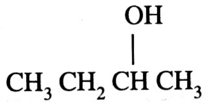


Fig. 28.2: *Hydrogen bonding in alcohol molecules*

You can see that the negatively polarised oxygen atom of one alcohol molecule attracts the positively polarised hydrogen atom of the other molecule. 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_3CH_2OH	Ethanol	158.3	351.5	∞
CH_3CH_3	Ethane	189.7	184.4	-
CH_3CH_2Cl	Chloroethane	136.6	285.3	-
$CH_3CH_2CH_2OH$	Propan-1-ol		378.04	∞
$CH_3CH_2CH_3$	Propane	85.3	230.9	-
 $CH_3\overset{\overset{OH}{\vert}}{CH}CH_3$	Propan-2-ol	184	355	∞
$CH_3CH_2CH_2\ CH_2OH$	Butan-1-ol	183	391	83
 $CH_3CH_2\overset{\overset{OH}{\vert}}{CH}CH_3$	Butan-2-o1	159	373	10.0

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.

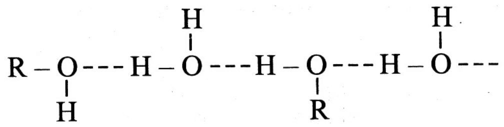


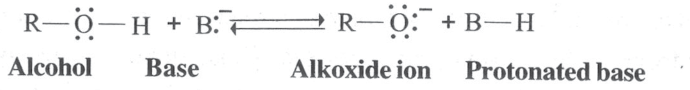
Fig. 28.3: *Hydrogen bonding in a solution of methanol and water*

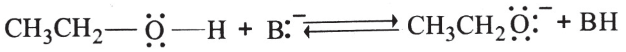
28.1.4 Reactions of Alcohols

Alcohols exhibit the following reactions:

1. Acidic and Basic behaviour

Alcohol behave both as acids and bases. They are weakly acidic. A strong base such as a hydride ion (H^-) in sodium hydride (N aH), can remove the proton from the alcohol molecule and an alkoxide ion results.





Ethanol Base Ethoxide ion rotonated base

When water is used as a base, the *acid dissociation constant (K_a)* and *pK_a* can be written as follows:

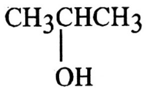
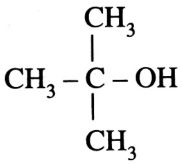
$$R-O-H+H_2O \underset{}{\overset{K_a}{\rightleftarrows}} R-O^- + H_3O^+$$

$$K_a = \frac{[H_3O^+][RO^-]}{[ROH]}$$

$$pK_a = -\log\ K_a$$

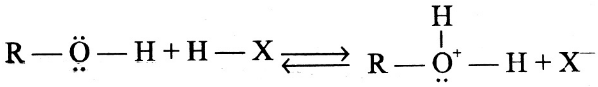
Some pK_a values are listed in Table 28.3.

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_a 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:



$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H-X \rightleftharpoons R-\overset{H}{\underset{\cdot\cdot}{\overset{|}{O^+}}}-H + X^-$$

Alcohol **Acid** **Oxonium ion**

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

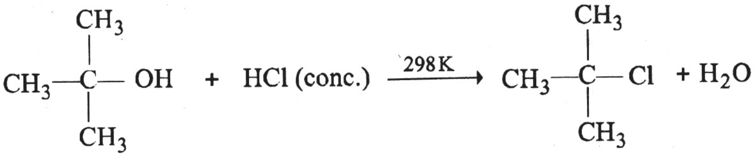
$$(CH_3)_3C-OH \;+\; K \longrightarrow (CH_3)_3C-O^-K^+ + \frac{1}{2}H_2(g)$$

tert-Butyl alcohol Potassium metal Potassium *tert-butoxide*

Alkoxides are used in the synthesis of organic compounds.

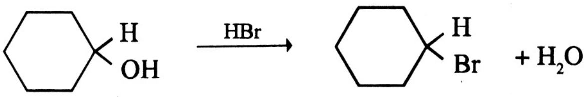
3. Conversion to Alkyl Halides

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.

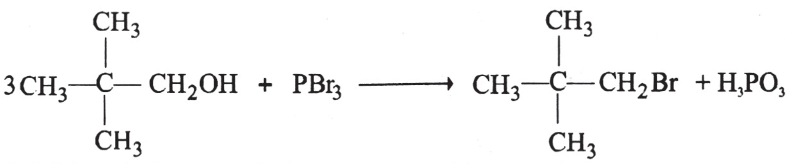


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HCl\,(conc.) \xrightarrow{298K} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + H_2O$$

2-Methyl propan-2-ol **2-chloro-2-methyl propane**



Cyclohexanol **Bromocyclohexane**



$$3CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH + PBr_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br + H_3PO_3$$

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.

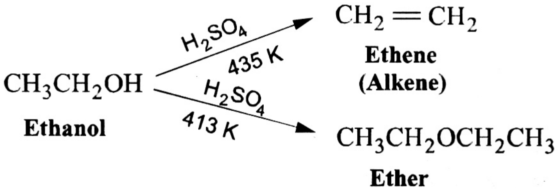
4. Formation of Alkenes

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 $KMnO_4$, crO) and $Na_2Cr_2O_7$ or $K_2Cr_20_7$ 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

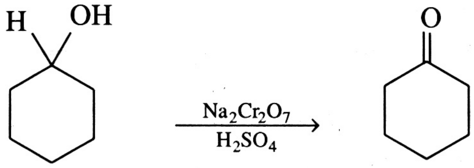
The aldehydes obtained by oxidation of the primary alcohols get further oxidised to carboxylic acids as shown above. You will study more about these classes of compounds in the next lesson.

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 :



Cyclohexanol **Cyclohexanone**

7. **Formation of Esters**

Alcohols react with carboxylic acids to form esters. This reaction is discussed in the next lesson.

$$CH_3COOH + CH_3CH_2OH \overset{H+}{\rightleftharpoons} CH_3COOCH_2CH_3 + H_2O$$

Ethanoic acid Ethanol Ethyl ethanoate Water

This reaction is called esterification reaction and is reversible in nature.

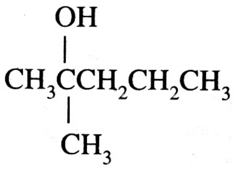
Uses

Alcohols find a large variety of uses as follows :

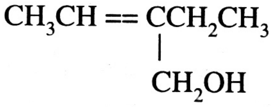
1. As solvents
2. As laboratory reagents
3. In medicines
4. As thinners in paints, varnishes, etc.

Intext Questions 28.1

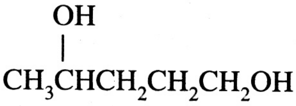
1. Give the IUPAC names of the following alcohols:

(i) 

$CH_3C(OH)(CH_3)CH_2CH_2CH_3$

(ii) 

$CH_3CH{=}C(CH_2OH)CH_2CH_3$

(iii) 

$CH_3CH(OH)CH_2CH_2CH_2OH$

....

2. How Will you prepare propan-l-o1 from propanal?

....

3. Give the synthesis of 2-methylpropan-2-o1 using Grignard reagent.

....

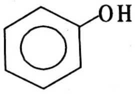
4. Give the product of the following reactions:

(i) Hexan-l-ol $\xrightarrow[H_2O,\ H^+]{CrO_3}$

(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.

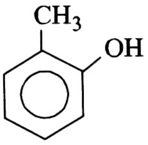


Phenol

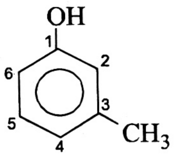
It is also used as a general name for the class of compounds derived from the above compound. Phenol is a disinfactant. Phenols are widely distributed in nature. They are also important in the synthesis of organic compounds such as aspirin and in the preparation of dyes. Phenol is also used in the manufacture of bakelite which is a very useful polymer.

28.2.1 Nomenclature of Phenols

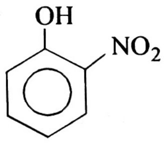
Some representative examples of phenolic compounds are given below:



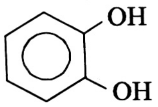
2-Methylphenol
(*o*-Cresol)



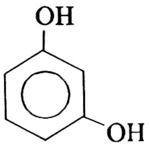
3-Methylphenol
(*m*-Cresol)



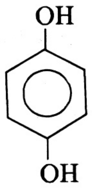
2-Nitrophenol
(*o*-Nitrophenol)



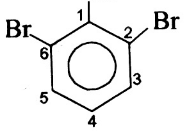
1,2-Benzenediol
(Catechol)



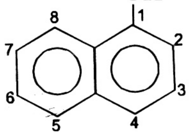
1,3-Benzenediol
(Resorcinol)



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.

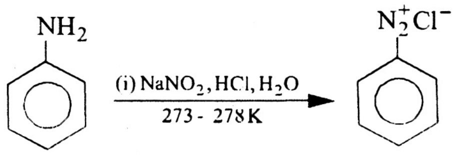
28.2.2 General Methods of Preparation

We can categorise the methods of preparation as methods of *laboratory synthesis* and *industrial synthesis* of phenols.

A. Laboratory Synthesis of Phenols

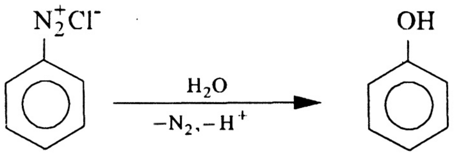
1. From Arenediazonium Salts

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:



Benzenamine **Benzenediazonium chloride**
(Aniline)
(an aromatic amine)

The arenediazonium salt on hydrolysis yields phenol.

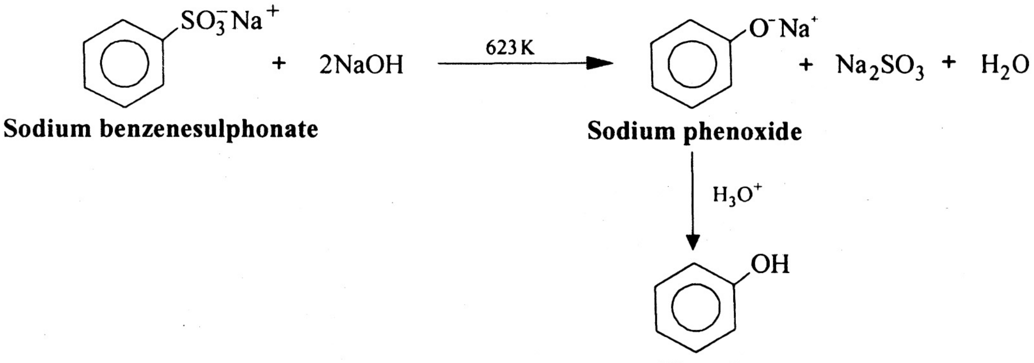


Benzenediazonium chloride **Phenol**

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.



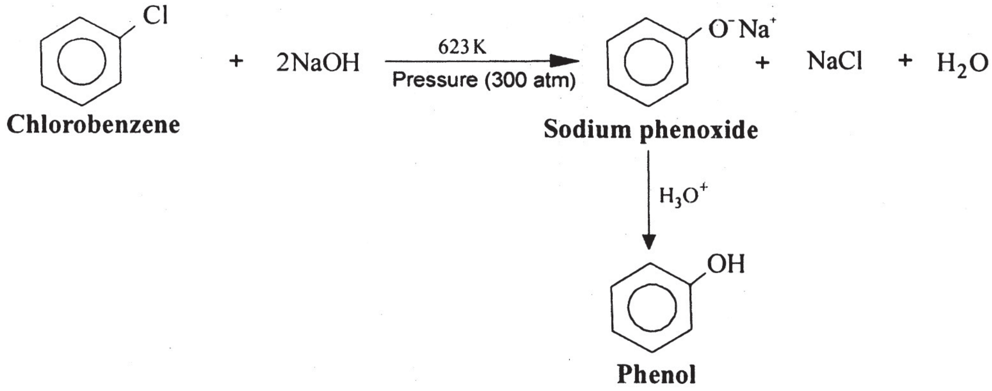
Sodium benzenesulphonate **Sodium phenoxide**

Phenol

B. Industrial Synthesis of Phenols

1. Dow Process

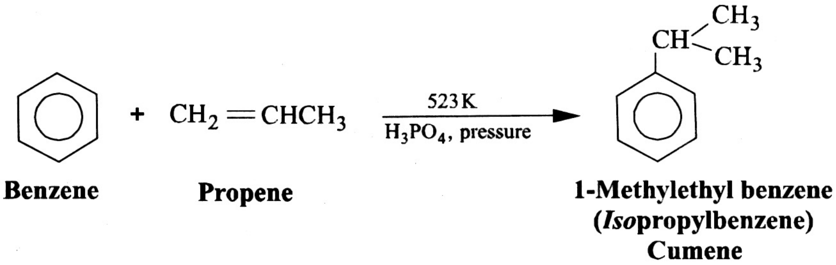
In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.



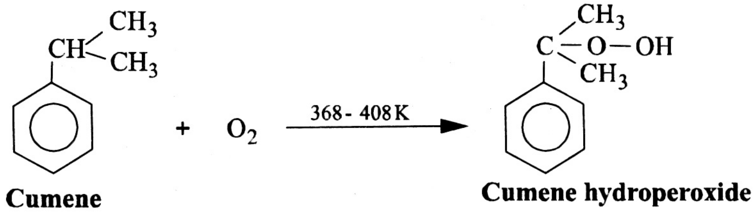
This method was in use for many years but now phenol is synthesised via cumene hydroperoxide which is discussed below.

2. From Cumene Hydroperoxide

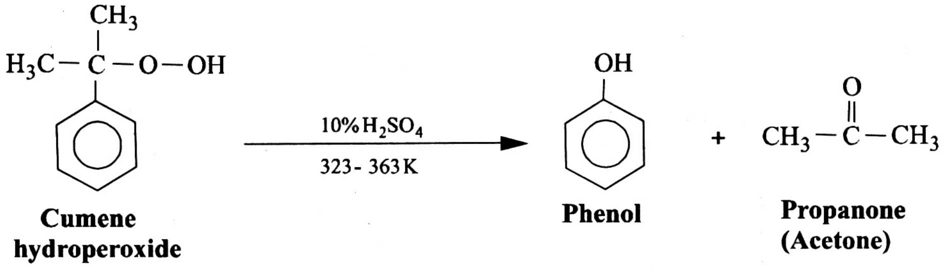
The reaction between benzene and propene in presence of phosphoric acid yields cumene.



Cumene is then oxidised to cumene hydroperoxide by air.



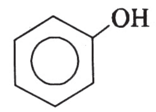
In the final step, cumene hydroperoxide is treated with 10% sulphuric acid to give phenol and acetone on hydrolytic rearrangement.



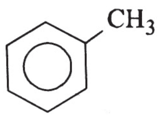
Note that propanone is obtained as a valuable byproduct in this reaction.

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.

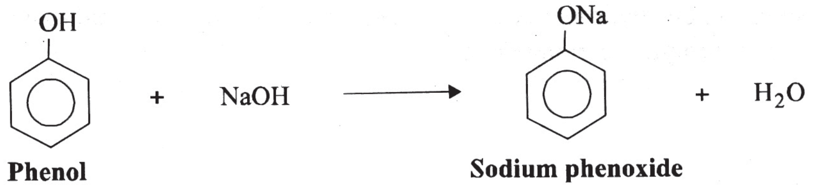
1. Acidic and Basic Nature

Phenols are much more acidic than alcohols. pK_a values of some phenols are listed in Table 28.4.

Table 28.4: pK_a 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.

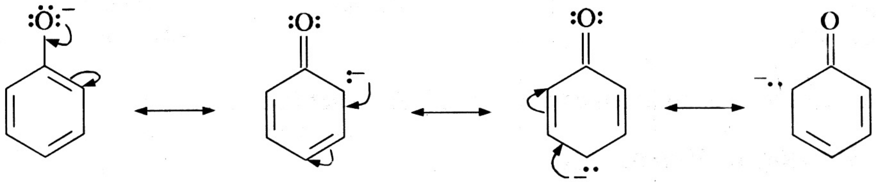


Fig. 28.4: Resonance structures of phenoxide ion

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.

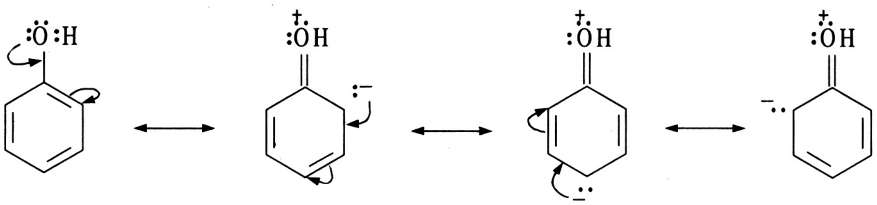
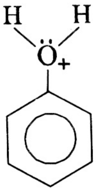


Fig. 28.5 : *Resonance structures of phenol*

If you carefully go through the $p'K_a$ 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 pK_a values as compared to phenol itself. On the other hand, electron withdrawing substituents increase the acidity and phenols having these substituents (-CI, -N0_2, etc.) have lower pK_a 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.

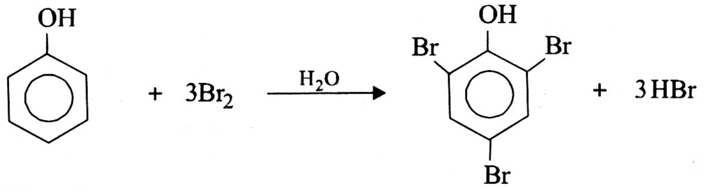


Phenyloxonium ion

2. Electrophilic Substitution Reactions

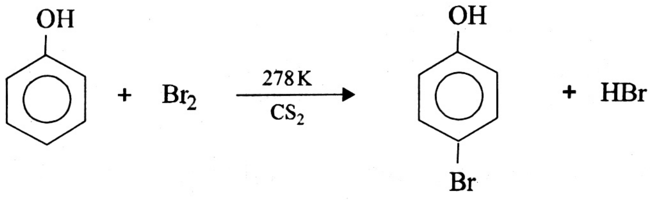
The hydroxyl group is a powerful activating group and hence phenols readily undergo electrophilic substitution reactions. In this reaction, an electrophile (electron loving species) attacks the benzene ring and replaces one of its hydrogen atoms. Since the *ortho* and *para* positions of the phenol are 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.



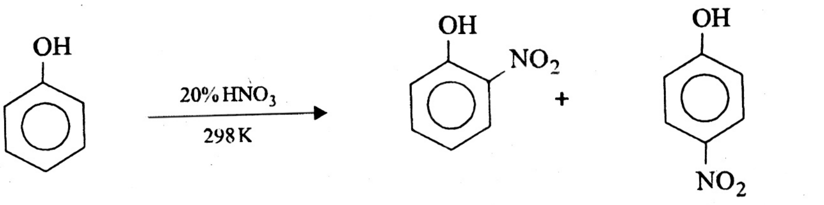
Phenol **2,4,6-Tribromophenol**

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 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 Is 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.

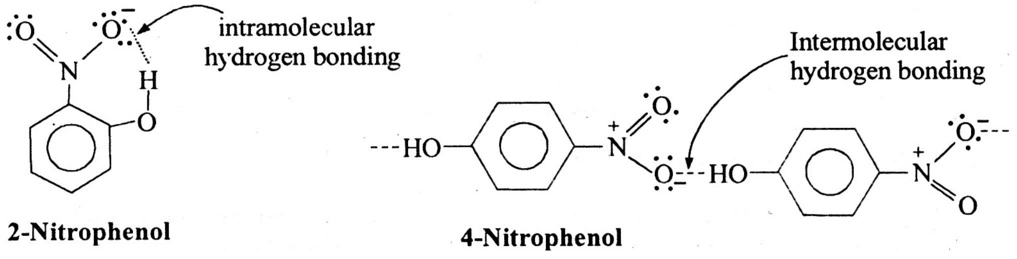


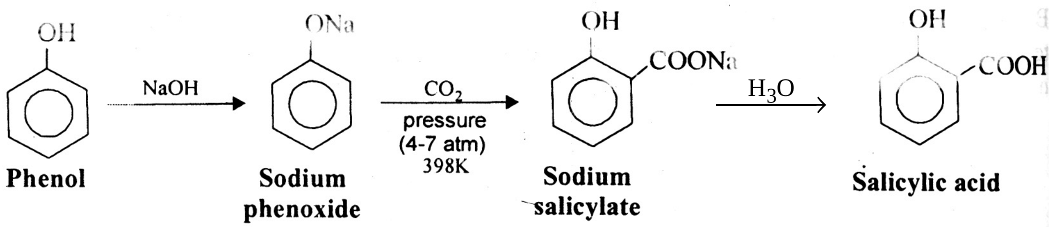
Fig. 28.5 : *Intramolecular and intermolecular hydrogen bonding in nitrophenols*

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

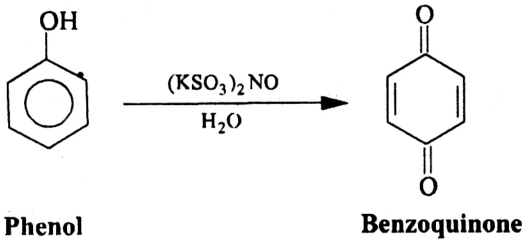
It involves sodium phenoxide which is allowed to absorb carbon dioxide and then heated under a pressure of CO_2 to 398K. Sodium salicylate so obtained on acidification yields salicylic acid.



By reaction with acetic anhydride, salicylic acid yields *aspirin*, which is the common pain reliever.

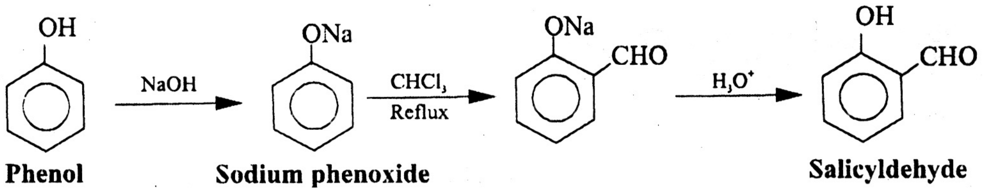
4. Oxidation

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.

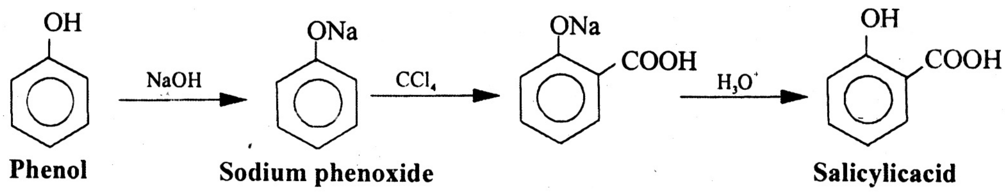


5. Reimer Tiemann Reaction

Phenols react with chloroform in the presence of sodium hydroxide (or potassium hydroxide) solution followed by acidification to give hydroxy aldehydes.

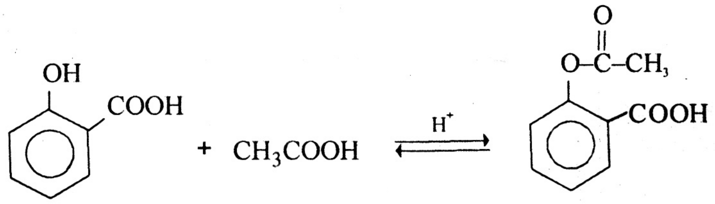


Use of carbon tetrachloride in place of chloroform gives salicylic acid.



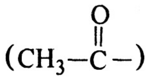
6. Esterification

Similar to alcohols, phenols react with carboxylic acids to give esters.



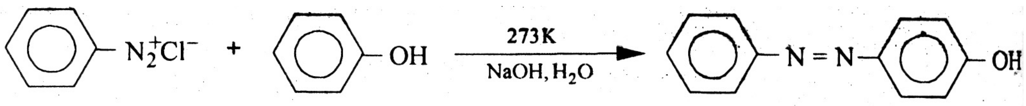
2-Hydroxybenzoic acid **Ethanoic acid** **Acetyl salicylic acid**

This reaction is an acetylation reaction as the H of - OH the phenol is replaced by the acetyl


$(CH_3-\overset{O}{\overset{||}{C}}-)$ 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.*



Benzenediazonium chloride **Phenol** **orange solid**
***p*-Phenylazophenol**
(*p*-Hydroxyazobenzene)

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?

....

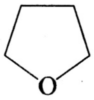
28.3 Ethers

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)

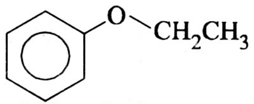
Ethers are commonly used as solvents for organic reactions. The symmetrical ether shown here is diethyl ether and is commonly also referred to simply as *ether* because of its nature as solvent for reactions and extraction of organic compounds. It was also used as an anaesthetic for over hundred years.

28.3.1 Nomenclature of Ethers

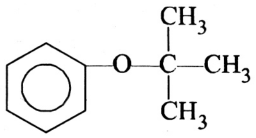
Common names of ethers are arrived by alphabetically naming the two groups attached to the oxygen followed by the word ether. The common names for some ethers are given below:

$CH_3OCH_2CH_3$
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

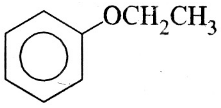
In IUPAC nomenclature, the larger alkyl (or aryl) group is used as the root name as the *alkane* and the smaller alkyl group is treated as an *alkoxy* substituent on this alkane. For example, in ethyl methyl ether having ethyl and methyl groups, the ethyl group is larger than methyl group and hence this 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.

$$<ROH + Na \longrightarrow RO^{-}Na^{+} + \frac{1}{2}H_2>$$

Metal alkoxide

$$<ROH + NaH \longrightarrow RO^{-}Na^{+} + H_2>$$

Metal alkoxide

$$< RO^{-}Na^{+} + R'–X \longrightarrow R–O–R' + NaX>$$

Metal alkoxide   Alkyl halide   Ether

$$CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2ONa \xrightarrow{CH_3CH_2I} CH_3CH_2CH_2OCH_2CH_3 + NaI$$

propan-l-ol   Sodium propoxide   l-Ethoxypropane (Ethyl propyl ether)

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 sp^3 hybridised. There are two lone pairs of electrons present on the oxygen atom as is shown in Fig. 2.8.6.

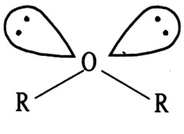


Fig. 28.6 : *Geometry of an ether molecule*

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.

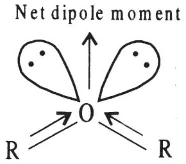
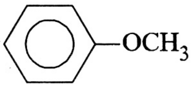


Fig. 28.7: *Polar ether molecule*

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.

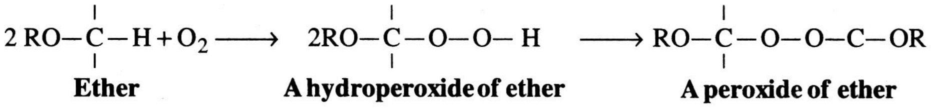
Table 28.5 : Boiling points of some common ethers

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.

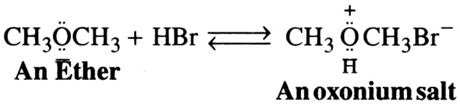


$$\underset{\textbf{Ether}}{2\,RO-\overset{|}{\underset{|}{C}}-H+O_2} \longrightarrow \underset{\textbf{A hydroperoxide of ether}}{2RO-\overset{|}{\underset{|}{C}}-O-O-H} \longrightarrow \underset{\textbf{A peroxide of ether}}{RO-\overset{|}{\underset{|}{C}}-O-O-C-OR}$$

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.



$$\underset{\textbf{An Ether}}{CH_3\ddot{\underset{..}{O}}CH_3} + HBr \rightleftharpoons \underset{\textbf{An oxonium salt}}{CH_3\,\overset{+}{\underset{H}{\ddot{O}}}CH_3Br^-}$$

3. Acidic Cleavage

Heating dialkyl ethers with strong acids such as HI, HBr or H_2SO_4 leads to their cleavage.

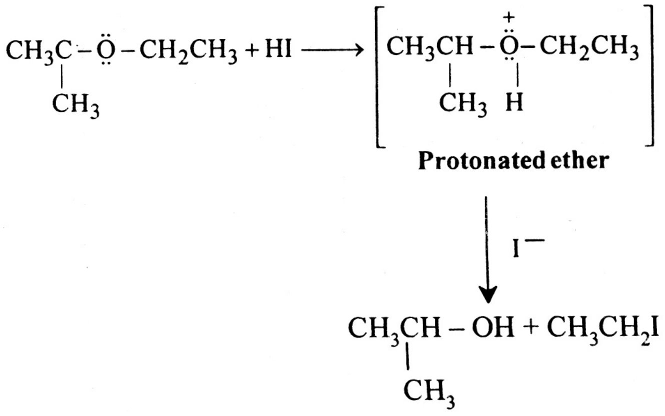
$$CH_3CH_2OCH_2CH_3 + HBr \longrightarrow CH_3CH_2Br + CH_3CH_2OH$$

Ethoxyethane Bromoethane Ethanol

The alcohol formed further reacts with additional HBr to give bromoethane. Hence,

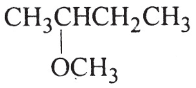
$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

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) 

$CH_3\underset{\displaystyle OCH_3}{\underset{|}{C}}HCH_2CH_3$

(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.

....

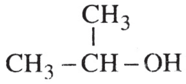
What You Have Learnt

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.

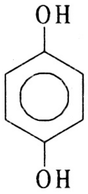
Terminal Exercise

1. Give the IUPAC names of the following compounds:

(i) 

$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-OH$

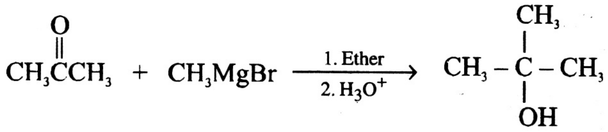
(ii) $C_6H_5OCH_2CH_3$

(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

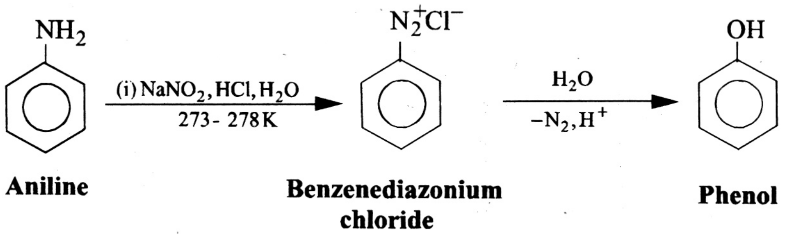
28.1

1. (i) 2-Methylpentan-2-ol (ii) 2-Ethylbut-2-en-1-ol (iii) 1, 4-Pentanediol
2. By reduction with $NaBH_4$ or $LiAlH_4$
3. 

$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ Ether} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

4. (i) Hexanoic Acid (ii) Hexanal

28.2

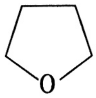
1. 

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) $CH_3CH_2CH_2O^- + CH_3Br \longrightarrow CH_3CH_2 - O - CH_3 + Br^-$

   (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.

29

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

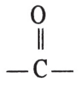
In the last lesson, you studied about organic compounds containing functional groups having carbon-oxygen single bond. There are other classes of organic compounds in which the functional group contains the carbon- oxygen double bond. The examples of these classes of compounds being carbonyl compounds 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

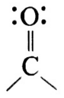
After reading this lesson, you should be able to

- 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.

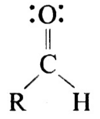
29.1 Aldehydes and Ketones

You have some familiarity with these classes of compounds from previous lessons. These compounds are also referred to as *carbonyl compounds* and have  $-\overset{O}{\overset{\|}{C}}-$ 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.

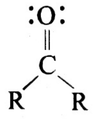
Aldehydes have at least one hydrogen atom bonded to the carbonyl group, the other group may be either a hydrogen or an alkyl (or aryl) group. In *ketones*, the carbonyl group is bonded to two alkyl or aryl groups. The two groups bonded to a ketone may be similar or different resulting in a symmetrical or an unsymmetrical ketone, respectively.



Carbonyl group

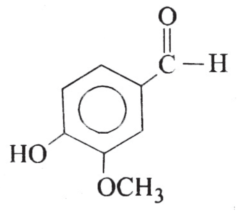


an aldehyde

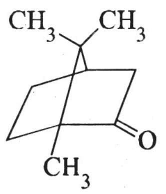


a ketone

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)

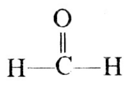


Camphor

29.1.1 Nomenclature of Aldehydes and Ketones

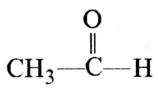
In the IUPAC system of nomenclature, aliphatic *aldehydes* are named as *alkanals.* The final *-e* in the name of the corresponding alkane is substituted by *-al.*

Some common examples of aldehydes and their names are given below:



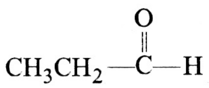
$H-\overset{O}{\overset{\|}{C}}-H$

Methanal
(Formaldehyde)



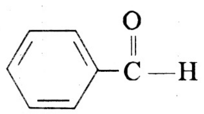
$CH_3-\overset{O}{\overset{\|}{C}}-H$

Ethanal
(Acetaldehyde)



$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$

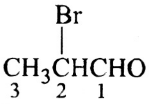
Propanal
(Propionaldehyde)



Benzenecarbaldehyde
(Benzaldehyde)

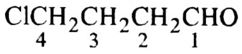
Note that when the -CHO group is attached to a ring, then the compound is called a *carbaldelzyde.*

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.



$\underset{3}{CH_3}\underset{2}{\overset{\overset{Br}{|}}{C}H}\underset{1}{CHO}$

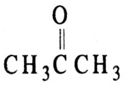
2-Bromopropanal



$Cl\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CHO}$

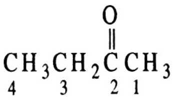
4-Chlorobutanal

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:



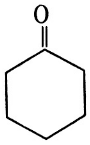
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

Propanone
(Acetone)

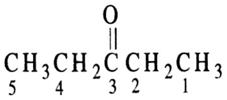


$\underset{4}{CH_3}\underset{3}{CH_2}\underset{2}{\overset{\overset{O}{\|}}{C}}\underset{1}{CH_3}$

Butan-2-one
(Ethyl methyl ketone)

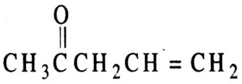


Cyclohexanone



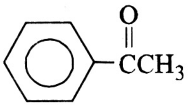
$\underset{5}{CH_3}\underset{4}{CH_2}\underset{3}{\overset{\overset{O}{\|}}{C}}\underset{2}{CH_2}\underset{1}{CH_3}$

Pentan-3-one
(Diethyl ketone)

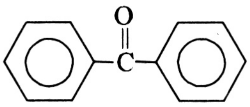


$CH_3\overset{\overset{O}{\|}}{C}CH_2CH=CH_2$

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

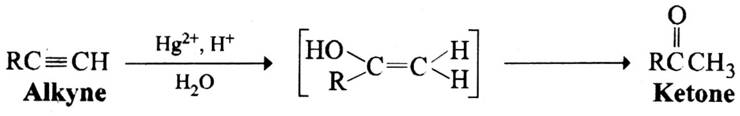
From the last lesson, you know that primary alcohols can be oxidised to aldehydes and secondary alcohols can be oxidised to ketones.

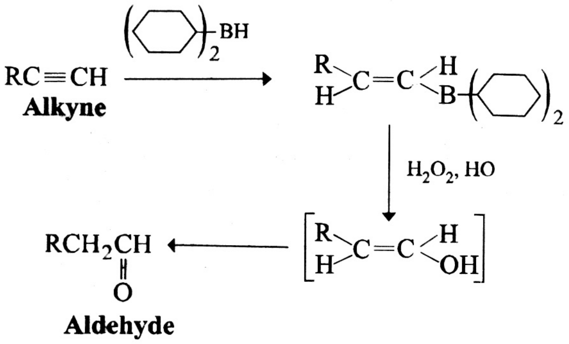
2. Ozonolysis of Alkenes

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.

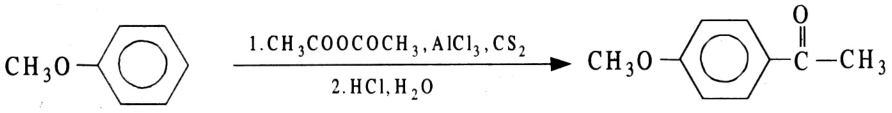




You can go through the details of these reactions as discussed in lesson 26.

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 and oxygen atoms are *Sp*^{2} hybridised. Therefore, the groups attached to the carbon atom and oxygen are present in a plane. This is shown in Fig. 29.1.

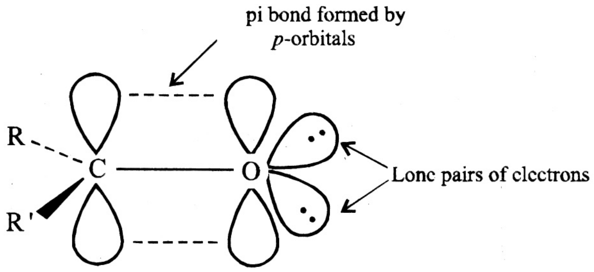
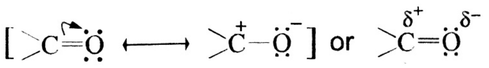


Fig. 29.1 : *The structure of the carbonyl functional group*

You can see in the figure that a π-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.



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.

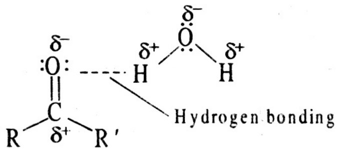
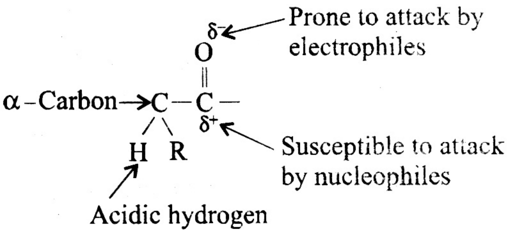


Fig. 29.2 : *Hydrogen bonding between carbonyl compound and water molecule*

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 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 :

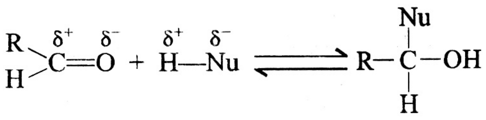
(i) Aldehydes have only one alkyl group whereas ketones have two. Since the alkyl groups are electron donating in nature, the carbonyl carbon in ketones which is bonded to two alkyl groups, is less positive (electrophilic) as compared to the aldehydic carbonyl carbon. Hence, it is less susceptible to 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:

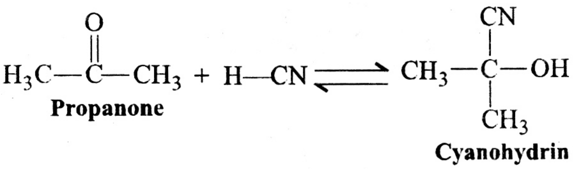


$$\underset{H}{\overset{R}{>}}\overset{\delta^+}{C}=\overset{\delta^-}{O} + \overset{\delta^+}{H}-\overset{\delta^-}{Nu} \rightleftharpoons R-\underset{H}{\overset{Nu}{\overset{|}{\underset{|}{C}}}}-OH$$

Some specific reactions of this category are discussed below :

1. Formation of Cyanohydrins

Carbonyl compounds react with hydrogen cyanide to yield *cyanohydrins.*



$$\underset{\textbf{Propanone}}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3} + H-CN \rightleftharpoons \underset{\textbf{Cyanohydrin}}{CH_3-\underset{CH_3}{\overset{CN}{\overset{|}{\underset{|}{C}}}}-OH}$$

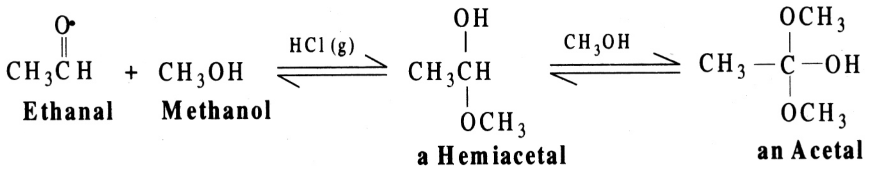
Note that one more carbon atom is present in the cyanohydrin as compared to the starting carbonyl compound.

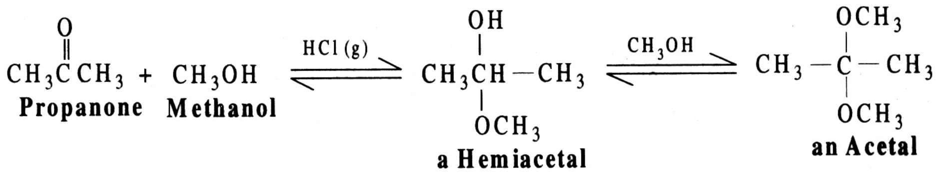
Cyanohydrins are useful in the synthesis of carboxylic acids about it you will study in the next section.

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.*



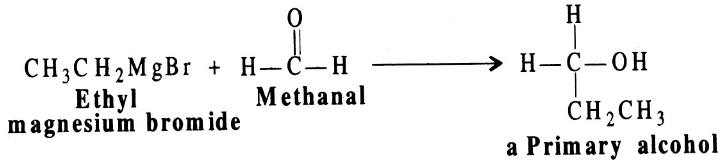


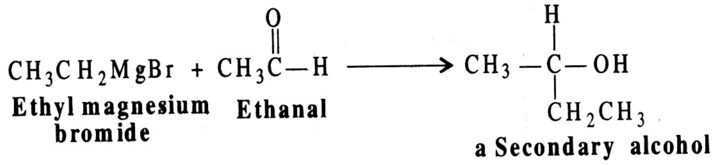
Note that an acetal has two -OR groups attached to the same carbon atom.

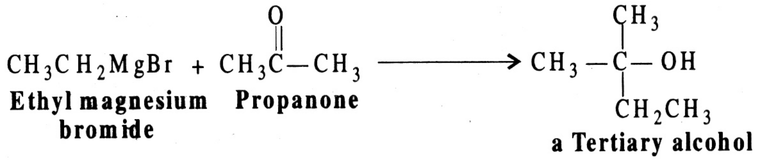
Acetals are stable in basic solutions and are 'therefore' used as protecting groups for aldehydes and ketones. Acetals can be converted back to the carbonyl compounds by treating them with dilute acids because of the reversible nature of the above reaction.

3. Formation of Alcohols

Grignard reagents (RMgX) react with aldehydes and ketones to give alcohols as shown below:





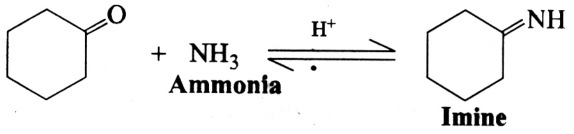


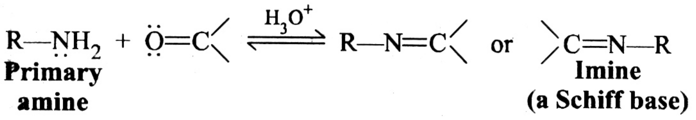
You have already studied these reactions under the preparation of alcohols in lesson 28.

B. Addition-Elimination or Condensation Reactions

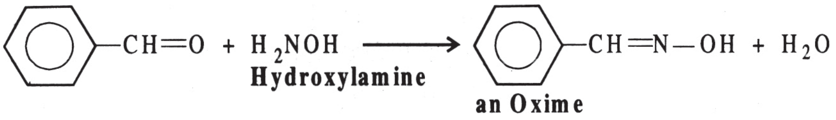
1. Reaction with Ammonia and its Derivatives

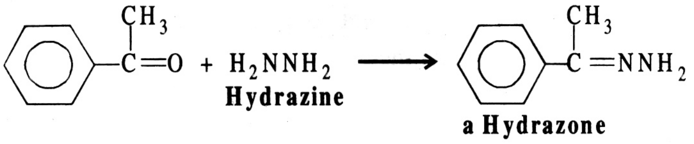
Aldehydes and ketones react with ammonia and primary amines to give imines which are compounds having carbon-nitrogen double bond.

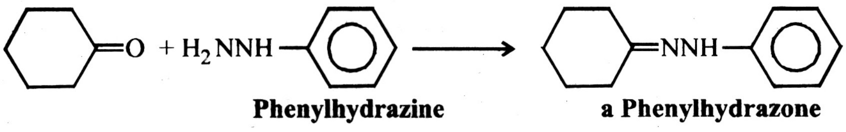


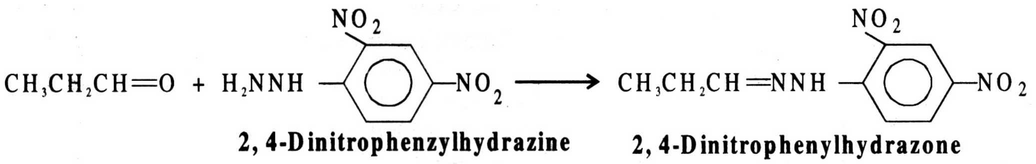


It appears that during the above reaction a molecule of water is lost from the primary amine and the carbonyl compound. The reactions with other derivatives of ammonia are given below:









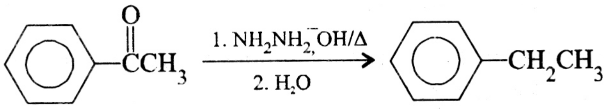
The compounds formed above are relatively insoluble solids and have characteristic melting points. These compounds can be prepared for the unknown aldehyde or ketone and their melting points can be determined. These melting points are matched with the derivatives of already known aldehydes and ketones 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

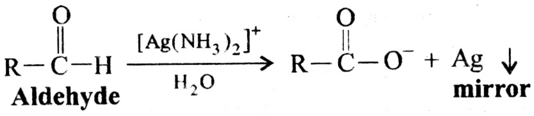
It is carried out in acidic medium using amalgamated zinc and hydrochloric acid.

$$CH_3(CH_2)_5CHO \xrightarrow[HCl,\ H_2O]{Zn(Hg)} CH_3(CH_2)_5-CH_3$$

Heptanal **Heptane**

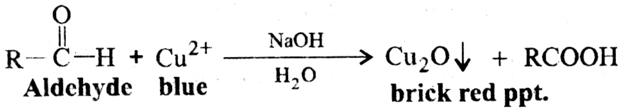
D. Oxidation of Aldehydes

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.



$$\underset{\textbf{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} \xrightarrow[H_2O]{[Ag(NH_3)_2]^+} R-\overset{\overset{O}{\|}}{C}-O^- + \underset{\textbf{mirror}}{Ag\downarrow}$$

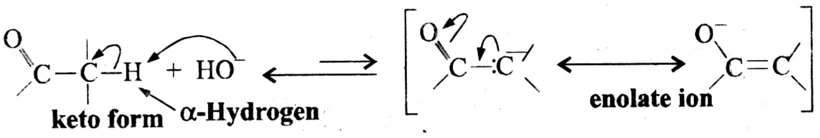
Aldehydes are also oxidised by *Fehling solution,* which contain Cu^2+ (cupric) ions complexed with tartarate ions as the oxidant. These Cu^{2+} ions are reduced by the aldehydes in alkaline medium to give a brick red precipitate of cuprous oxide.



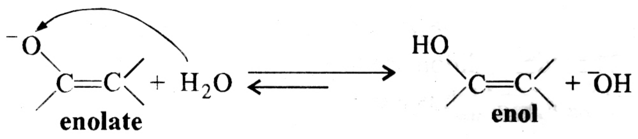
$$\underset{\textbf{Aldchydc}}{R-\overset{\overset{O}{\|}}{C}-H} + \underset{\textbf{blue}}{Cu^{2+}} \xrightarrow[H_2O]{NaOH} \underset{\textbf{brick red ppt.}}{Cu_2O\downarrow} + RCOOH$$

E. Reactions at *a* - carbon

The α - hydrogen in aldehydes and ketones is quite acidic and can be easily abstrated 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.*

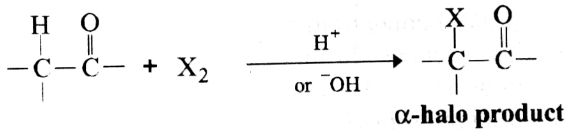


Thus, keto form and enol form are in equilibrium. This is also known as *keto-enol tautomerism.*

Other reactions feasible due to the presence of a. hydrogen are as follows:

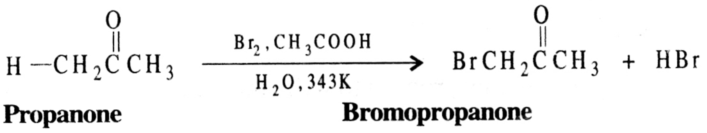
1. Halogenation

Ketones having an α . hydrogen-atom react readily with halogens and a. haloketones are obtained as the product. The reaction is promoted both by acids and bases.



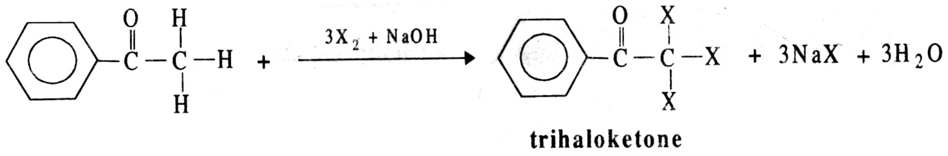
$$-\overset{\overset{H}{|}}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}- + X_2 \xrightarrow[\text{or }^{-}OH]{H^+} -\overset{\overset{X}{|}}{\underset{|}{C}}-\overset{\overset{O}{\|}}{C}-$$

$(X_2 = Cl_2, Br_2 \text{ or } I_2)$

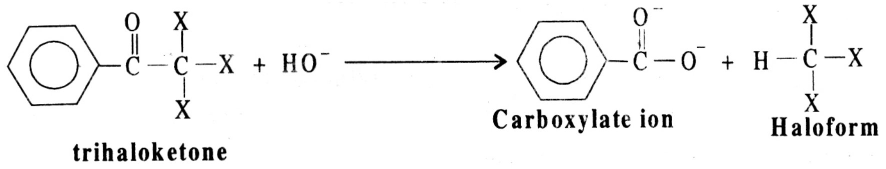


$$H-CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[H_2O,\,343K]{Br_2,\,CH_3COOH} BrCH_2\overset{\overset{O}{\|}}{C}CH_3 + HBr$$

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.

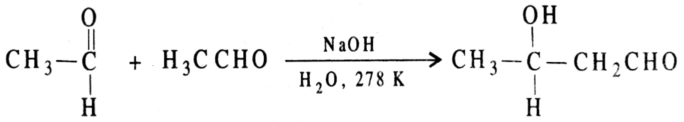


This reaction is called the *halform reaction* after the name of the product.

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

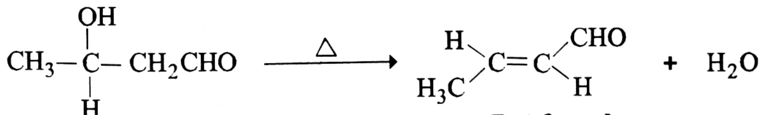
Aldehydes having α - hydrogen atom on reaction with dil. NaOH give *aldols.* The reaction is illustrated below by using ethanal as the example.



$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle O}{\overset{\|}{C}}} + H_3CCHO \xrightarrow[H_2O,\ 278\ K]{NaOH} CH_3-\underset{\displaystyle H}{\overset{\displaystyle OH}{C}}-CH_2CHO$$

Ethanal **Ethanal** **3-Hydroxybutanal (an Aldol)**

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.



Aldol ***trans*-But-2-enal**

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:

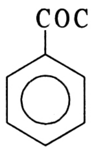
A-A, B-B, A-B and B-A.

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) a cyanohydrin (ii) an acetal (iii) a hemiacetal

....

5. How can you convert the carbonyl $\left(\gt C{=}O\right)$ group to $\left(\gt CH_2\right)$ group?

....

6. What is an aldol?

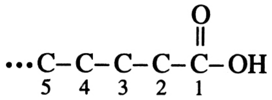
....

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

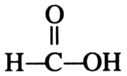
Several carboxylic acids have been known since long and their common names are based on their sources. However, in the IUPAC nomenclature, carboxylic acids are named by choosing the longest carbon chain containing the -COOH group. The final *·e* in the name of the alkane is replaced by *-oic acid.* While numbering the carbon chain, the -COOH carbon is always given number 1 as shown below:



$$\cdots \underset{5}{C}-\underset{4}{C}-\underset{3}{C}-\underset{2}{C}-\underset{1}{\overset{\overset{\displaystyle O}{\|}}{C}}-OH$$

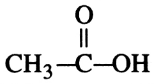
The other groups and substituents are numbered and named according to the usual rules of nomenclature which you have already studied.

Some common carboxylic acids and their names are given below:



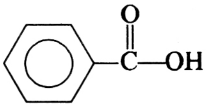
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Methanoic acid
(Formic acid)



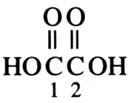
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Ethanoic acid
(Acetic acid)



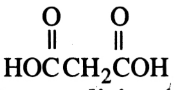
Phenylmethanoic acid
(Benzoic acid)

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.



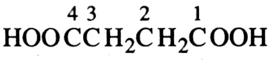
$HO\underset{1}{\overset{O}{\overset{\|}{C}}}\underset{2}{\overset{O}{\overset{\|}{C}}}OH$

Ethanedioic acid
(Oxalic acid)



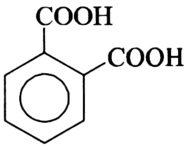
$HO\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OH$

Propanedioic acid
(Malonic acid)

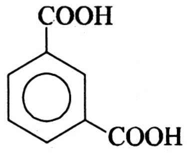


$HOO\overset{4}{C}\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$

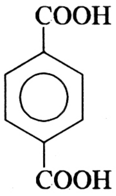
Butane-1,4-dioic acid
(Succinic acid)



***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.

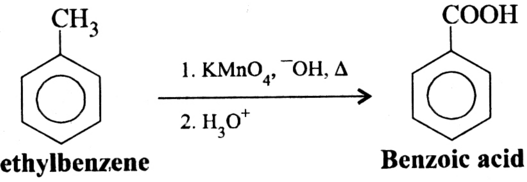
$$RCH{=}CHR' \xrightarrow[2.H_3O^+]{1.KMnO_4,\ ^-OH} RCOOH + R'COOH$$

2. Oxidation of Alcohols and Aldehydes

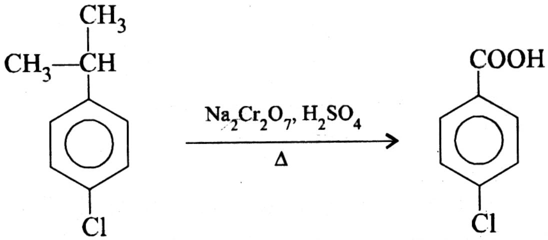
You have read in the last lesson and the previous section of this lesson that alcohols and aldehydes can be oxidized to carboxylic acids using a variety of oxidising agent. You can refer back to the details of these reactions.

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.



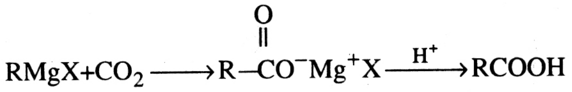
Acidified sodium dichromate can also be used for this oxidation.



***p*-Chlorobenzoic acid**

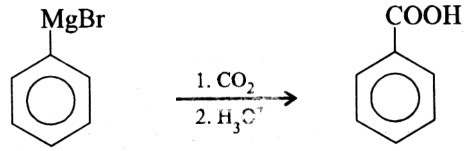
4. Carbonation of Grignard Reagents

Grignard reagents (RMgX) react with carbon dioxide to give magnesium carboxylates which on acidification yield carboxylic acids.



$$RMgX + CO_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}O^-Mg^+X \xrightarrow{H^+} RCOOH$$

$$\underset{\substack{\textbf{Chloroethane}\\\textbf{(an alkyl halide)}}}{CH_3CH_2Cl} \xrightarrow[Et_2O]{Mg} \underset{\textbf{Grignard reagent}}{CH_3CH_2MgCl} \xrightarrow[2 \cdot H_3O^+]{1 \cdot CO_2} \underset{\textbf{Propanoic acid}}{CH_3CH_2COOH}$$

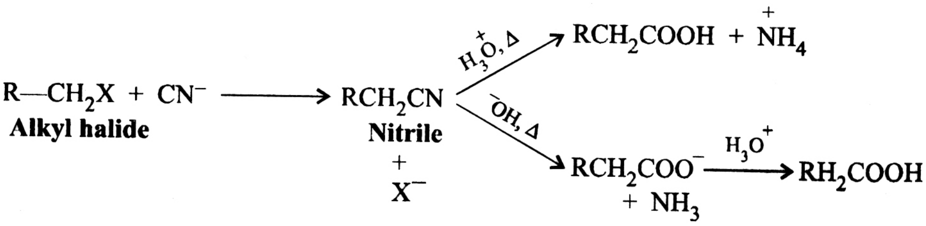


Phenyl magnesium bromide **Benzoic acid**

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

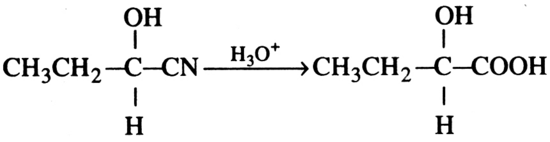
Alkyl halides can be converted to *nitriles* which on hydrolysis yield carboxylic acids having *one more carbon atom than the starting alkyl halide.*



$$Br\text{-}CH_2CH_2-Br \xrightarrow{NaCN} NC-CH_2CH_2-CN \xrightarrow{H_3O^+} HOOCCH_2CH_2COOH$$

1,2-Dibromoethane Butanedinitrile Butanedioicacld

Cyanohydrins obtained from aldehydes also yield 2-hydroxycarboxy1ic acids on hydrolysis.



$$CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CN \xrightarrow{H_3O^+} CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-COOH$$

2 - Hydroxybutanenitrile **2 - Hydroxybutanoic acid**

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 120^0 between them, see Fig. 29.3.

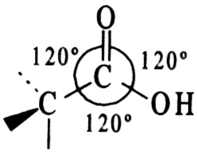
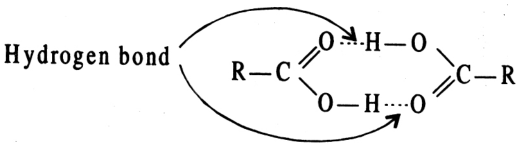


Fig. 29.3 : *Structure of the carboxyl group*

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 :



Dimer of a carboxylic acid

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 ds in water. This is ,also due to the presence of hydrogen bonding between the carboxylic acid molecule and solvent water molecules.

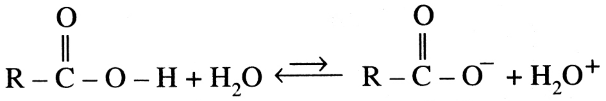
Table 29.2 : Some Physical Properties of Carboxylic Acids

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_sCOOH	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

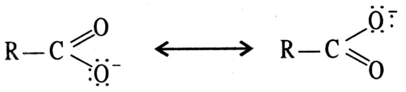
Carboxylic acids are acidic in nature. They dissociate in water according to following equilibrium to give a proton and the carboxylate ion.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + H_2O \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

Carboxylic acid **Carboxylate ion**

The pK_a values of some carboxylic acids are given in the last column of Table 29.2. Remember that the *lower pK_a indicates greater acidity.* If you compare these pK_a 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.

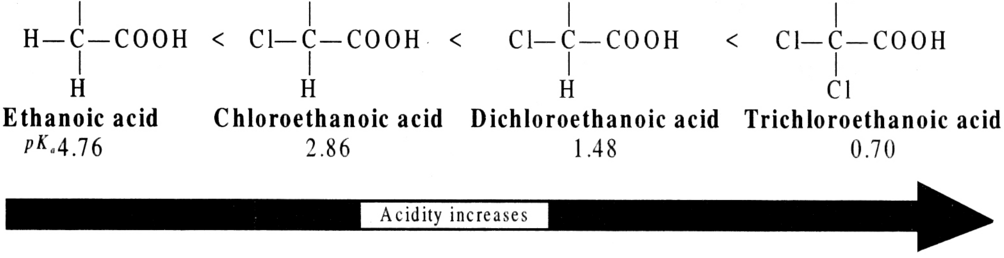
If you compare this situation with the alkoxide ion (RO-) obtained by the dissociation of an alcohol molecule, you will see that no such resonance stabilisation is possible in the alkoxide Ion.

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 pK_a 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**.

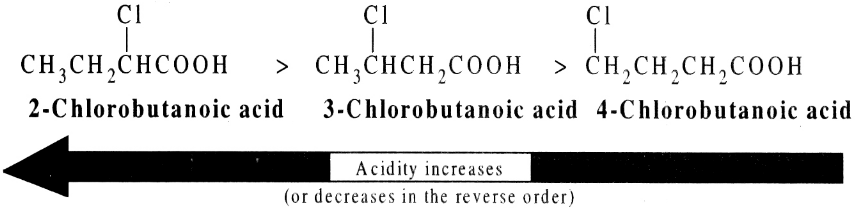
Let us next see what will be the effect of electron withdrawing substituents such as halogens and nitro-group on the acidity. The comparison of pK_a values of ethanoic acid (4.76) and chloroethanoic acid (2·86) suggests that chloroethanoic acid is a stronger acid than ethanoic acid. The chloro substituent 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.



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-COOH < Cl-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-COOH < Cl-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-COOH < Cl-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-COOH$$

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).*



$$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCOOH \; > \; CH_3\overset{\overset{Cl}{|}}{C}HCH_2COOH \; > \; \overset{\overset{Cl}{|}}{C}H_2CH_2CH_2COOH$$

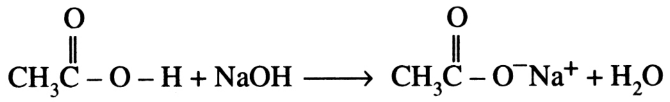
2-Chlorobutanoic acid **3-Chlorobutanoic acid** **4-Chlorobutanoic acid**

29.2.5 Reactions of Carboxylic Acids

Let us now study the reactions given by carboxylic acids.

1. Formation of Salts

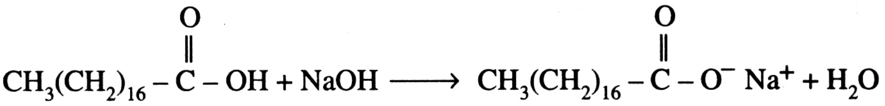
Carboxylic acids are completely deprotonated by strong bases such as metal hydroxides to give salts.



$$CH_3\overset{\overset{O}{\|}}{C}-O-H + NaOH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-O^-Na^+ + H_2O$$

Ethanoic acid **Sodium ethanoate**

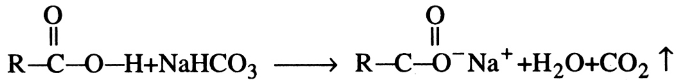
It will be interesting to know that *soaps* are sodium salts of long chain carboxylic acids which are called fatty acids.



$$CH_3(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow CH_3(CH_2)_{16}-\overset{\overset{O}{\|}}{C}-O^- Na^+ + H_2O$$

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.



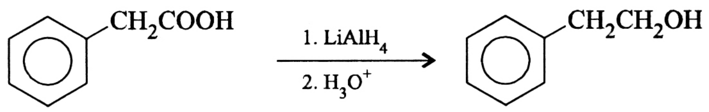
$$R-\overset{\overset{O}{\|}}{C}-O-H+NaHCO_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + H_2O + CO_2\uparrow$$

This reaction is also used as a test for carboxylic acids in the laboratory. The liberation of CO_2 in the form of bubbles on treatment with $NaHCO_J$ 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

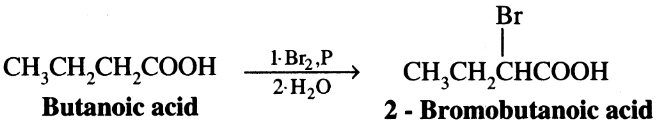
Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride ($LiAlH_4$).



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 $C1_2$) in the presence of phosphorus or phosphorus trihalide.



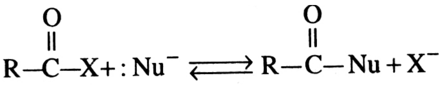
$$\underset{\textbf{Butanoic acid}}{CH_3CH_2CH_2COOH} \xrightarrow[2\cdot H_2O]{1\cdot Br_2,P} \underset{\textbf{2 - Bromobutanoic acid}}{CH_3CH_2\overset{\overset{Br}{|}}{C}HCOOH}$$

a -Haloacids so obtained are useful intermediates in the synthesis of other organic compounds.

4. Synthesis of Acid Derivatives

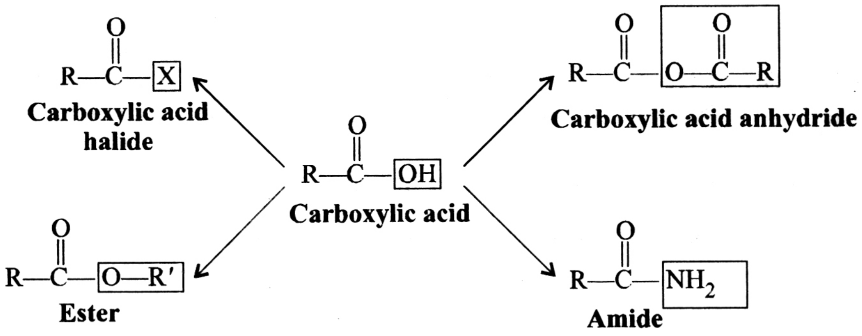
This is one of the very important reactions of carboxylic acids. The nucleophilic addition to the carboxyl carbon of the carboxylic acids is followed by elimination of the leaving group leading to a substitution product. If you remember the reactions of aldehydes and ketones, the addition of nucleophile 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**.



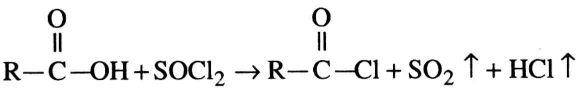
$$R-\overset{\overset{O}{\|}}{C}-X+:Nu^- \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-Nu+X^-$$

Here, X = OH in case of the carboxylic acids and Nu- can be a halide ion, $^-O-\overset{\overset{O}{\|}}{C}-R$, $^-O-R'$ 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.



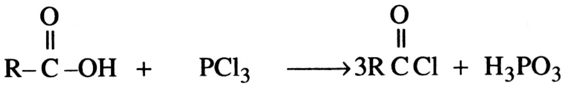
(i) Formation of Acid Chlorides

Carboxylic acids react with $SOCI_2$, PCl_3 or PCl_5 to give carboxylic acid chlorides also known as acyl chlorides, as shown below :



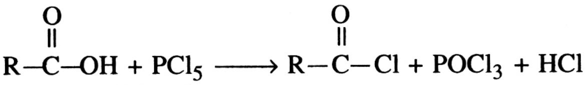
$$R-\overset{\overset{O}{\|}}{C}-OH+SOCl_2 \rightarrow R-\overset{\overset{O}{\|}}{C}-Cl+SO_2\uparrow+HCl\uparrow$$

Carboxylic acid	Thionyl chloride	an acid chloride



$$R-\overset{\overset{\large O}{\|}}{C}-OH + PCl_3 \longrightarrow 3R\overset{\overset{\large O}{\|}}{C}Cl + H_3PO_3$$

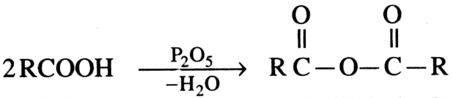
Phosphorus trichloride



$$R-\overset{\overset{\large O}{\|}}{C}-OH + PCl_5 \longrightarrow R-\overset{\overset{\large O}{\|}}{C}-Cl + POCl_3 + HCl$$

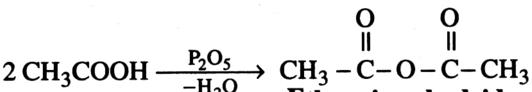
Phosphorus pentachloride

(ii) Formation of Acid Anhydrides



$$2RCOOH \xrightarrow[-H_2O]{P_2O_5} R\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-R$$

a Carboxylic acid **an Acid Anhydride**



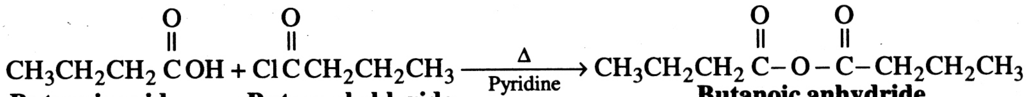
$$2\,CH_3COOH \xrightarrow[-H_2O]{P_2O_5} CH_3-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_3$$

Ethanoic anhydride

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.

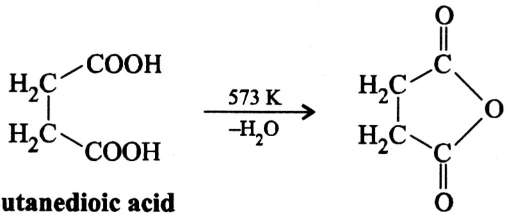


$$CH_3CH_2CH_2\overset{\overset{\large O}{\|}}{C}OH + Cl\overset{\overset{\large O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow[\text{Pyridine}]{\Delta} CH_3CH_2CH_2\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_2CH_2CH_3$$

Butanoic acid **Butanoyl chloride** **Butanoic anhydride**

We can prepare unsymmetrical anhydrides by this method.

Cylic anhydrides are obtained by the dehydration of dicarboxylic acids at higher temperature.

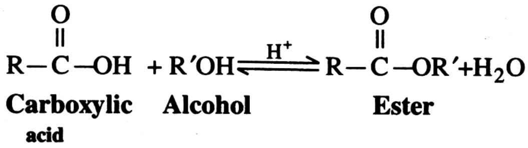


Butanedioic acid
(Succinic acid)

Butanedioic anhydride
(Succinic anhydride)

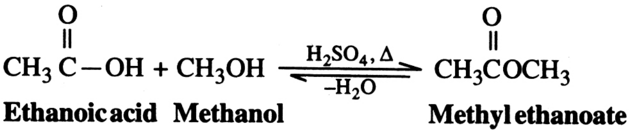
(iii) Formation of Esters

Carboxylic acids react with alcohols to form esters.



$$R-\overset{\overset{O}{\|}}{C}-OH + R'OH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{O}{\|}}{C}-OR' + H_2O$$

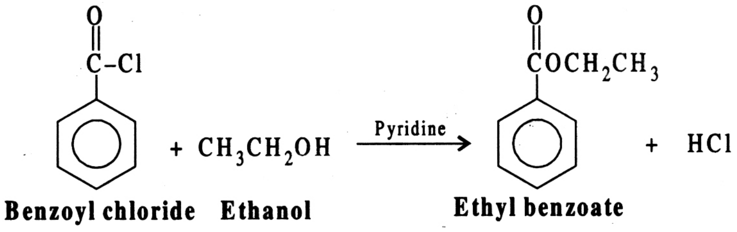
Note that the acid catalysed esterification is an equilibrium reaction. The equilibrium can be shifted to the right side towards products if we are able to remove water or the ester from the reaction mixture. Also if we use excess of one reagent, then the equilibrium shifts towards the right side to give the ester. Normally, we take excess of alcohol and use it as a solvent to carry out esterification.

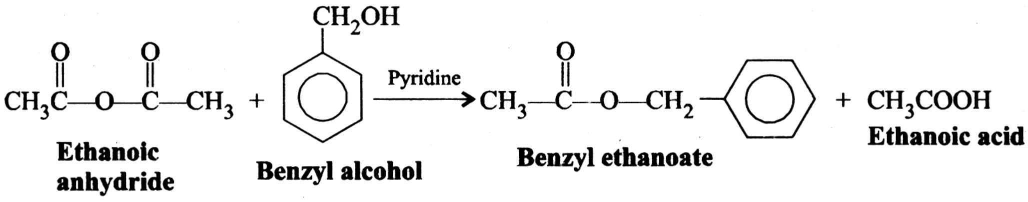


$$CH_3\overset{\overset{O}{\|}}{C}-OH + CH_3OH \underset{-H_2O}{\overset{H_2SO_4,\Delta}{\rightleftharpoons}} CH_3\overset{\overset{O}{\|}}{C}OCH_3$$

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**.

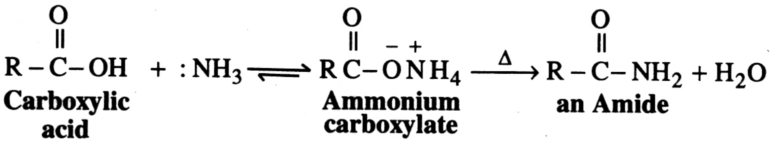
Esters can also be prepared by the reaction of acid chlorides or acids anhydrides with alcohols. Thus we can see that these acid derivatives can be converted to one-another.



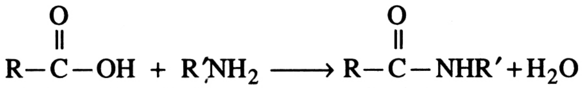


(iv) Formation of Amides

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.



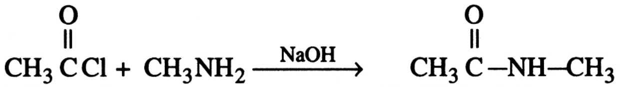
$$R-\overset{\overset{O}{\|}}{C}-OH + :NH_3 \rightleftharpoons R\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{\Delta} R-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$



$$R-\overset{\overset{O}{\|}}{C}-OH + R'NH_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-NHR'+H_2O$$

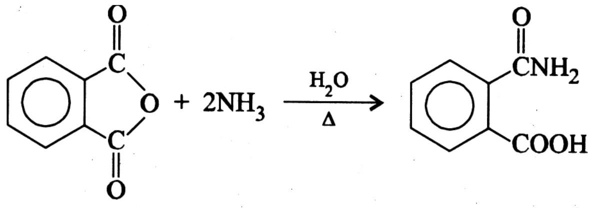
Carboxylic acid **Primary amine** **Amide (Substituted)**

Amides can also be obtained by the reaction of ammonia or amines with carboxylic acid halides, anhydrides and esters.

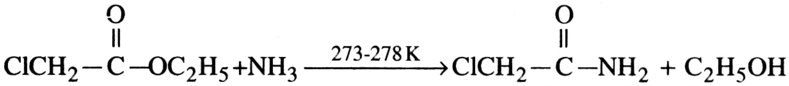


$$CH_3\overset{\overset{O}{\|}}{C}Cl + CH_3NH_2 \xrightarrow{NaOH} CH_3\overset{\overset{O}{\|}}{C}-NH-CH_3$$

Ethanoyl chloride ***N*** **- Methylethanamide**



Phthalic anhydride **Pnhthalamic acid**



$$ClCH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5+NH_3 \xrightarrow{273\text{-}278\,K} ClCH_2-\overset{\overset{O}{\|}}{C}-NH_2 + C_2H_5OH$$

Ethyl chloroethanoate **Chloroethanamide** **Ethanol**

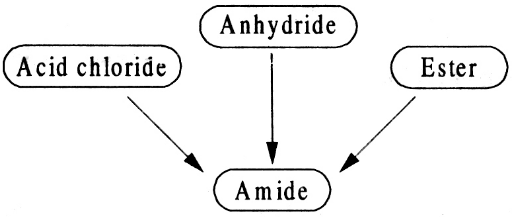
Thus, we can make one carboxylic acid derivative from another. Generally, the less reactive acid (acyl) derivatives can be prepared from the more reactive ones.

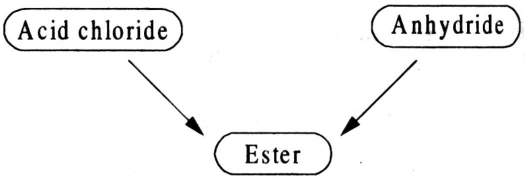
The order of reactivity of various carboxylic acid derivatives is as follows:

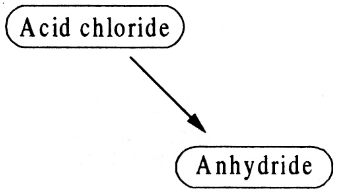
Acid chloride > Acid anhydride > Ester > Amide

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_3COCI	(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

....

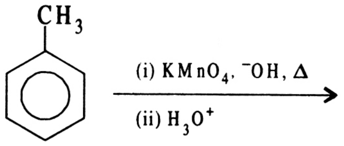
3. Which one of the following will be most acidic and why?

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) 

(iii) $CH_3COOH + PCl_3 \longrightarrow$

....

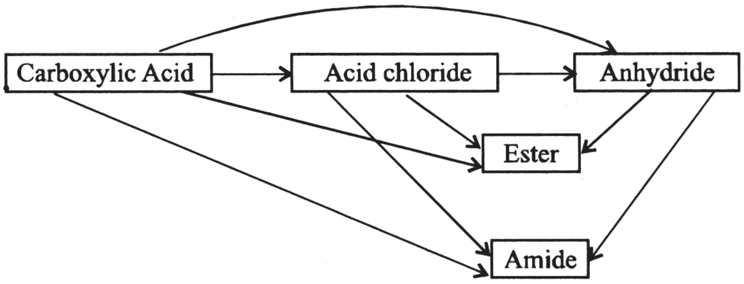
5. Why are carboxylic acids more acidic than alcohols?

....

What You Have Learnt

In this lesson, you have learnt that

- Aldehydes and ketones constitute the carbonyl compounds. Aldehydes are known as **a1kanals** 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 $LiAIH_4$.
- 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

Answersto Intext Questions

29.1

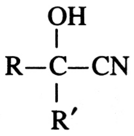
1. (i) aldehyde, Ethanal

   (ii) ketone, Butane-2-one

   (iii) ketone, I-Phenylethanone

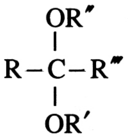
   (iv) aldehyde, Propanal
2. Using hydration with Hg^{2+}, H^+.
3. Because they have one alkyl group whereas a ketone has two alkyl groups. Hence, the carbonyl carbon in aldehydes is more positive.

   Also, the two alkyl groups lead to more crowding in ketones.
4. (i)



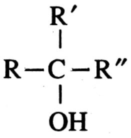
$R-\underset{R'}{\overset{OH}{C}}-CN$

(ii)



$R-\underset{OR'}{\overset{OR''}{C}}-R'''$

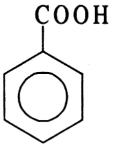
(iii)



$R-\underset{OH}{\overset{R'}{C}}-R''$

5. By Wolff- Kishner reduction or Clemmensen reduction.
6. 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.

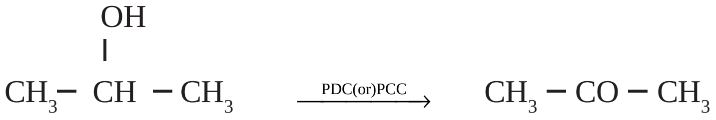
29.1.2.a Methods of preparation of Carbonyl compounds: Acetaldehyde and acetone preparations:

1) From alcohols:

Ethyl alcohol (I 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.

$$CH_3CH_2OH \xrightarrow[CH_2Cl_2]{PDC(or)PCC} CH_3CHO$$

Ethyl alcohol acetal dehyde



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{PDC(or)PCC} CH_3-CO-CH_3$$

Iso propyl alcohol acetone

2) From alkenes (wacker process):

When ethylene is passed through an acidified aqueous solution of $PdCl_2$ and $CuCl_2$ acetal dehyde is formed. Acetone is formed propane by the same method.

$$CH_2 = CH_2 + PdCl_2 + H_2O \xrightarrow[H^+]{CuCl_2} CH_3\text{–}CO\text{–}CH_3 + Pd + 2\ HCl$$

Ethylene acetal dehyde

$$CH_3-CH = CH_2 + PdCl_2 + H_2O \xrightarrow[H^+]{CuCl_2} CH_3\text{–}CO\text{–}CH_3 + Pd + 2\ HCl$$

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.

$$Ca(HCOO)_2 + Ca\ (CH_3COO)_2 \xrightarrow{\Delta} 2\ CH_3CHO + 2\ CaCO_3$$

$$Ca\ (CH_3COO)_2 \xrightarrow{\Delta} 2\ CH_3COCH_3 + CaCO_3$$

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.

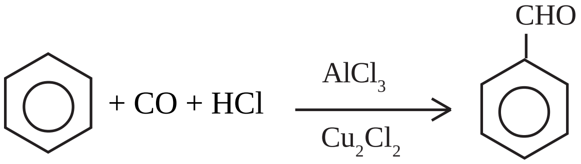
$$CH_3COCl + H_2 \xrightarrow{Pd-BaSO_4} CH_3CHO + HCl$$

Acetyl chloride acetal dehyde

Aromatic aldehyde (Benzaldehyde) preparation:

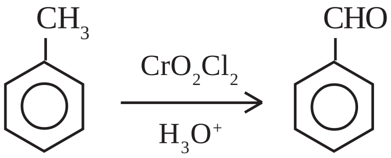
1. **Gatterman – kock reaction:**

   When benzene is treated with Co and HCl in the presence of anhydrous $AlCl_3$ and Cu_2Cl_2 benzal dehyde is formed.



2. **Etard reaction:**

   When toluene is treated with chromyl chloride followed by hydrolysis benzal dehyde 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.

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

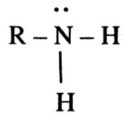
After reading this lesson, you will be able to:

- 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.

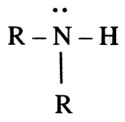
30.1 Amines

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.

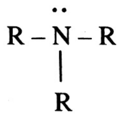
This is illustrated below.



A primary amine

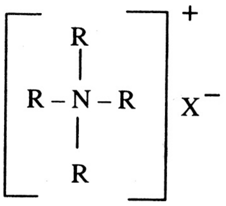


A secondary amine



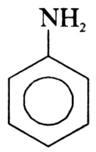
A tertiary amine

If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.



A quaternary ammonium salt

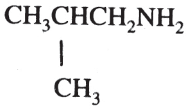
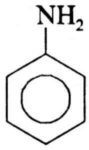
The amino group in aromatic amines is directly bonded to the benzene ring. Aromatic amines are aryl derivatives of ammonia. The parent aromatic amine is known as aniline.



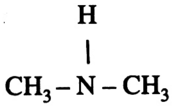
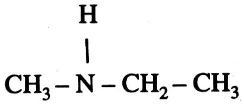
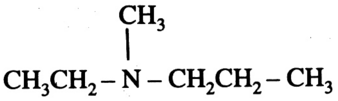
Aniline

30.1.1 IUPAC Nomenclature of Amines

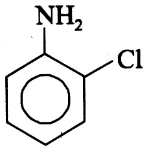
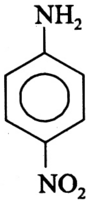
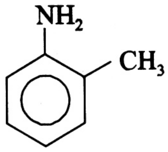
Similar to other classes of compounds which you have studied, amines can also be named according to the IUPAC system. In case of primary aliphatic amines, the longest continuous chain of carbon atoms determines the root name of the compound. The ending *-e* in the name of the corresponding alkane is 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
 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2NH_2$	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.

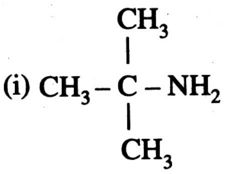
Compound	IUPAC name	Common name
 $CH_3-\overset{\overset{H}{\vert}}{N}-CH_3$	N-Methylmethanamine	Dimethylamine
 $CH_3-\overset{\overset{H}{\vert}}{N}-CH_2-CH_3$	N-Methylethanamine	Ethylmethylamine
 $CH_3CH_2-\overset{\overset{CH_3}{\vert}}{N}-CH_2CH_2-CH_3$	N-Ethyl-N-methylpropan-I-amine	-

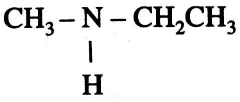
The IUPAC names of other aromatic amines are given as derivatives of aniline shown below:

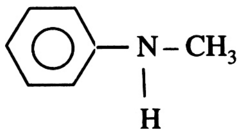
Compound	IUPAC name	Common name
	2-Chloroaniline	o-Chloroaniline
	4- Nitroaniline	*p*- Nitroaniline
	Methylaniline	*o*- Toluidine

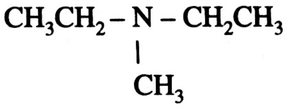
Intext Questions 30.1

1. Classify the following as primary, secondary, tertiary amines and quaternary ammonium salts :

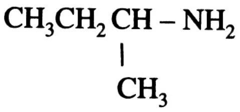
(i)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NH_2$

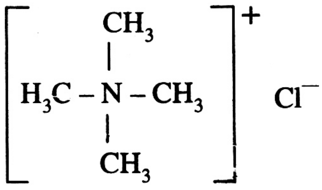
(ii)

$CH_3-\underset{H}{N}-CH_2CH_3$

(iii)


(iv)

$CH_3CH_2-\underset{CH_3}{N}-CH_2CH_3$

....

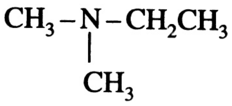
(v)

$CH_3CH_2\underset{CH_3}{CH}-NH_2$

(vi)

$\left[H_3C-\overset{CH_3}{\underset{CH_3}{N}}-CH_3\right]^+ Cl^-$

....

2. Write IUPAC names for the following amines :

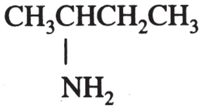
(i) CH_3 - $CH_2CH_2CH_2CH_3$

(ii)

$CH_3-\underset{CH_3}{N}-CH_2CH_3$

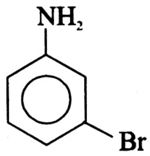
....

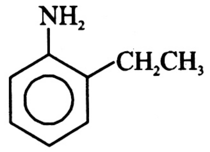
(iii)

$CH_3-\underset{H}{N}-CH_2CH_2CH_2CH_3$

(iv)

$CH_3\underset{NH_2}{CH}CH_2CH_3$

....

(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.

$$\underset{\text{Bromoethane}}{C_2H_5Br} + 2\,NH_3 \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

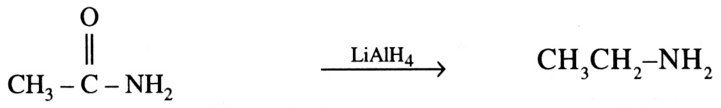
(ii) By reduction of nitriles (cyanides), amides and nitro compounds

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.

$$\underset{\text{Propanenitrile}}{CH_3CH_2C \equiv N} \xrightarrow[\text{or } Na/C_2H_5OH]{H_2/Pt} \underset{\text{Propan-1-amine}}{CH_3\,CH_2CH_2-NH_2}$$

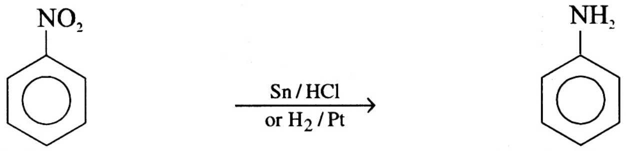
Similarly, amides are reduced by $LiAlH_4$ to primary amines having same number of carbon atoms as in the starting amide. For example, ethanamide gives ethanamine on reduction.



$$CH_3-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2-NH_2$$

Ethanamide **Ethanamine**

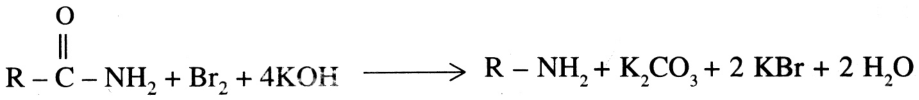
Reduction of nitro compounds can be carried out by using hydrochloric acid and a metal , such as Sn or Fe. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. Such a reduction of nitrobenzene by any of these methods provides aniline.



Nitrobenzene **Aniline**

(iii) By Hofmann bromamide reaction

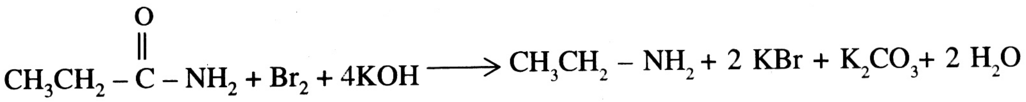
Aliphatic amides on treatment with bromine and a strong base like potassium hydroxide are converted into primary amines having one carbon less than those present in the starting amide.



$$R-\overset{\overset{\large O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow R-NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$$

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

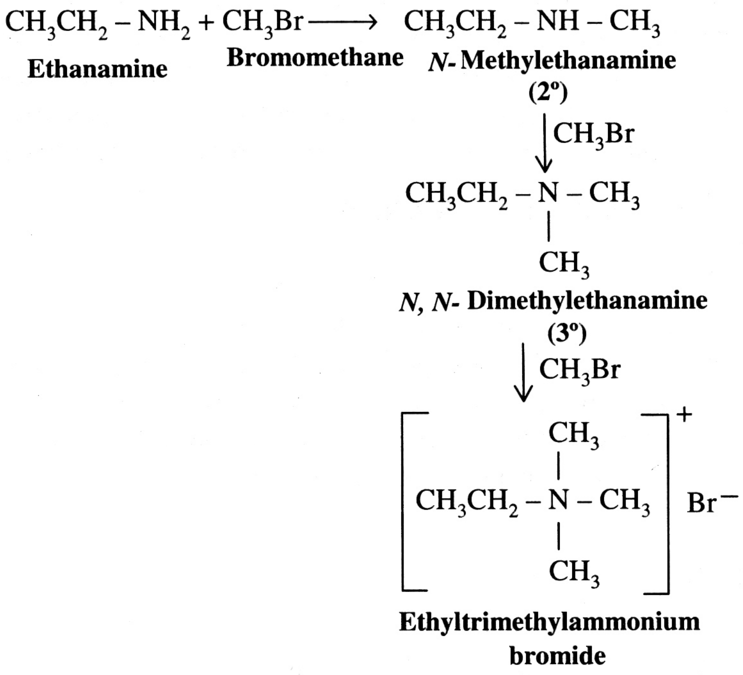
$$\underset{\text{Primary }(1^0)}{R-NH_2} \quad < \quad \underset{\text{Secondary }(2^0)}{R_2NH} \quad > \quad \underset{\text{Tertiary }(3^0)}{R_3N}$$

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.



$$CH_3CH_2-NH_2 + CH_3Br \longrightarrow CH_3CH_2-NH-CH_3$$

Ethanamine **Bromomethane** ***N*****- Methylethanamine (2°)**

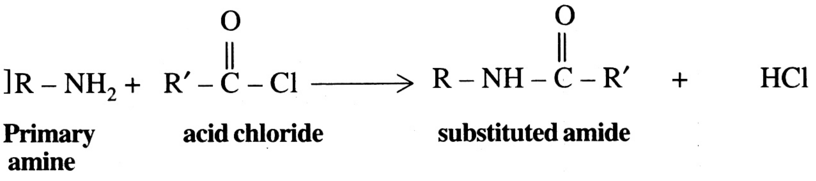
$$\xrightarrow{CH_3Br} CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$$

N, N**- Dimethylethanamine (3°)**

$$\xrightarrow{CH_3Br} \left[CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N}}}}-CH_3 \right]^+ Br^-$$

Ethyltrimethylammonium bromide

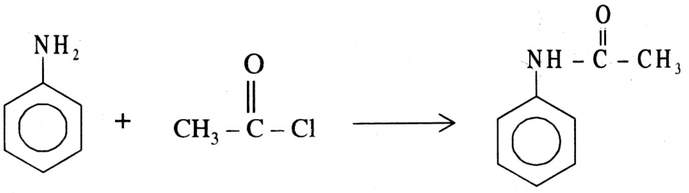
(iii) Acylation : Primary amines on reaction with acid chlorides or acid anhydrides give N-substituted amides.



$$]R-NH_2 + R'-\overset{\displaystyle O}{\overset{\|}{C}}-Cl \longrightarrow R-NH-\overset{\displaystyle O}{\overset{\|}{C}}-R' + HCl$$

Primary amine **acid chloride** **substituted amide**

For example, aniline on reaction with ethanoyl chloride (acetyl chloride) gives acetanilide.



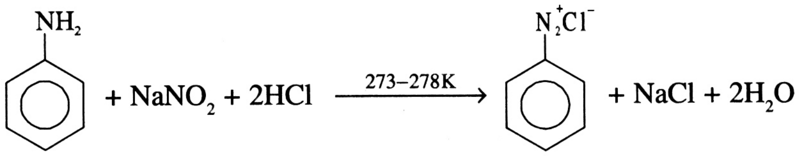
Aniline **Ethanoyl chloride** **Acetanilide**

(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.

$$\underset{\text{Ethylamine}}{CH_3CH_2-NH_2} + CHC1_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Ethyl carbylamine}}{CH_3CH_2\,N\equiv C} + 3KCl + 3H_2O$$

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 can not 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.

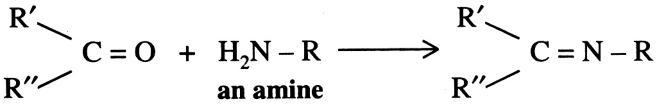


Aniline **Benzene diazonium chloride (a diazonium salt)**

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.

$$\underset{\text{Ethanamine}}{CH_3CH_2-NH_2} \xrightarrow{NaNO_2/HCl} \underset{\substack{\text{Ethyldiazonium chloride}\\ \text{Unstable diazonium salt}}}{[CH_3CH_2\overset{+}{N_2}\,Cl^-]} \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2-OH} + N_2 + HCl$$

(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:

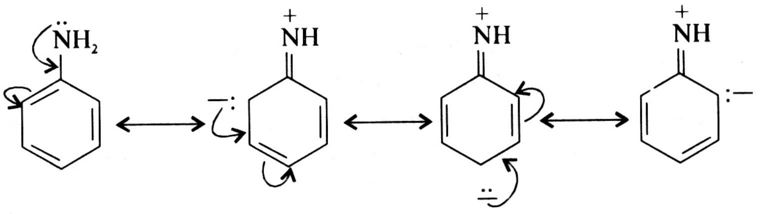


$$\begin{matrix}R'\\ \quad\end{matrix}\!\!>C=O + \underset{\text{an amine}}{H_2N-R} \longrightarrow \begin{matrix}R'\\ \quad\end{matrix}\!\!>C=N-R$$

$$R'' \qquad\qquad\qquad\qquad R''$$

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.

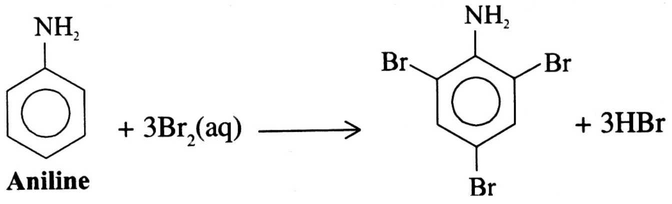


Resonance structures of aniline

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

2,4,6-Tribromoaniline

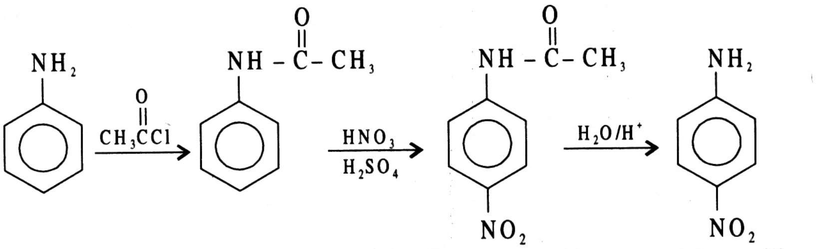
Aniline is very reactive and all the three hydrogen atoms at *ortho*- and *para*- positions are substituted with bromine atoms.

(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.

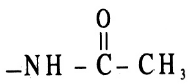
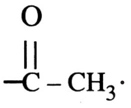
(i) The free amine is very susceptible to oxidation and thus much of it is lost in the form of a black-sticky material which is formed as result of its oxidation.

(ii) The free amine is very reactive but acetyl the group protects it and reduces its reactivity.

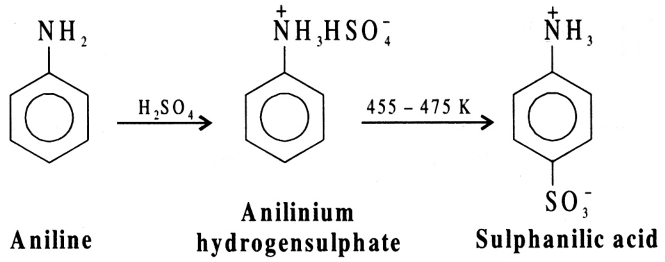
The nitration of aniline with the protection of the amino group is shown below:



Aniline **Acetanilide** ***p*-Nitroacetanilide** ***p*-Nitroaniline**

The first step consists of acetylation of the amino group in aniline. The conversion of $-NH_2$ to  $-NH-\overset{O}{\overset{\|}{C}}-CH_3$, lowers the activity of -NH_2 group because of electron withdrawal by  $-\overset{O}{\overset{\|}{C}}-CH_3$. 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) ***Sul phonation*** **:** 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.



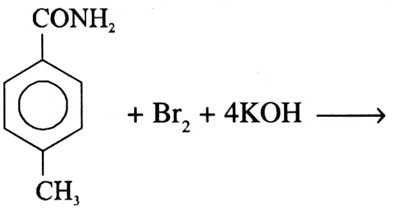
30.1.5 Uses of Amines

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

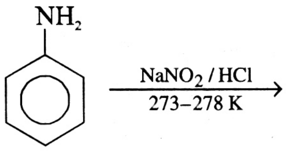
1. Predict the major product of the following reactions:

(a)

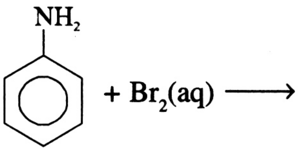


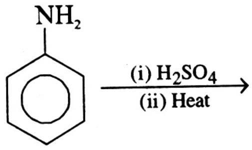
(b) $CH_3CH_2NH_2 \xrightarrow{NaNO_2/HCl}$

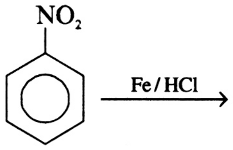
(c)



(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?

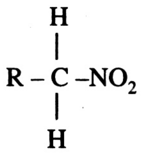
....

5. How will you obtain sulphanilic acid from benzene?

....

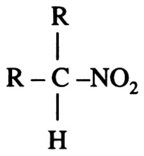
30.2 Nitro Compounds

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom is replaced by a nitro ($-NO_2$) 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.



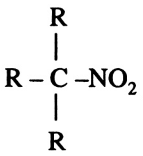
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-NO_2$$

***p*-nitroalkane**



$$R-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-NO_2$$

sec-nitroalkane

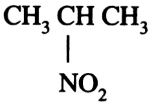
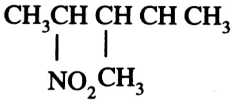
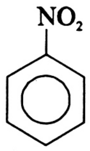
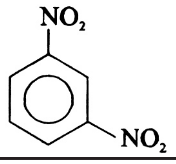


$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-NO_2$$

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
 $\underset{\substack{\vert\\NO_2}}{CH_3\,CH\,CH_3}$	2-Nitropropane
 $CH_3\underset{\substack{\vert\\NO_2}}{CH}\,\underset{\substack{\vert\\CH_3}}{CH}\,CH\,CH_3$	2-Nitro - 3- methylbutane
	Nitrobenzene
	1,3 - Dinitrobenzene (m - Dinitrobenzene)

30.2.2 Preparation of Nitro Compounds

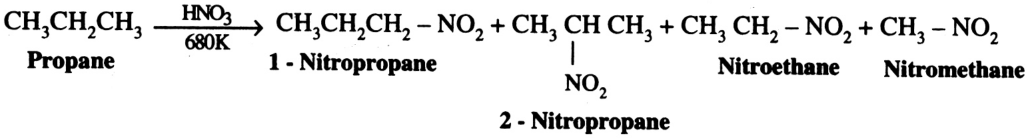
(i) ***From alkylhalides:*** Nitroalkanes are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite. In this reaction, a small amount of isomeric alkyl nitrites (R-O-N = 0) is also obtained.

$$R-X+AgNO_2 \longrightarrow R-NO_2+AgX$$

For example. bromoethane on reaction with silver nitrite gives nitroethane.

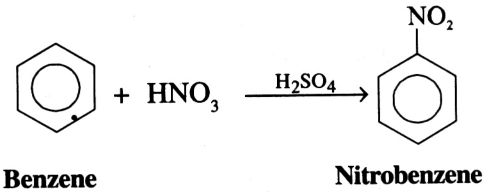
$$\underset{\text{Bromoethane}}{CH_3CH_2Br}+AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{CH_3CH_2NO_2}+AgBr$$

(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 680 K. 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.



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[680K]{HNO_3} \underset{\text{1 - Nitropropane}}{CH_3CH_2CH_2-NO_2} + \underset{\text{2 - Nitropropane}}{\underset{\substack{|\\NO_2}}{CH_3\,CH\,CH_3}} + \underset{\text{Nitroethane}}{CH_3\,CH_2-NO_2} + \underset{\text{Nitromethane}}{CH_3-NO_2}$$

(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.



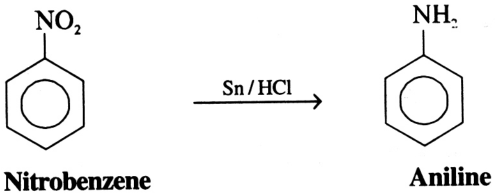
30.2.3 Physical Properties of Nitro Compounds

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.

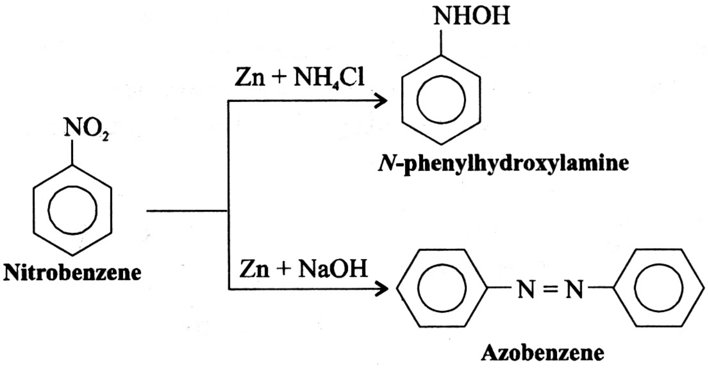
30.2.4 Chemical Properties of Nitro Compounds

(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.

$$\underset{\text{Nitroethane}}{CH_3CH_2 - NO_2} + 3H_2 \xrightarrow{Ni} \underset{\text{Ethanamine}}{CH_3CH_2 - NH_2} + 2H_2O$$



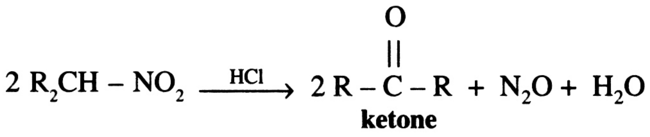
Nitrobenzene on reduction in neutral medium, using zinc dust and ammonium chloride yields N-phenylhydroxylarnine whereas its reduction in alkaline medium using zinc and sodium hydroxide yields azobenzene.



(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.



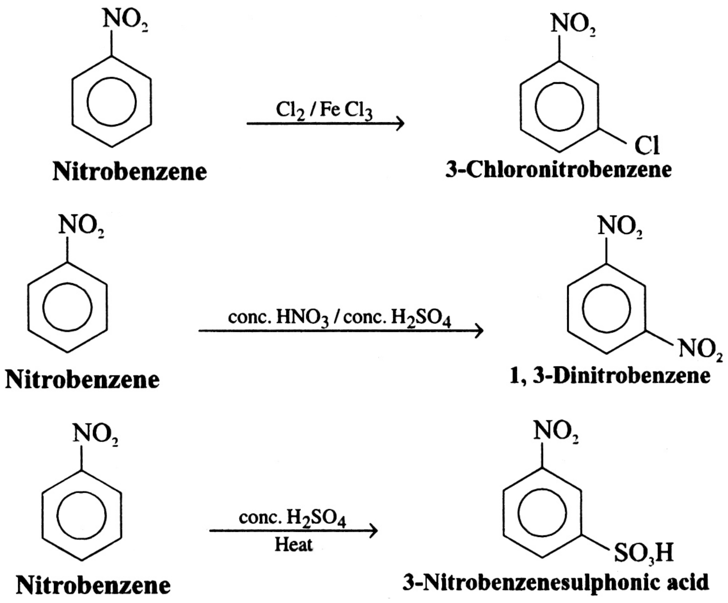
$$2\,R_2CH - NO_2 \xrightarrow{HCl} \underset{\textbf{ketone}}{2\,R - \overset{\overset{\displaystyle O}{||}}{C} - R} + N_2O + H_2O$$

(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.

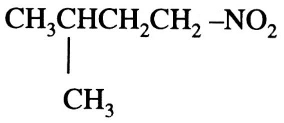


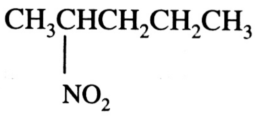
30.2.5 Uses of Nitro Compounds

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.

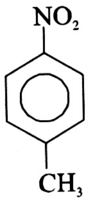
Intext Questions 30.3

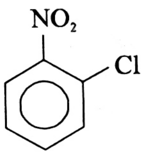
1. Write IUPAC names of the following:

(a) 
$CH_3\underset{\begin{array}{c}|\\ CH_3\end{array}}{CH}CH_2CH_2-NO_2$

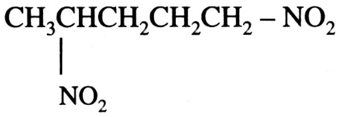
(b) 
$CH_3\underset{\begin{array}{c}|\\ NO_2\end{array}}{CH}CH_2CH_2CH_3$

....

(c) 

(d) 

....

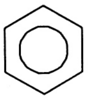
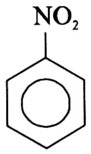
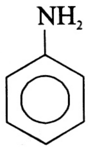
(e) 
$CH_3\underset{\begin{array}{c}|\\ NO_2\end{array}}{CH}CH_2CH_2CH_2-NO_2$

....

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.

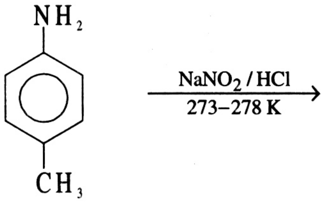
- Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines along with quaternary ammonium salts.
- Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms.
- In Hofmann bromamide reaction, the amine formed has one 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.

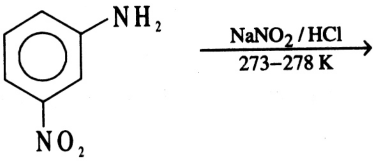
Terminal Exercise

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.

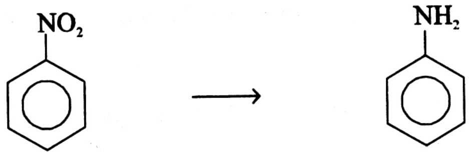
(i) 

(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.

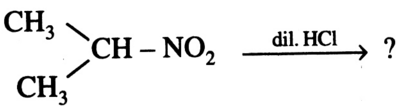
6. How will you prepare sulphanilic acid from nitrobenzene?

7. What happens when ethanamine is treated with excess of chloroethane?

8. Write the reaction sequence to convert nitromethane into ethanamine.

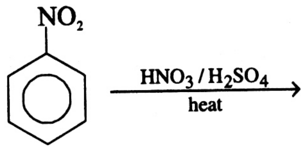
9. How will you prepare *para-bromoaniline* from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.

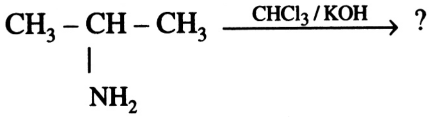
10. Complete the following reactions:

(i) 

$(CH_3)_2CH-NO_2 \xrightarrow{dil.\ HCl} ?$

(ii) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2/KOH} ? \xrightarrow[273-278K]{NaNO_2/HCl}$

(iii) 

(iv) 

$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3 \xrightarrow{CHCl_3/KOH} ?$

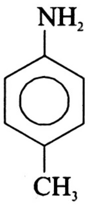
(v) $CH_3\,CH_2CH_2-Br + AgNO_2 \xrightarrow{\text{alcohol}} ?$

Answers to Intext Questions

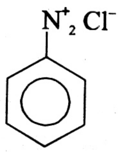
30.1

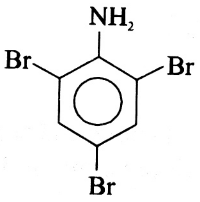
1. (i) Primary amine (ii) Secondary amine (iii) Secondary amine
   (iv) Tertiary amine (v) Primary amine (vi) Quaternary ammonium salt
2. (i) Butan-l-amine
   (ii) N, N-Dimethylethanamine
   (iii) N-Methylbutan-l- amine
   (iv) Butan-2-amine
   (v) 3-Bromoaniline
   (vi) 2-Ethylaniline

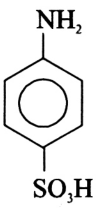
30.2

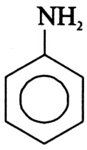
I. (i) 

(ii) CH_3CH_2OH

(iii) 

(iv) 

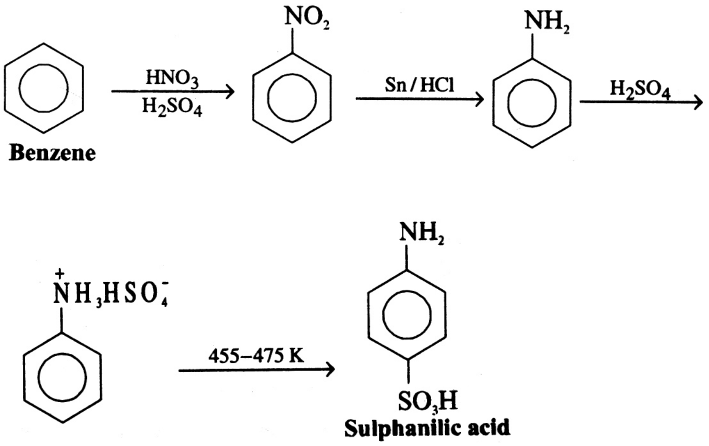
(v) 

(vi) 

2. Aniline is very reactive towards bromination because the -NH_2 group is a highly activating group.

3. Carbylamine test.

4. No

5. 

30.3

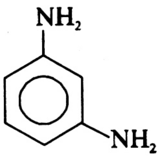
1. (i) 3-Methyl-l-nitrobutane

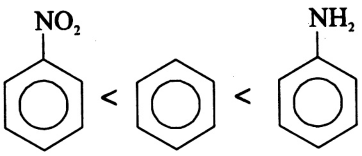
   (ii) 2-Nitropentane

   (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.

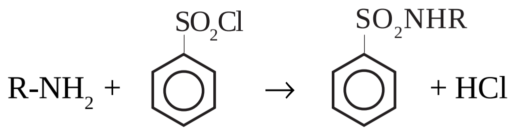
30.1.3.a Identification of Primary, Secondary and tertiary amines

1. Hinsberg's test:

Amine reacts with benzene sulphonyl chloride primary amine gives N-alkyl benzene sulphonamide and it dissolves in alkali.

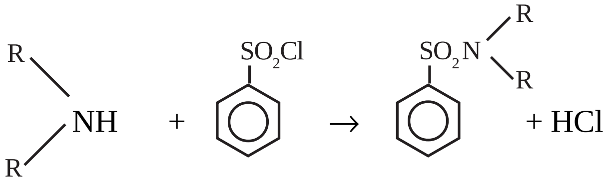
Secondary amine gives N, N- dialkyl benzene sulphonamide and it is insoluble in alkali.

Tertiary amine does not reacts with benzene sulphonyl chloride.



1^0 amine

N - alkyl benzene sulphonamide



N, N - alkyl benzene sulphonamide

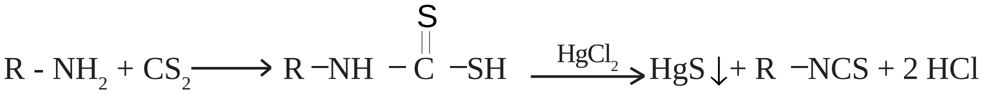
2. Hofmann mustard oil reaction:

Here amine is reacted with CS_2 followed by $HgCl_2$.

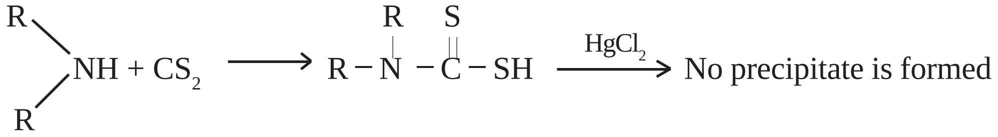
Primary amine reacts with CS_2 and the products reacts with $HgCl_2$ and black precipitate is formed.

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.

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 build up living organisms and are also 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

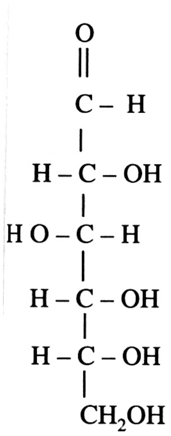
(ii) Disacccharides: Carbohydrates which give two monosaccharide molecules on hydrolysis are called disaccharides e.g. sucrose, maltose, lactose etc.

(iii) Polysaccharides : Carbohydrates which yield a large number of monosaccharide units on hydrolysis e.g. starch, glycogen, cellulose etc.

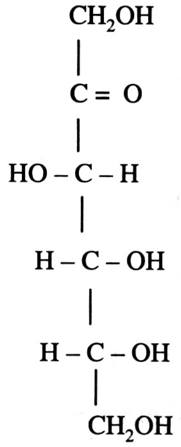
31.1.2 Structure of Monosaccharides·

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.

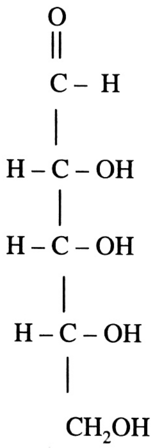
D-Glucose (an aldohexose) is the monomer for many other carbohydrates. Alone or in combination, glucose is probably the most abundant organic compound on the earth. D-Fructose (a ketohexose) is a sugar that is found with glucose in honey and fruit juices. D-Ribose (an aldopentose) is found in ribonucleic 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.



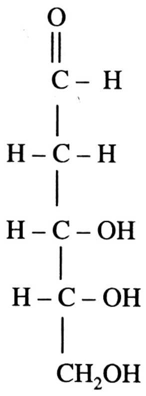
D-Glucose



D-Fructose



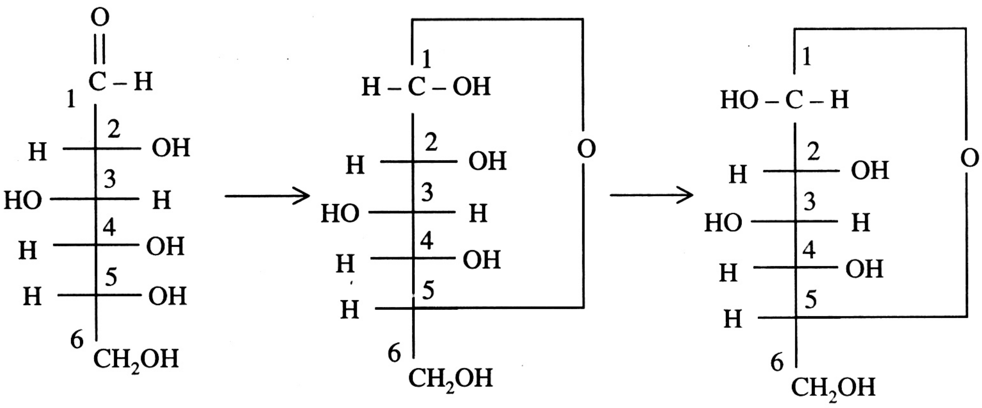
D-Ribose



2-Deoxy-D-ribose

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 and 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.

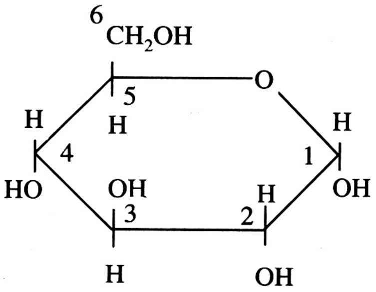
Formation of these cyclic structures (I and II) from the open chain structure can be shown as follows.



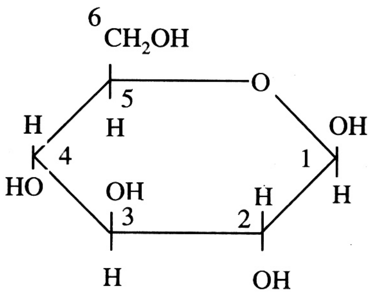
(I) α – D – glucose

(II) β – D –glucose

The cyclic structures I and II are more appropriately represented as Ia and IIa.

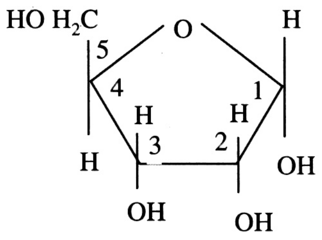


(Ia)

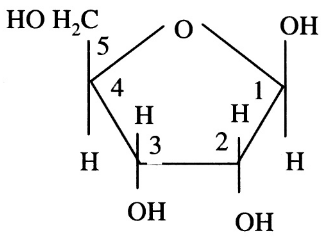


(IIa)

The α and β-forms of other sugars also exist in the cyclic form. D-Ribose forms a five membered ring structure as shown below

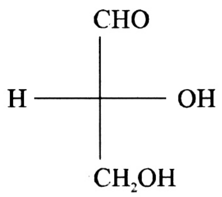


α – D – ribose

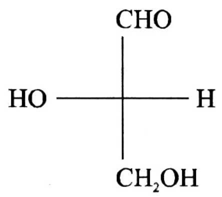


β – D – ribose

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.

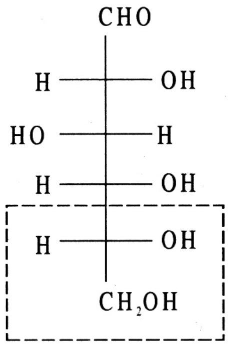


(+) –glycaraldehyde

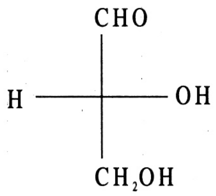


(–) –glyceraldehyde

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.



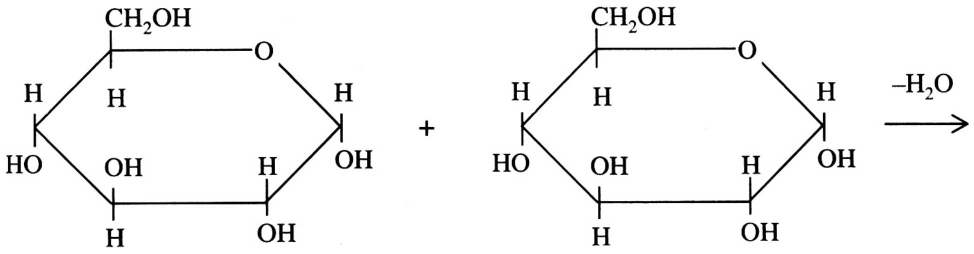
(+) – glucose or
D-glucose



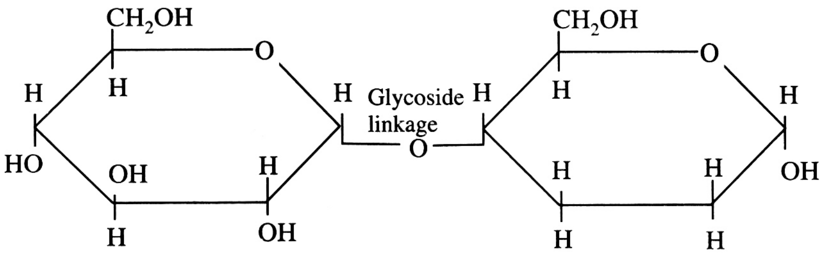
(+) – glyceraldehyde or
D-glyceraldehyde

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 β-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).

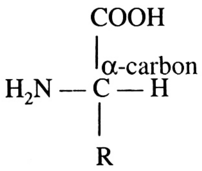
Proteins can also be classified on the basis of functions they perform, as summarized in table 31.2.

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 physiological activity	Insulin

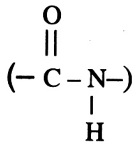
31.2.2 Structure of Proteins

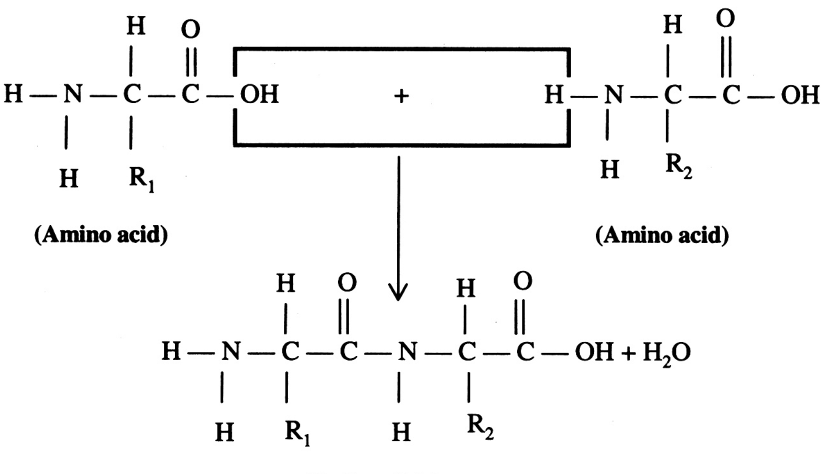
Protein molecules are polymers of different sizes and shapes with different physical and chemical properties. The monomer units for proteins are amino acids. All the amino acids that are found in proteins have an amino group($-NH_2$) on the carbon atom adjacent to carbonyl group, hence are called α -amino acids. The general formula of α-amino acids is shown below.



$$H_2N-\underset{\underset{R}{|}}{\overset{\overset{COOH}{|}}{C}}-H$$

All proteins found in nature are the polymers of about twenty (20) different α-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 $-\underset{\underset{O}{||}}{C}-$ 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.

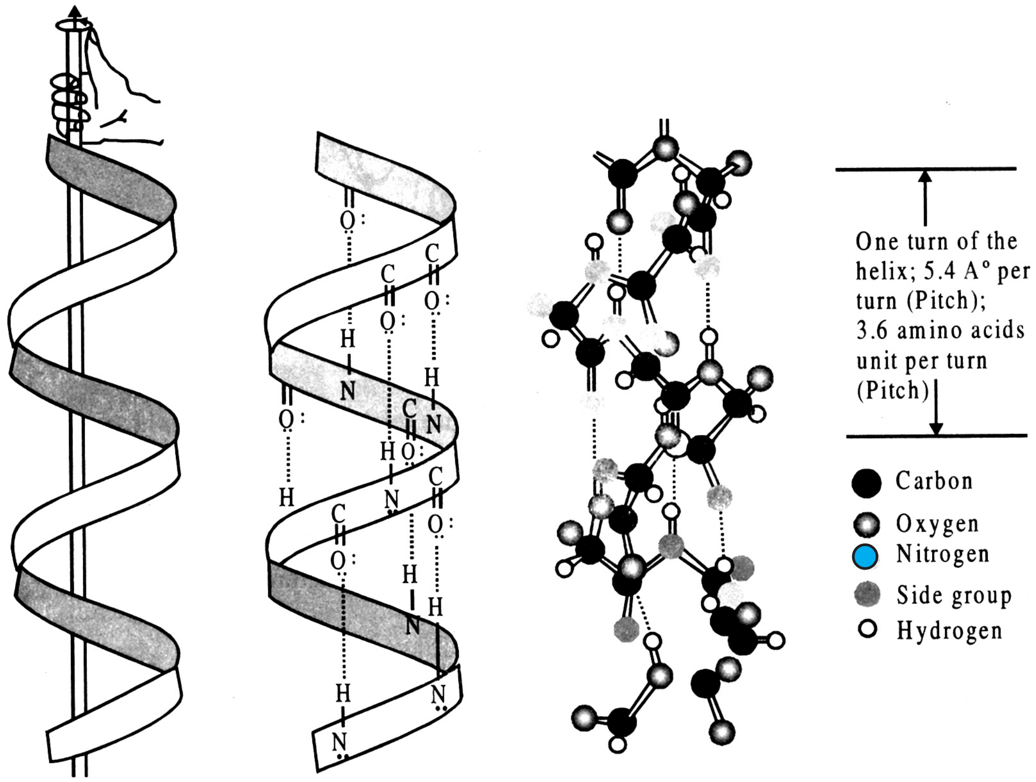
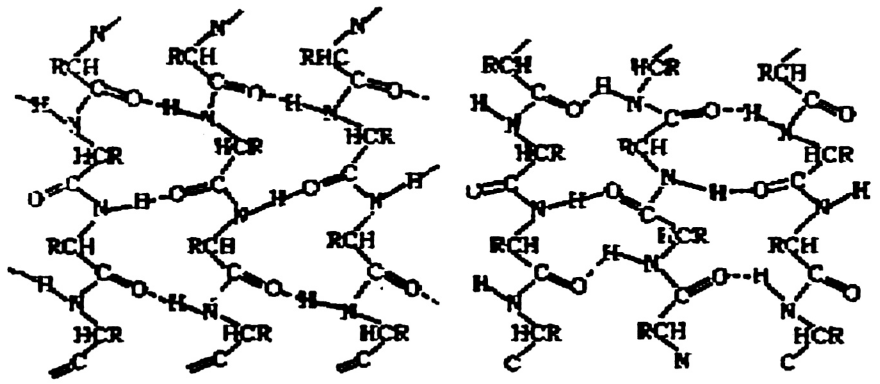


Fig. 31.1 : *The α -helix structure of protein*



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.

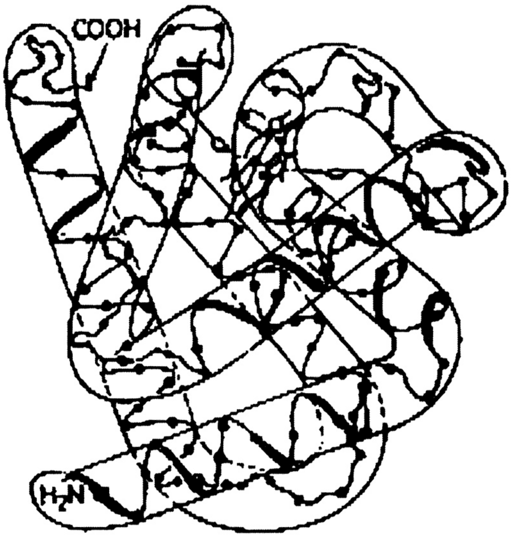


Fig. 31.3 : *Structure of myoglobin*

(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 *p*H 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 produce 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 defence 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 α-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.

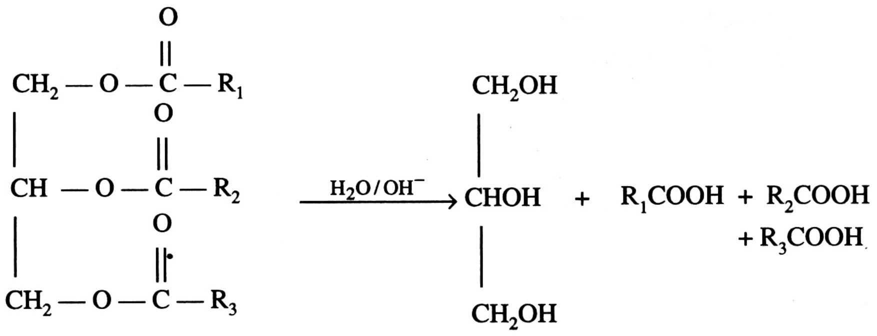
(iii) **Derived Lipids:** Compounds which are formed from oils, fats etc. during metabolism. They include steroids and some fat soluble vitamins.

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:

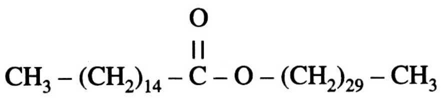


(Oil or fat) **Glycerol** **(Fatty acids)**

By definition, a fat is that triglyceride which is solid or semisolid at room temperature and an oil is the 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 has for storing the energy from unused , carbohydrates. The vegetable oils are found primarily in the seeds of plants.

The second type of simple lipids are 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

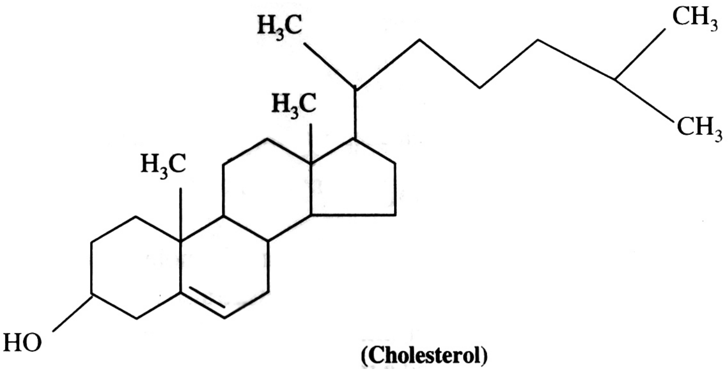
The waxes discussed above should not be confused with household paraffin wax which is a mixture of straight chain hydrocarbons.

(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 can not 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?

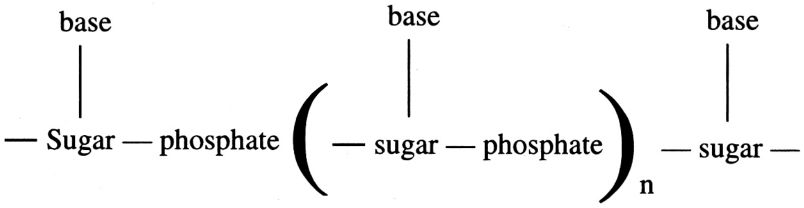
   ....

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.



$$-\overset{\text{base}}{\overset{|}{\text{Sugar}}}-\text{phosphate}\left(-\overset{\text{base}}{\overset{|}{\text{sugar}}}-\text{phosphate}\right)_n-\overset{\text{base}}{\overset{|}{\text{sugar}}}-$$

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

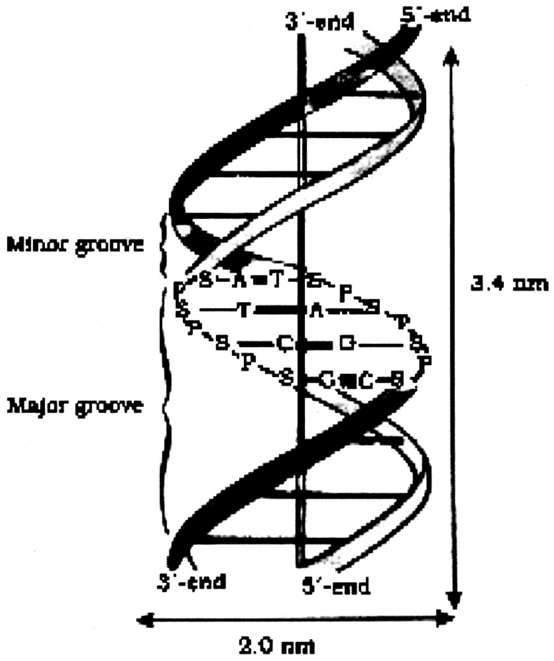


Fig. 31.4: *Watson and Crick's double helix structure of DNA*

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.

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).

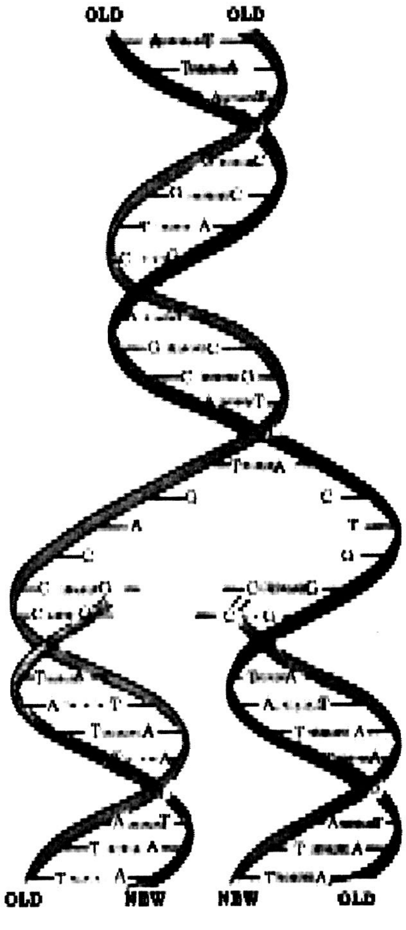


Fig. 31.5 : *Replication of DNA*

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.

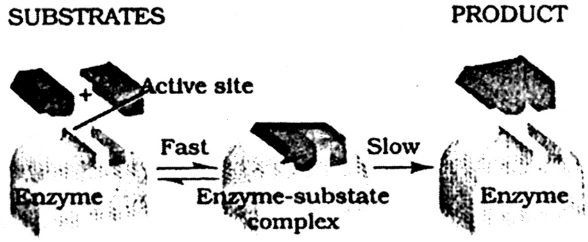


Fig. 31.6 : *Lock and Key arrangement of enzyme action*

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 *p*H.

(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 *coenzymes*. For example nicotinamide adenine dinucleotide (NAD) is a coenzyme 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 α-amino acids which are linked by peptide bonds.
- All proteins are the yolymers of twenty different α-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?

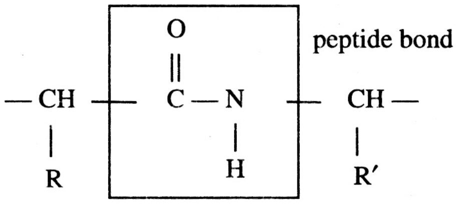
Answers to Intext Questions

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.

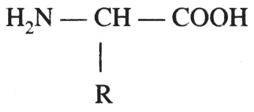
31.2

1. Information regarding the sequence of amino acids in a protein chain is called its primary structure.
2. Proteins are made up of many α-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.



$$-\underset{\underset{R}{|}}{CH}-\boxed{\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}}-\underset{\underset{R'}{|}}{CH}-$$

3. An α-amino acid may be represented as



$$H_2N - \underset{\underset{R}{|}}{CH} - COOH$$

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

De oxy 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 3^1-5^1 direction so that mRNA can be synthesized in 5^1-3^1 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 indicates 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 $5^1 \rightarrow 3^1$ direction.

A sequence of three bases, called codon specifies a particular amino acid that is to be incorporated into a protein.

Eg:- UCA on mRNA codes for the amino acid serine and CAG codes for glutamine. There are 64 codons, but 20 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.

$$\text{DNA} \underset{\text{Reverse transcription}}{\overset{\text{Transcription}}{\rightleftharpoons}} \text{RNA} \xrightarrow[\text{Translation}]{} \text{Proteins}$$

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:

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.

Fat Soluble Vitamins :

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 comers 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:

2. Deficiency of Vitamin ‘C’ Causes scurvy and deficiency of vitamin ‘D’ causes Rickets.