Bachelor of Science

(B.Sc.)

Basics of Chemistry

Semester-II

Author- Dr.Tarun Patodiya

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CONTENTS

Subject Name: Basics of Chemistry

Course Objective:

Objective of this chapter is to provide students with a brief detail on the basic fundamentals of the organic chemistry. Topics covered in this chapter such as hybridization, delocalized bonding and electronic effects, isomerism, aliphatic and aromatic hydrocarbons. The chapter is developed to stimulate interest of the reader into the organic chemistry and at the same time to build the deep understanding of the fundamental concepts of organic chemistry.

Course Outcomes:

After learning this chapter, students will be able to:

Explain the Fundaments of Organic Chemistry

Define Isomerism

Classify Aliphatic Hydrocarbons

Illustrate Aromatic Hydrocarbons, Alkyl and Aryl Halides

Identify Alcohols, Phenols and Ethers

Syllabus

Basics of Chemistry

Block-I: Molecules and Bonding

Unit 1: Unit and dimensions

Introduction, basic units, derived unites, SI Prefixes. Grammatical Rules for Representing the SI Unites. Conversion of Non- SI unit to SI units

Unit 2: Atom and Molecules

Bohr's Atomic theory (only postulates), structure of an atom; nuclear particles, atomic number, mass number and Isotopes, Atomic orbitals, filling of electrons in various orbitals-Aufbau energy diagram, Pauli's Exclusion Principle, Hund's rule of maximum multiplicity

Unit 3: Molecules and bonding

Molecules and chemical formulae, molar mass and Avogadro's number, ionic bond and ionic compounds, Covalent compounds-bonding, VSEPR concept and geometry, Valence Bond theory, Hybridization

Unit 4: Electronegativity and polarization of covalent bond

Electronegativity and polarization of covalent bond, inductive, mesmeric, electrometric effect, hydrogen bonding and its significance

Block-II: Periodic Properties and Gaseous State

Unit 5: Periodic Properties

Periodic table and periodic law, Periodic relationship among the elements, periodic properties-atomic size, ionization energy, electron affinity, electronegativity

Unit 6: Gaseous State

Pressure of a gas, pressure volume relationship-Boyle's law, the temperature volume relationship-Charle's law, Ideal gas equation, definition of acid and base

Block-III: Hydrocarbon and biomolecule

Unit 7: Hydrocarbons and functional groups

Alkanes, alkenes, alkynes, aromatic hydrocarbons, Preparation and properties of ethene and ethyne. Functional groups in organic compounds-alcohols, ethers, aldehydes, ketones and carboxylic acids.

Unit 8: Carbohydrates and nucleic acid

Carbohydrates: Classification and nomenclature. Monosaccharides, mechanism of ozone formation

Unit 9: Nucleic acid

Introduction, Nitrogen bases, purines, pyrimidines, nucleosides, nucleotides, structure of RNA and DNA molecule

Unit 10: Metal ion in biological system

A brief introduction to bio-inorganic chemistry. Role of metal ions present in biological systems with special reference to Na^+, K^+ and Mg^{2+} ions: Na/K pump; Role of Mg^{2+} ions in energy production and chlorophyll.

Block-IV: Redox reactions and catalysis

Unit 11: Oxidation and reduction

Use of redox potential data- analysis of redox cycles, redox stability in water-Frost, Latimer and Roubaix. Principles involved in the extraction of the element.

Unit 12: Catalysis

Catalysis, characteristics of catalysed reactions, Classification of catalysis, miscellaneous examples.

UNIT 1: UNITES AND DIMENSIONS

CONTENTS:

1. 1 INTRODUCTION

All the physical quantities are given by a few fundamental quantities or their combinations. The units of such fundamental quantities are called base units, combinations of them being called derived units. The system in which length, mass, velocity, density and time are adopted as the basic quantities, and from which the units of other quantities are derived, is called the absolute system of units.

1.2 OBJECTIVES

- Use the SI system.

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- Know the SI base units.

- State rough equivalents for the SI base units in the English system.

- Read and write the symbols for SI units.
- Recognize unit prefixes and their abbreviations.

- Build derived units from the basic units for mass, length, temperature, and time.

- Convert measurements from SI units to English and from one prefixed unit to another.

- Use derived units like density and speed as conversion factors.

- Use percentages, parts per thousand, and parts per million as conversion factors.

- Use and report measurements carefully.

- Consider the reliability of a measurement in decisions based on measurements.

- Clearly distinguish between precision and accuracy

- Exact numbers and measurements

-

1.3 BASIC UNITS, DERIVED UNIT AND SI PREFIXES

A unit is a particular way of attaching a number to the quantitative dimension.

Measured physical properties have a basic dimension in which they are measured. There may be many units that are used to measure this dimension. This is best shown by example. The thickness of an object has the dimension of length. Length can be measured in a wide range of units including inches, feet, yards, meters, kilometers, micrometers, Angstrom units, furlongs, fathoms, light-years and many more. The thickness of an object cannot be measured in kilograms, however. That is because the kilogram is a unit used to measure quantities that have the fundamental dimension of mass.

 The term units usually start by making arbitrary definitions of a unit for fundamental dimensions. Typically these fundamental dimensions are mass, length, time, electric charge and temperature. Once these units are selected for the fundamental dimensions the units for other physical quantities can be determined from the physical relations among quantities having the fundamental units. For example velocity is found as distance divided by time. Thus the dimensions of velocity must be length/time. Similarly the dimensions of acceleration, found as velocity divided by time, must be length/time^2, and the dimensions of force can be found from Newton's second law: force equals mass times acceleration. This gives the dimensions of force as the dimensions of mass times the dimensions of acceleration or (mass) times (length) divided by (time). The symbols M, L, and T are usually used to represent dimensions of mass, length, and time, respectively. (In table 1.1)

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1.3.1. System of Units

(a) C.G.S (Centimeter-Grand-Second) system

(b) F.P.S. (Foot-Pound-Second) system

(c) M.K.S. (Meter-Kilogram--Second) system. (d) M.K.S.A. (Meter-Kilogram-Second-Ampere) unit

Table 1.1- General Base Units:

PHYSICAL QUANTITY	SYMBOL	DIMENSION	MEASUREMENT UNIT	UNIT
Length	S	L	Meter	m
Mass	M	M	Kilogram	Kg
Time	T	T	Second	Sec
Charge	Q	Q	Coulomb	C
Temperature	T	K	kelvin	^{0}C
Area	A	L^2	Square meter	m^2
Volume	V	L^3	Cubic meter	m^3
Velocity	V	L/T	Meter per second	m/sec.
Angular velocity	W	T_{-1}	Radians per sec.	1/sec
Force	F	MLT^{-2}	Newton	Kg m/sec
Energy	E	ML2T-2	Joule	Kg m2/sec2
Heat	Q	ML2T-2	Joule	Kg m2/sec2
Density	P	ML-3	kilogram per cubic meter	Kg/m3
Pressure	P	ML-1T-2	Newton per square meter	Kg m$^-$^{1}/sec^2

1.3.2. The seven base units of the SI

1.   Length- Meter, m: The meter is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second.

2.   Mass- kilogram, kg: The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram.

3.   Time- second, s: The second is the durationof 9 192 631 770 periods of the radiationcorresponding to the transition betweenthe two hyperfine levels of the ground stateof the caesium 133 atom.

4.   Electric current- ampere, A: The ampere is that constant currentwhich, if maintained in two straight parallelconductors of infinite length, of negligible circular cross-section, and placed 1 metre apart in vacuum,would produce between these conductors a forceequal to 2×10^{-7}newton per metre of length**.**

5.   Thermodynamic temperature - Kelvin, K: the Kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

6.   Amount of substance- Mole, mol: The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12. When the mole is used, the elementary entities must be specie and may be atoms, molecules, ions, electrons, other particles, or specie groups of such particles.

7.   Luminous intensity- candela, cd: The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steroidal.

Table -1.2 The seven independent SI base units

Quantity	Unit name	Unit symbol
Length	Meter	M
Time	Second	S
Mass	Kilogram	Kg
Temperature	Kelvin	K
Electric current	Ampere	A
Amount of substance	Mole	Mol
Luminous intensity	Candela	Cd

The International System of Units

Seven physical quantities have been selected as base quantities in the 14th General Conference onWeights and Measurements, held in France in 1971. These quantities form the basis of the International System of Units, abbreviated **SI** (from its French name *Système International*)

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and popularly known as the *metric system*. Table 3 depicts these quantities, their unit names, and their unit symbols. (H. A. Radi and J. O. Rasmussen, *Principles of Physics*,)

Prefixes for SI units

An additional convenient way to deal with very large or very small numbers in physics is to use the prefixes listed in **Table 1.3**. Each one of these prefixes represents a certain power of 10.

Table -1.3

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{24}	yotta-	Y	$10-24$	yocto	-y
10^{21}	zeta-	Z	$10-21$	zepto	-z
10^{18}	exa-	E	$10-18$	atto	-a
10^{15}	peta-	P	$10-15$	femto-	-f
10^{12}	tera-	T	$10-12$	pico	-p
10^{9}	giga-	G	$10-9$	nano	-n
10^{6}	mega	- M	$10-6$	micro	$-\mu$
10^{3}	kilo	-k	$10-3$	milli	-m
10^{2}	hecta	-h	$10-2$	centi	-c
10^{1}	deca	-da	$10-1$	deci	-d

Common metric prefixes:

The units often have **prefixes**, indicating the power(s) of 10 by which a unit may be multiplied (for example, the prefix kilo in kilometer indicates that the unit kilometer is 1000 times larger than the meter). They are attached to an SI unit name or symbol to form what are properly called "multiples" and "submultiples" (i.e., positive or negative powers of 10) of the SI unit. These prefixes are helpful when referring to very small or very large quantities. Instead of creating a new unit, a prefix is added. For example, when measuring short lengths such as 1/1000th of a meter, we simply write millimeter; milli denotes 1/1000th. The some common metric prefixes are giving below: **(Table 1.4)**

Example 1.1

Convert the following: (a) 1 kilometre per hour to meter per second, (b) 1 mile per hour to meter per second, and (c) 1 mile per hour to kilometre per hour [to a good approximation 1mi = 1.609 km].

Table -1.4

Multiplication Factor	Prefix Name	Prefix Symbol
$1\ 000\ 000\ 000\ 000 = 10^{12}$	tera	T
$1\ 000\ 000\ 000 = 10^{9}$	giga	G
$1\ 000\ 000 = 10^{6}$	mega	M
$1\ 000 = 10^{3}$	kilo	k
$100 = 10^{2}$	hecto	h
$10 = 10^{1}$	deka	da
$0.1 = 10^{-1}$	deci	d
$0.01 = 10^{-2}$	centi	c
$0.001 = 10^{-3}$	milli	m
$0.000\ 001 = 10^{-6}$	micro	μ
$0.000\ 000\ 001 = 10^{-9}$	nano	n
$0.000\ 000\ 000\ 001 = 10^{-12}$	pico	p

1.4 GRAMMATICAL RULES FOR REPRESENTING THE   SI UNITES

The term SI Units is an abbreviation of the French Le System International Unites. It is the modern metric system of measurement. SI unit is now universally accepted as a standard system of measurement.

The SI units consist of

(a) Seven base units

(b) A set of prefixes

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(c) Several derived units

1.4.1 Representation of SI units

Step I: The SI Base Units

The SI base units represent seven mutually independent base quantities. These quantities, their names, and the symbols that represent them are given in **Table-1.5.**

Quantity	Name	Symbol
Length	meter	m
Mass	Kilogram	Kg
Time	Second	s
Current	ampere	A
Temperature	Kelvin	K
Amount of mols	Mole	mol

Step II: The Prefixes

A prefix may be added to any unit to produce an integer multiple of ten of the base unit. For example, a kilogram denotes a multiple of 1000gm and a milligram denotes a multiple of a 1000 gram. **Table 1.6** gives the prefixes that are accepted to be used in the SI units. Prefixes are never combined. For example, mill millimeter is not written; micrometer is written instead.

Table 1.6:

Name	yotta	zetta	Exa	peta	tera	giga	mega	kilo	hecto	deca
Symbol	Y	Z	E	p	T	G	M	K	H	D
Factor	10^{24}	10^{21}	10^{18}	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{2}	10^{1}
Name	deci-	cent-	milli-	micro-	nano-	pico-	femto-	atto	zepto-	yacto-
Symbol	d	C	M	µ	n	p	f	A	z	y
Factor	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}	10^{-21}	10^{-24}

Step III: The SI Derived Units

A system of equations involving the seven base quantities defines the derived quantities. The SI derived units follow these equations to represent the derived quantities. **Table 1.7** gives examples of a number of SI derived units.

Table1.7: Examples of SI Derived Units

Derived quantity	Name	Symbol
Area	square meter	m^2
Volume	cubic meter	m^3
Wave number	reciprocal meter	m^{-1}
Mass density	kilogram per cubic meter	kg/m^3
Specific volume	cubic meter per kilogram	m^3/kg
Mass fraction	kilogram per kilogram	$kg/kg = 1$
Speed, velocity	meter per second	m/s
Acceleration	meter per second squared	m/s^2
Current density	ampere per square meter	A/m^2
Magnetic field strength	ampere per meter	A/m
Amt-of-substance concentration	mole per cubic meter	mol/m^3
Luminance	candela per square meter	cd/m^2

A few notable points are given below:

1.Electrical energy is often measured in kilowatt-hours (kWh) instead of mega joules.

2."Calorie" is used as a heat unit indicating the amount of heat required to increase the temperature of 1 gm of water by 1^0C.

3.Blood pressure is measured in mmHg instead of Pa.

4.Atomic scale units used in Physics and Chemistry are angstrom, electron volt, atomic mass unit (amu), and barn.

5.Travel distance and speed of ships and aircraft are measured in nautical mile and knot (nautical mile per hour).

6.The year is not specifically included as an SI unit.

7.A metric ton is called "tone" in a few countries.

8.It is preferred to use numbers between 0.1 and 1 000 in expressing the quantity of any SI unit. Thus the quantity 15 000 m is expressed as 15 km, and 0.002 cubic centimetre is preferably written as 2 mm^3.

1.5 CONVERSION OF NON SI UNIT TO SI UNIT

1.5.1Non SI Unit: A number of non-SI units are commonly used, even though the SI system of units allows for complete coverage of all scientific measurements.

1.5.2 Some commonly used non-SI units

Physical quantity	Non-SI unit	Symbol	Conversion Factor
Energy	calorie	cal	1 cal = 4.184 J
Length	Ångstrom	Å	1 Å = 10^{-10} m
Mass	tonne	t	1 t = 10^3 kg
Pressure	atmosphere	atm	1 atm = 1.013 x 10^5 Pa
Temperature	degree Celsius	°C	1 °C = 1 K
Time	minute	min	1 min = 60 s
	Hour	h or hr	1 h = 3600 s
	Day	d	1 d = 86 400 s
Volume	litre	L	1 L = 1 dm^3 = 10^{-3} m^3

1.5.3 SI Unit

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The International System of Units (SI) is a scientific method of expressing the magnitudes or quantities of important natural phenomena. There are seven base units in the system, from which other units are derived. This system was formerly called the meter-kilogram-second (MKS) system. See **Table-1.8**

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1.5.4 Conversion Factors for SI and non-SI Units (Table 1.8)

To convert Column 1 into Column 2, multiply by	Column 1 SI Unit	Column 2 NonSI Unit	To convert Column 2 into Column 1, multiply by
Length			
0.621	kilometer, km (103 m)	mile, mi	1.609
1.094	meter, m	yard, yd	0.914
3.28	meter, m	foot, ft	0.304
1.0	micrometer, m (10 6 m)	micron,	1.0
3.94×10^2	millimeter, mm (10 3 m)	inch, in	25.4
10	nanometer, nm (10^9 m)	° Angstrom, A	0.1
Area			
2.47	hectare, ha	acre	0.405
247	square kilometer, km2 (103 m)2	acre	4.05×10^3
0.386	square kilometer, km2 (103 m)2	square mile, mi2	2.590
2.47×10^4	square meter, m2	acre	4.05×10^3
10.76	square meter, m2	square foot, ft2	9.29×10^2
1.55×10^3	square millimeter, mm2 (10 3 m)2	square inch, in2	645
Volume			
9.73×10^3	cubic meter, m3	acre-inch	102.8
35.3	cubic meter, m3	cubic foot, ft3	2.83×10^2
6.10×10^4	cubic meter, m3	cubic inch, in3	1.64×10^5
2.84×10^2	liter, L (10 3 m3)	bushel, bu	35.24
1.057	liter, L (10 3 m3)	quart (liquid), qt	0.946
3.53×10^2	liter, L (10 3 m3)	cubic foot, ft3	28.3
0.265	liter, L (10 3 m3)	gallon	3.78
33.78	liter, L (10 3 m3)	ounce (fluid), oz	2.96×10^2
2.11	liter, L (10 3 m3)	pint (fluid), pt	0.473
Mass			
2.20×10^3	gram, g (10 3 kg)	pound, lb	454
3.52×10^2	gram, g (10 3 kg)	ounce (avdp), oz	28.4
2.205	kilogram, kg	pound, lb	0.454

0.01	kilogram, kg	quintal (metric), q	100
1.10×10^3	kilogram, kg	ton (2000 lb), ton	907
1.102	megagram, Mg (tonne)	ton (U.S.), ton	0.907
1.102	tonne, t	ton (U.S.), ton	0.907
Pressure			
9.90	megapascal, MPa (106Pa)	atmosphere	0.101
10	megapascal, MPa (106Pa)	bar	0.1
1.00	megagram per cubic meter, Mg m 3	gram per cubic centimeter, g cm 3	1.00
2.09×10^2	pascal, Pa	pound per square foot, lb ft 2	47.9
1.45×10^4	pascal, Pa	pound per square inch, lb in 2	6.90×10^3

1.6 SUMMARY

In this chapter you have studied Use the SI system, know the SI base units, Recognize unit prefixes and their abbreviations, Convert measurements from SI units to English and from one prefixed unit to another. With the help of unit and dimensions we can derive the various derivations by making use units and converted units.

1.7 TERMINAL QUESTIONS

A. Short answers type questions:

1. What is the importance of base units?

2. Does the measurement of a physical quantity depend upon the system of units used? **B. Objective type questions:**

1.In the S.I. system, the unit of temperature is-

    A. Degree centigrade   B. Kelvin

    C. Degree Celsius   D.degree Fahrenheit

2. In the S.I. unit of energy is-

    A. Erg   B. calorie   C. joule   D. electron volt

3.   If Force = (x/density) +Cis dimensionally correct, the dimension of x are -

    A. MLT_{-2} B. MLT_{-3} C. ML_2T_{-3} D. $M_2L_{-2}T_{-2}$

4. Intensity of electric current is expressed in

    A. Volts   B. Watts   C. Amperes   D. Joules

5. One Newton force equals.

    A. 10^5 dynes   B. 10^4 dynes   C. 10^3 dynes   D. 10^2 dynes

6. In S.I. system, the symbol for density is

    A. N/m^3 B. kg/m^3 C. m^3/s D. kg

7. The thickness of a micron, is

    A. 10^{-3} m   B. 10^{-6} m   C. 10^{-9} m   D. 10^{-12} m

8. The fundamental units in S.I. system are the same as that of

    A. C.G.S. units   B. F.P.S. units   C. M.K.S. units   D. None of these

9. Pick up the correct statement from the following:

A. In S.I. system, surface tension is expressed in Newton per meter

B. In S.I. system, force is expressed in Newton

C. In S.I. system, power is expressed in watts

D. All the above.

10. 100 kN/m^2 pressure is equal to

    A. 1 atm   B. 1 bar   C. 1 m bar   D. 1 mm Hg

Answers : 1B. 2 C. 3. A 4.C 5. A 6. 7. B 8. C 9. E 10. B

1.8 REFERENCES AND FURTHER STUDIES

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1. H. A. Radi and J. O. Rasmussen, *Principles of Physics*, Undergraduate Lecture Notes in Physics, DOI: 10.1007/978-3-642-23026-4_1, Springer-Verlag Berlin Heidelberg 2013.

2. Kenneth Butcher Linda Crown Elizabeth J. Gentry Weights and Measures Division

Technology Services

UNIT-2: ATOM AND MOLECULES

CONTENTS:

2.1. INTRODUCTION

In the beginning of nineteenth century, John Dalton (1766-1844) put forward his atomic theory, he regarded atom as hard and smallest indivisible particle of matter that takes part in chemical reactions; the atoms of one particular element are all identical in mass and atoms of defferent elements differ in mass and other properties.

Later on, various investigators around the end of nineteenth century and beginning of twentieth centurydid several experiments and revealed the presence of much smaller negatively charged particles, named electrons by J.J. Thomson (1897) and positively charged particles, named protons by Rutherford (1911) within an atom. These tiny particles were called subatomic particles. It was also established by Rutherford that the whole positive charge and most of the mass of an atom lies at nucleus. The positive charge on the nucleus was attributed to the presence of protons called the atomic number by Moseley (1912). The electrons were said to be arranged around the nucleus in the extra nuclear region in certain well defined orbits called energy shells and were said to be in constant motion (N. Bohr, 1913). Chadwick's experiments (1932) also revealed the existence of yet another subatomic particle in the nucleus which did not have any charge and named as neutrons. Further investigations established that there were also present some other subatomic particles in the nucleus in addition to electrons, protons and neutrons. These particles are positrons, neutrinos, antineutrinos, pions (π-mesons) etc. The pions (Yukawa, 1935) are said to be continuously consumed and released by proton-neutron exchange processes.

Thus, it is concluded that the atom no longer is an ultimate and indivisible particle of matter and the outer or valence shell electrons are responsible for chemical activity of the elements.

2.2. OBJECTIVES

The objective of the preparation of the text of this unit is to acquaint the readers with the fascinating and exciting realm of the atoms. Accordingly, an attempt has been made to through light on the arrangement of the internal constituents of the atoms (the subatomic particles), their peculiarities and characteristics along with their behaviour towards their neighbours, i.e.

the arrangement of protons and neutrons in the nucleus and the rules governing the arrangement of electrons in the extra nuclear region of an atom and filling of orbital's belonging to higher energy shells prior to the entry of electrons in the orbitals of lower energy shells. At the same time, the problem "what makes the electron cloud to acquire different shapes in three dimensional space around the nucleus?" has been entertained and various other interesting problems have also been taken into account.

2.3 BOHR'S ATOMIC THEORY

A Danish physicist named Neil Bohr in 1913 proposed the Bohr atomic model. He modified the problems and limitations associated with Rutherford's model of an atom. Earlier in Rutherford Model, Rutherford explained in an atom a nucleus is positively charged and is surrounded by electrons (negatively charged particles). Whereas Bohr took the model one step ahead, he explained about electrons and the different energy levels associated with them.

2.3.1. Postulates of Bohr's model of atom :

Bohr's atomic model explains the structure of atoms, basically of the Hydrogen atom, and is therefore also called Bohr's model of Hydrogen atoms. Bohr's atomic model suggests that electrons surround the nucleus moving in orbit like planets around the sun. The main postulates of Bohr's model of the Hydrogen atom are:

1. In an atom, electrons revolve around positively charged nucleus in a fixed cicular path

   called orbits or shells. The orbits are reprsented as 1, 2, 3, …..etc., and the shells are

   represented by K, L, M, N,………..etc.

2. The energy of the electrons in a particular energy level remains constant, and hence

   accounts for the stability of an atom.

3. Only those orbits are permitted whose angular momentum is the integral multiple of

   $h/2\pi$ i.e. $mvr = nh/2\pi$. This postulates suggest that electron's angular momentum is

quantized

4 .An elctrons jumps from higher energy level to lower energy level when it absorbs

energy, while looses energy when the transition occurs from higher energy level to

lower energy level. The difference in energy between two energy states is hv i.e.

$\Delta E = E_2 - E_1 = h\nu$
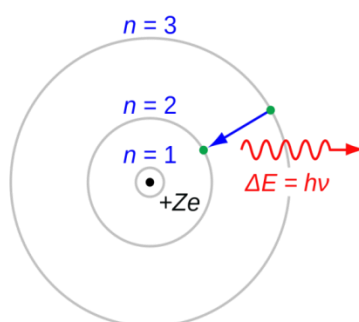
Bohr's Atomic Model

Merits of Bohr's model of atom

- Bohr's atomic model explains the stability of an atom on the basis that electrons energy remain constant in an orbit or shell.

- It gives basis to find energy of electron in a particular orbit, and the radius of an orbit from which electron revolves around positively charged nucleus.

- Bohr's atomic model succesfully explain the atomic spectra of Hydrogen atom.

Limitations of Bohr's model :

- Bohr's atomic model fails to explain Stark effect (splitting of spectral lines under the influence of magnetic field) and Zeeman effect (splitting of spectral lines under the influence of electric field).

- This theory violates Heisenberg Uncertainty Principle.

- Fails to explain spectra for multielectron systems/largerr atoms

- Fails to explain the shape of the molecule, and so on.

2.4. STRUCTURE OF AN ATOM

In atomic structure, you will learn about the different parts of the atom, along with the subatomic particles found in each region. You will also learn about the properties that can be found through the subatomic particles.

An atom is a building block of matter, used to determine the characteristics of an element. An atom is the smallest unit of matter that retains the chemical properties of an element. Atoms are able to interact with each other through bonding, to form more complex substances, also known as molecules.

2.5 NUCLEAR PARTICLES

Atoms are made up of various parts; the nucleus contains minute particles called protons and neutrons, and the atom's outer shell contains other particles called electrons.
Protons :Protons are positively charged subatomic particles, found in the nucleus of all atoms. The charge of a proton is +1. An protons carries a charge of +1.6 x 10-19 coulombs The atomic number of an element is equal to the number of protons in the nucleus and has a mass of 1.007277 amu (atomic mass units).

Neutron:Neutron is a undeniably a neutrally charged subatomic particle, found in the nucleus of all atoms except hydrogen. The mass of a neutron is slightly more than of a proton, and It has a mass of 1.008665 amu (atomic mass units).

Electron: Electrons are the subatomic particles that orbit the nucleus of an atom. They are negative in charge and are much smaller than protons or neutron. In fact, they are 1,800 times smaller. They also carry electricity. The charge of an electron is -1. An electron carries a charge of -1.6 x 10-^{19} coulombs and they have a mass of 0.000549 amu (atomic mass units).

2.6.ATOMIC NUMBER

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The total number of proton in the nucleus of an atom is called the atomic number.It is same as the number of electrons in the neutral atom and it is denoted by symbol, (Z).

For example: Calculate the atomic number and number of electron in magnisum($_{12}Mg^{24}$).

Answer :   Atomic Number = Z = 12

Atomic Mass Number = A = 24

Number of protons = atomic number = 12

Number of electrons = atomic number = 12

2.7. MASS NUMBER AND ISOTOPES

2.7.1. MASS NUMBER:

The sum of the protons and neutrons in the nucleus of an atom of the element is called mass number. The mass number is denoted by 'A'.

$$A = P + N$$

Or $$A = Z + N$$

For Example: Calculate the number of electrons, protons, and neutrons in the ($_{15}P^{31}$) atoms.

Answer: Atomic Number = Z = 15

Atomic Mass Number = A = 31

Number of protons = atomic number = 15

Number of electrons = atomic number = 15

Neutron number = Number of neutrons = A – Z = 31 – 15 = 16

Number of nucleons = Atomic mass number = 31

2.7.2 ISOTOPES :

Isotopes are distinct nuclear species of the same element. They have the same atomic number (number of protons in their nuclei) , but differ in nucleon numbers (mass numbers) due to different numbers of neutrons in their nuclei. All isotopes have almost the same chemical properties, they have different atomic masses and physical properties.

For example: 1. Hydrogen has three naturally occurring Isotopes: Protium (1H),

Deuterium(2H) and Tritium(3H), with mass number 1,2,3 respectivly.

2.Carbon-12, Carbon-13, and Carbon-14 are three isotopes of the

element carbon with mass numbers 12, 13, and 14, respectively.

2.8. SHAPES OF ATOMIC ORBITALS

The shapes of atomic orbitals depend θ and ϕ i.e. the product $[\Theta (\theta) \times \Phi (\phi)]$ or $_{l,m} \times \Phi_m$ is related with the shapes of the orbitals. The values of $\Theta_{l,m} \times \Phi_m$ for s-orbital (l=0,m=0), porbital (l = 1, m = 0, ±1), and d-orbitals (l = 2, m = 0, ±1, ±2) can be obtained and correlated with the shapes of orbitals.

For s-orbitals (l = 0, m = 0), the angular wave function $\Theta_{o,o} \times \Phi_o$ is independent of the angles Θ and ϕ, i.e. there is no angular wave function and hence orbitals have only one orientation and are spherically symmetrical over all the directions, hence have spherical shape as well as are non-directional. Thus, s-orbitals are usually represented by circles. Greater the value of n and higher the number of nodal points for s-orbital, larger is the size of orbital. The electron density in s-orbitals could be shown by concentric shades as follows:
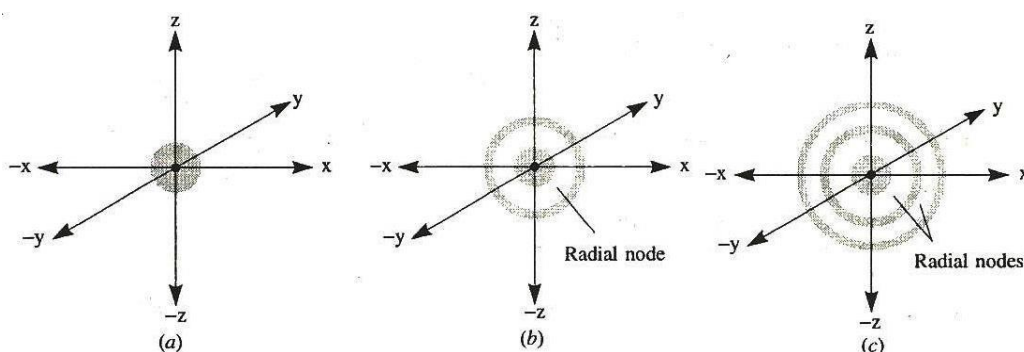
1s-orbital	2s-orbital	3s-orbital
(no nodal point)	(1 nodal point)	(2 nodal points)

Electron charge density pictures for 1s, 2s and 3s-orbitals. Nucleus has been shown by thick dot.

For **p orbitals** (l = 1, m = 0, ±1), there are three values of m and therefore, there are three orientations of lobes of orbitals along cartesian coordinates *viz.* p_x, p_y and p_z. The subscripts x, y and z indicate the axes along which orbitals are oriented. The three p-orbitals are similar in size, shape and energy but differ in orientation only. The angular wave function for these

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orientations is the product $\Theta_{,m}$ x Φ_m. For l=1, m =0 orientation, the angular wave function $\Theta_{1,0}$ Φ_0 is a real quantity and corresponds to p_z orbital which is dumb-bell shaped curve along zaxis in three dimensional space (**Fig. 2.1 c**).

For l = 1,m = +1 and l =1, m= -1 orientations, angular wave functions are $\Theta_{1,+1}$ x Φ_{+1} and $\Theta_{1,-1}$ x Φ_{-1} which have imaginary quantities and are avoided. The real values are obtained by the normalised linear combinations (addition and subtraction) of angular angular wave functions. Thus, addition process, i.e. $\Theta_{1,+1}$ x Φ_{+1} + $\Theta_{1,-1}$ x Φ_{-1} gives normalised wave function corresponding to p_x orbital. In three dimensional space, this gives dumb-bell shaped curve along x- axis (Fig.1.4a) The subtraction process, i.e. $\Theta_{1,+1}$ x Φ_{+1} - $\Theta_{1,-1}$ x Φ_{-1} gives normalised wave function corresponding to p_y orbital which is again dumb-bell shaped curve in three – dimensional space along y-axis (**Fig. 2.1b**).

P_x orbital	P_y orbital	p_z orbital
(a)	**(b)**	**(c)**
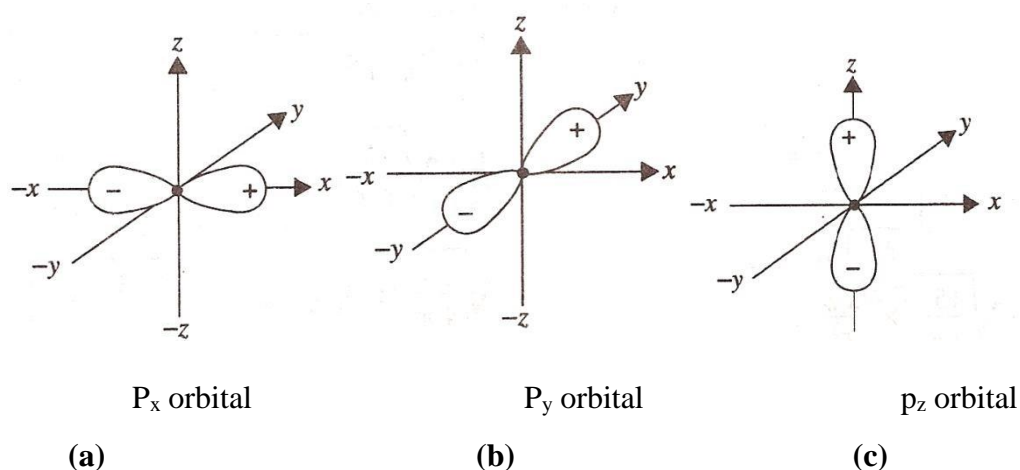
Fig.2.1 The orientation of p- orbitals along x, y and z- axis.

The (+) and (–) signs are algebraic signs of angular wave function and not the charge. The angular part of the wave function ψ (Θ, Φ) has (+)sign on one lobe and (–)sign on the opposite lobe although $ψ^2$ (Θ, Φ) will be positive on both the lobes. Thus, for p-orbitals, the important points to be noted are:

(i) Since x, y and z axes are perpendicular to each other, the three p-orbitals are   also perpendicular to each other.

(ii) Each of the three p-orbitals has two lobes on each side of the nucleus which is at the origin of the axes, hence the probability of finding the electron (s) in both lobes is equal. These lobes are

separated by nodal planes passing through the nucleus. The electron density on the nodal plane is zero.

(iii) Greater the value of n (principal quantum number or the shell number), larger is the size of p orbital i.e. 3p orbital is larger in size than 2p orbital though the shapes of both the orbitals are the same.

(iv) The energy of the three p-orbitals with the same value of n is same i.e. all the three p-orbitals are degenerate.

For **d-orbitals** (l = 2, m = 0, ±1, ±2), five orientations (or orbitals) are there corresponding to five values of m for l = 2. Depending on the permitted combinations of l and m, values for five d-orbitals, angular wave functions corresponding to different d-orbitals are as follows:

For l = 2 and m=0, the angular wave function $\Theta_{2,0}$ x Φ_0 has a real value and corresponds to $d_z{}^2$-orbital. For l =2 and m = ±1, we have two angular wave functions, $\Theta_{2,+1}$ x Φ_{+1} and $\Theta_{2,-1}$ x Φ_{-1}. The values of these angular wave functions contain imaginary quantity and hence, these values are not accepted. The real and acceptable values are obtained from these by normalised linear combinations (addition and subtraction) of above functions. The addition process of above angular wave functions, i.e. $\Theta_{2,+1}$ x Φ_{+1} + $\Theta_{2,-1}$ x Φ_{-1} gives the wave function for d_{zx} (or d_{xz}) orbital and subtraction process, i.e. $\Theta_{2,+1}$ x Φ_{+1} - $\Theta_{2,-1}$ x Φ_{-1}, gives the wave function for dyz, orbital, for l = 2 and m = ±2, we have two wave functions *viz.* $\Theta_{2,+2}$ x Φ_{+2} and $\Theta_{2,-2}$ x Φ_{-2}. Again the values of these wave functions contain imaginary quantity and hence are not accepted. Real and acceptable values are obtained by the nornalised linear comlimation of the two angular wave functions. The addition process of above angular wave functions, i.e., $\Theta_{2,+2}$ x Φ_{+2} + $\Theta_{2,-2}$ x Φ_{-2}, gives the wave function for d_{x2-y2} orbital and subtraction process i.e., $\Theta_{2,+2}$ x Φ_{+2} - $\Theta_{2,-2}$ x Φ_{-2}, gives the wave subtraction for d_{xy} orbital. When these five angular wave functions for different orbitals obtained above are plotted in three dimensional space, we get the solid curves which give the orientations along the axes or in between the axes as shown below:
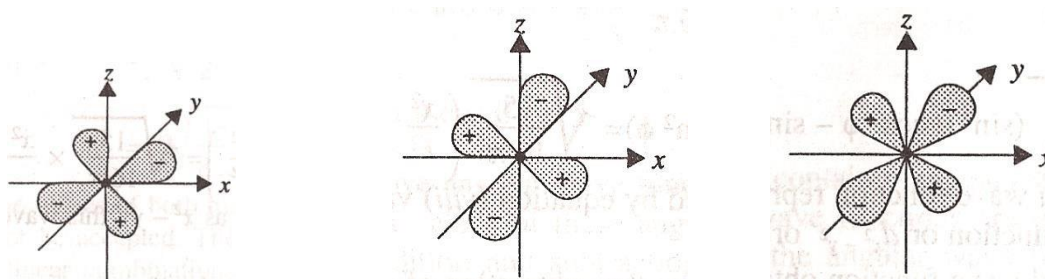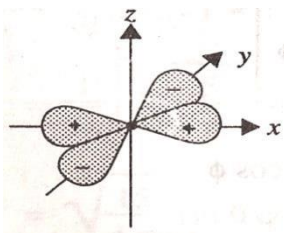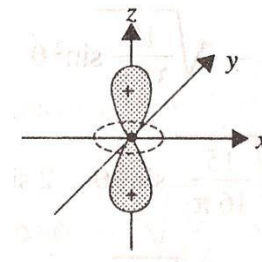
d_{xy} orbital d_{yz} (or d_{xz}) orbital d_{zx}orbital

d_{x2-y2} orbital d_{z2} orbital

Fig. 2.2   Angular dependence and shapes of d-orbitals.

The probability density is the square of the wave function and is positive everywhere. The lobes on the positive or negative side of both the axes are assigned (+) sign and those on positives side of one axis and negative side of the other or vice versa are assigned (–)sign.

The characteristics of the d-orbitals may be summarised as follows:

(i) d_{xy}, d_{yz} and d_{zx} (or d_{xz}) as well as d_{x2-y2} orbitals are double dumb-bell shaped and contain four lobes. The lobes of the first three orbitals are concentrated between xy, yz and zx planes, respectively and lie between their coordinate axes. The lobes of d_{x2-y2} orbital are concentrated along x and y axes. d_{z2} orbital has a dumb-bell shape with two lobes along z-axis with (+) sign and a concentric collar or ring around the nucleus in xy plane with (–)sign.

(ii) The d-orbitals belonging to same energy shell are degenerate, i.e. have the same energy in a free atom.

(iii)The d-orbitals belonging to all main energy shells have similar shape but their size goes on increasing as the value of n and number of nodal points increase. For example, the size of 5dorbital (number of nodal points = 5 – 2–1=2) is larger than that of 4d-orbital (number of nodal points = 4 – 2 – 1=1).

N.B. The shapes of f, g etc. orbitals are beyond the scope of the text.

2.9. *FILLING OF ELECTRON IN VARIOUS ORBITALS :THE AUFBAU PRINCIPLE*

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Aufbau is a German word which means building up or construction. The building up of orbitals implies the filling of orbitals with electrons. This principle gives us the sequence in which various orbitals are filled with electrons. The principle can be stated as "**in the ground state of poly electronic atoms, the electrons are filled in various subshells in the increasing order of their energy".** This means the electrons are filled in the subshell of the lowest energy first followed by the higher energy subshells. There are certain rules which constitute the Aufbau principle:

i)In general, the subshells with lower n values are filled first followed by those with higher nvalues (called lower n rule).

ii)For any given principal quantum number n, the order of filling up of subshells is s, p, d and f.

iii) (n +l) Rule; sometime lower (n + l) rule is violated. In such cases (n+l) rule is applicable according to which the subshells are filled in order of increasing (n+l) values, e.g., 4s- subshell [(n+l) = 4+0 equal to 4] is filled before 3d subshell [(n+l) =3+ 2 equal to 5) due to lower (n+l) values. Keeping in mind the above discussion, various subshells can be arranged in the order of increasing energy as follows:
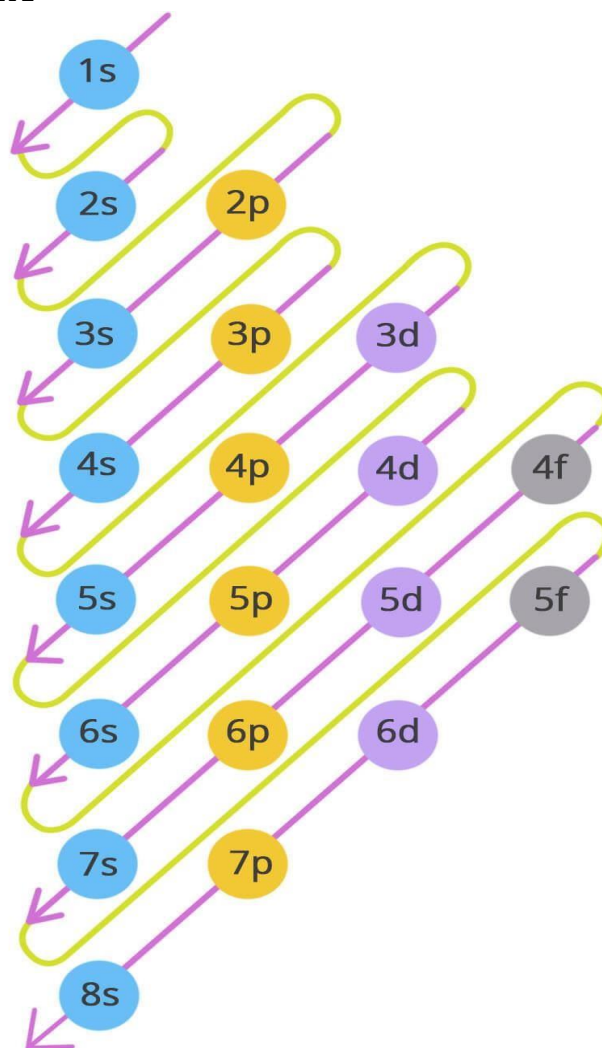
Energy sequence of sub shells for electron filling

This relative order of energy of various subshells of an atom may also be given as follows:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d …$
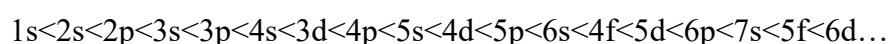
The electrons are filled according to this order only in polyelectron atoms. Configurations of lanthanum (La, Z = 57) and actinium (Ac, Z = 89) are the exceptions where the last electron enters 5d and 6d-subshells instead of 4f and 5f-subshells against the Aufbau's lower (n + l) rule though (n+l) values are same for 4f and 5d as well as 5f and 6d-subshells. **Electronic configuration of elements:**

Based on the Pauli's exclusion principle, Hund's maximum multiplicity rule and Aufbau principle, we can formulate a system for electron distribution in atoms and electronic

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configuration of the elements can be worked out. By electron distribution, we mean arrangement of electrons in various atomic orbitals and subshells.

Looking at the relative energy sequence of subshells of atoms in the elements, it can be concluded that we can work out and write down the electronic configuration of the elements straightaway up to argon (Ar, Z = 18) as follows:

Name of the element	Symbol with atomic number	Electronic configuration
Hydrogen	H (Z = 1)	$1s^1$
Helium	He (Z = 2)	$1s^2$
Lithium	Li (Z = 3)	$[He] 2s^1$
Beryllium	Be (Z = 4)	$[He] 2s^2$
Boron	B (Z = 5)	$[He] 2s^2 2p^1$
Carbon	C (Z = 6)	$[He] 2s^2 2p^2$
Nitrogen	N (Z = 7)	$[He] 2s^2 2p^3$
Oxygen	O (Z = 8)	$[He] 2s_2 2p_4$
Fluorine	F (Z = 9)	$[He] 2s^2 2p^5$
Neon	Ne (Z = 10)	$[He] 2s^2 2P^6$
Sodium (Natrium)	Na (Z = 11)	$[Ne] 3s^1$
Magnesium	Mg (Z = 12)	$[Ne] 3s^2$
Aluminium	Al (Z = 13)	$[Ne] 3s^2 3p^1$
Silicon	Si (Z = 14)	$[Ne] 3s^2 3p^2$
Phosphorus	P (Z = 15)	$[Ne] 3s^2 3p^3$
Sulphur	S (Z = 16)	$[Ne] 3s^2 3p^4$
Chlorine	Cl (Z = 17)	$[Ne] 3s^2 3p^5$
Argon	Ar (Z = 18)	$[Ne] 3s^2 3p^6$

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If we try to write down the electronic configuration of potassium (Kalium) (K, Z=19) according to above trend, the last electron must go to the 3d subshell, i.e. K_{19} = [Ne] $3s^2 3p^6 3d^1$ or [Ar] $3d^1$, but this electron is said to enter the 4s–subshell according to lower(n+l)rule of Aufbau principle. This may also be explained on the basis of effective nuclear charge given at the end of this topic. The (n + l) value for 4s = 4+0 is equal to 4 and for 3d, it is 3+2 is equal to5. Hence the electronic configuration of potassium (K, Z =19) is $[Ar_{18}]$ $4s^1$ and that for calcium (Ca, Z = 20), the next higher element, is [Ar] $4s^2$. Again, the last electron in the atom of the next element, Sc, (Z = 21) has the opportunity to occupy either 3d or 4p-subshell because both are available to it. The (n+l) values for 3d (3+2=5) and 4p (4+l = 5) are same and electron prefers to enter that subshell which has lower n value, i.e. 3d-subshell according to lower n rule of Aufbau principle. The filling of 3d-subshell goes on up to zinc (Z = 30).

The electronic configurations of the elements with Z = 21 to 30 are given below:

Name of the Symbol with atomic number	Electronic Configuration
Sc (Z = 21)	[Ar] $4s^2 3d^1$
Ti (Z = 22)	[Ar] $4s^2 3d^2$
V (Z = 23)	[Ar] $4s^2 3d^3$
Cr (Z = 24)	[Ar] $4s^1 3d^5$
Mn (Z = 25)	[Ar] $4s^2 3d^5$
Fe (Z = 26)	[Ar] $4s^2 3d^6$
Co (Z = 27)	[Ar] $4s^2 3d^7$
Ni (Z = 28)	[Ar] $4s^2 3d^8$
Cu (Z = 29)	[Ar] $4s^2 3d^{10}$
Zn (Z = 30)	[Ar] $4s^2 3d^{10}$

The next six elements, *viz*. Ga_{31}, to Kr_{36} belong to p-block and the last electron, as is evident, enters the 4p – subshell of the atoms of these elements. The electronic configurations of these elements are as follows:

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Gallium	Ga (Z = 31)	[Ar] $4s^2\, 3d^{10}\, 4p^1$
Germanium	Ge (Z = 32)	[Ar] $4s^2\, 3d^{10}\, 4p^2$
Arsenic	As (Z = 33)	[Ar] $4s^2\, 3d^{10}\, 4p^3$
Selenium	Se (Z = 34)	[Ar] $4s^2\, 3d^{10}\, 4p^4$
Bromine	Br (Z = 35)	[Ar] $4s^2\, 3d^{10}\, 4p^5$
Krypton	Kr (Z = 36)	[Ar] $4s^2\, 3d^{10}\, 4p^6$ or $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6 3d^{10} 4s^2\, 4p^6$

In next two elements of 5th period, the last electron goes to 5s- subshell. (s-block):

Rubedium	Rb (Z = 37)	[K_r] $5s^1$
Strontium	Sr (Z = 38)	[K_r] $5s^2$

Filling of 4d – subshell begins in the next element, yttrium, Y (Z = 39) and ends at cadmium, Cd (Z = 48) {Y: [Kr] $5s^2\, 4d^1$ to Cd: [Kr] $5s^2\, 4d^{10}$} with anomalies in the configurations of ^{42}Mo, ^{46}Pd and ^{47}Ag as shown below. In the next six elements of p-block, electron filling occurs in 5p – subshell, i.e. Indium ^{49}In: [Kr] $5s^2\, 4d^{10} 5p^1$ to Xenon, ^{54}Xe : [Kr] $5s^2\, 4d^{10}\, 5p^6$ or $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6 3d^{10} 4s^2\, 4p^6\, 4d^{10}\, 5s^2 5p^6$. Next two elements caesium ^{55}Cs and barium, ^{56}Ba are s-block elements and the last electron in these elements enters the 6s-subshell. ^{55}Cs: [Xe] $6s^1$ and ^{56}Ba: [Xe] $6s^2$. Next element lanthanum ^{57}La, belongs to d-block: [Xe] $6s^2\, 5d^1$ and is followed by 14 lanthanides: cerium, ^{58}Ce to lutetium, ^{71}Lu in which electron filling takes place in f-subshell except ^{64}Gd and ^{72}Lu in which the last electron enters d-subshell due to f^7 and f^{14} stable configuration but these show close resemblance with other f-block elements and have been placed with them in the periodic table.

It is observed that in case of chromium (Cr, Z = 24) and copper (Cu, Z = 29), the electronic configurations are against the trend. These configurations have been obtained experimentally by spectroscopic studies. Simple explanation to these anomalies can be given as under. For Cr and Cu, d-electrons being higher in number contribute more towards the stability of the atoms. Because d^5 (just half filled) and d^{10} (completely filled) configurations are more stable compared to d^4 and d^9 configurations, electronic transition occurs from s to d-subshells in these elements

(due to exchange energy effect and symmetry of orbitals), i.e. Cr: $4s^2 3d^4 \rightarrow 4s^1 3d^5$ and Cu : $4s^2 3d^9 \rightarrow 4s^1 3d^{10}$. s- electrons being less in number have little effect in this pursuit. Similar anomalies have also been observed in the higher homologues of these elements, *viz*. ,molybdenum (Mo, Z = 42) : [Kr] $5s^1 4d^5$ and silver (Ag, Z = 47) : [Kr] $5s^1 4d^{10}$. Palladium (Pd, Z = 46) contains another typical configuration: [Kr] $5s^0 4d^{10}$. Also there are anomalies in the configurations of lanthanides and actinides.

The important point to be noted here is that during the filling of electrons, these enter first in ns-subshell and then (n-1) d or (n-2) f-subshell. But during the removal of electron (s), it is first removed from n^{th}s orbital rather than (n-1) d or (n-2) f-subshell though $E_{ns} < E_{n-1d} < E_{n-2f}$ and removal of the electron must occur from higher energy subshell. For example, in case of first transition series (3d-series) elements filling and removal of 4-s-electrons occurs first followed by 3d-electrons. This is, perhaps, because after filling of d-subshell, it becomes of lower energy than 4s-subshell.

2.10. PAULI'S EXCLUSION PRINCIPLE

This principle was proposed by Pauli in 1924 and as an important rule, governs the quantum numbers allowed for an electron in an atom and determines the electronic configuration of poly electron atoms. In a general form, this principal states that "In **an atom, any two electrons cannot have the same values of four quantum numbers**". Alternatively, this can be put in the form "**any two electrons in an atom cannot exist in the same quantum state".** Consequently, it can be said that any two electrons in an atom can have same values of any three quantum numbers but the fourth (may be n or l or m or s) will definitely have different values for them. This can be shown as follows:

For any two electrons in an atom	Values of quantum numbers			
	n	l	m	s
	same	same	same	different
	same	same	different	same

same	different	same	same
same	same	same	same

Thus the values of all the four quantum numbers for any two electrons residing in the same orbital like s, p_x, p_y, p_z, d_{xy} etc. cannot be the same. For example, in case of 2 electrons in 1sorbital (i.e. $1s^2$), the values of n, l and m are same for both the electrons but s has different values as shown below:

	n	**l**	**m**	**s**
1st electron	1	0	0	$+\frac{1}{2}$
2nd electron	1	0	0	$-\frac{1}{2}$

For $1s^2$ electrons

The values of s may also be written in the reverse order but by convention the given order is preferred. The important conclusion drawn from this discussion is that "**an orbital can accommodate only two electrons with opposite spins**"

Application of Pauli's Exclusion Principle

This principle has been used to calculate the maximum number of electrons that can be accommodated in an orbital, a subshell and in a main shell. For example, for K-shell, n=1, l=0 and m=0 and s can have a value equal to either $(+)\frac{1}{2}$ or $(-)\frac{1}{2}$. These values of n, l, m and s give two sets of values of four quantum numbers as gives above. It is concluded that in Kshell,there shall be only one subshellwith one orbital i.e. the s-orbital is present which can contain only two electrons with s = $(+)\frac{1}{2}$ and $(-)\frac{1}{2}$.

For L-shell, n=2, l=0 and 1. The corresponding values of m are 0 (for l=0) and +1, 0, -1 (for l=1). For each value of m, s will have two values, $(+)\frac{1}{2}$ and $(-)\frac{1}{2}$. This leads to eight sets of quantum numbers belonging to eight different electrons. These are shown below:

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$n = 2,\ l = 0,\ m = 0,\ s = +\frac{1}{2}$ $\left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}$ These values correspond to two

$n = 2,\ l = 0,\ m = 0,\ s = -\frac{1}{2}$ elections in 2s – orbital.

$n = 2,\ l = 1,\ m = +1,\ s = +\frac{1}{2}$ $\left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}$ These values correspond to

two $n = 2,\ l = 1,\ m = +1,\ s = -\frac{1}{2}$ elections in $2p_x$ – orbital.

$n = 2,\ l = 1,\ m = 0,\ s = +\frac{1}{2}$ $\left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}$ These values correspond to two

$n = 2,\ l = 1,\ m = 0,\ s = -\frac{1}{2}$ elections in $2p_y$ – orbital.

$n = 2,\ l = 1,\ m = -1,\ s = +\frac{1}{2}$ $\left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}$ These values correspond to two $n =$

$2,\ l = 1,\ m = -1,\ s = -\frac{1}{2}$ elections in $2p_z$ – orbital.

By convention, the first p-orbital is denoted as p_x, second as p_y and third as p_z-orbital as given above.Therefore, we can say that an orbital can accommodate maximum two electrons. Further, since same values of 1 for a particular value of n corresponds to a particular subshell, total number of electrons in a subshell can be calculated, e.g., s-subshell contains two and psubshell (l=1) will accommodate six electrons, respectively. Thus total number of electrons in L-shell will be eight (2 in s and 6 in p-subshell). Likewise, one can calculate total number of electrons in M-shell (18) and N- shell (32) etc. as well as d (10) and f (14) subshells.

2.11 HUND'S RULE OF MAXIMUM MULTIPLICITY

This rule states that "**electron pairing in the orbitals of a subshell will not take place until each orbital is filled with single electron**" (due to same energy of orbitals of a subshell). This is because it is easier for an electron to enter an empty orbital than an orbital which already possesses an electron.

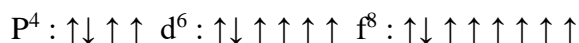If an atom has three electrons in p-subshell, these can be arranged in three p-orbitals as follows:

↓↑ ↑   ↑ ↓ ↑   ↑ ↑ ↑

(**a**)   (**b**)   (**c**)

Among these arrangements, the option(**c**) is the correct arrangement because this rule can be stated alternatively as "**the most stable arrangement of electrons in the orbitals of a subshell is that with greatest number of parallel spins**". It implies that before pairing starts, all the electrons of the subshell have the same spins (parallel).

This rule serves as a guideline for filling of multi orbital p, d and f subshells, e.g., the electron pairing in p, d and f-subshells will not start until each orbital of the given subshell contains one electron. Thus pairing starts in the three orbitals of p-subshell at fourth electron, in five orbitals of d-subshell at sixth electron and in seven orbitals of f-subshell at eighth electron, respectively. The electronic arrangements (or configurations) for p^4, d^6 and f^8 systems have been illustrated here along with p^3, d^5 and f^7:

$P^3 : \uparrow \uparrow \uparrow$ $d^5 : \uparrow \uparrow \uparrow \uparrow \uparrow$ $f^7 : \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$

$P^4 : \uparrow\downarrow \uparrow \uparrow$ $d^6 : \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$ $f^8 : \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$

Here p^3, d^5 and f^7 provide the examples of maximum multiplicity in the respective subshells and p^4, d^6 and f^8 provide the examples where pairing of electrons in these subshells starts.

2.12.SUMMARY

This unit contains the text related with the atom and molecules basic description and define the fundamental particles of nucleus. This unit also define the atomic number and mass number basic definition and how to calculated both one. Basically explain rules governing the filling of atomic orbitals such as Pauli's exclusion principle, Hund's rule and Aufbau principle has been given. The electronic configuration of elements has effectively been discussed with examples and the limitations are also given. At the last,applications have been given briefly.

2.13 TERMINAL QUESTIONS

i)Discuss the angular wave function and correlation between this wave function   and

shape of p-orbitals.

ii) Calculate the atomic mass of the following :

a) If P = 26 , N= 30   b) P= 18 , N= 16

iii)How many electrons can be contained in fourth hell of an atom and why?

iv) Write a short notes on Hund's rule of maximum multiplicity with example?

v)Explain the Pauli's Exclusion Principle with suitable Application ?

vi)Write down the electronic configurations of the elements with Z = 46, and 71.

vii) Define the energy sequence of subshells for electron filling by Aufbau Principle: viii)

Calculate the number of electrons, protons, and neutrons in the (16^8O) atoms.

ix) Short notes on: a) Isotopes   b) Mass number

x) Define the Bohr's atomic theory postulates?

2.14 REFERENCES AND FURTHER STUDIES

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UNIT 3: MOLECULES AND BONDING

CONTENTS

3.1 OBJECTIVES

The objective of writing the text of this unit is to enable the readers to understand various facts regarding the driving force that makes the isolated atoms to combine to form the polyatomic molecules or ions as well as to find the answers of certain interesting questions such as: What is a chemical bond? What is the basic difference between polar and non polar bond? What are ionic

bond? What happens to the energy of the atoms and the molecules? What happens in terms of electronic structure, while bond formation takes place? Why do the group 18 elements, i.e. the noble gases, generally not participate in bond formation and suffer from lack of reactivity while almost all other elements do so? etc.This unit also very helpful to explain the geometry of various compound on the basis of hyberization, VSEPRT concept and also define the various enery levels , filling of electron in various levels as well as magnetic behaviours ,various bond order etc.

3.2INTRODUCTION

The atoms are said to combine together because of the following two main reasons:

i) Concept of lowering of energy

It has been observed that the aggregate (or the molecules) are lower in energy than the individual atoms from which they have been formed. This means when the individual atoms combine to form molecules through a bond, the potential energy of the combining atoms decreases and the resulting molecules are more stable than the free atoms. This energy difference between the free atoms and bonded atoms (or molecules) is generally 40kJ mol^{-1} or more. It follows from this that the process of bond formationbetween the atoms decreases the energy of the molecule formed from these atoms and forms a system of lower energy and greater stability.

(i)   Electronic theory of valence (the octet rule)

The atoms of the noble gases-helium to radon- do not, except a few cases, react with any other atoms to form the compounds and also they do not react with themselves. Hence they stay in atomic form. These atoms are said to have low energy and cannot be further lowered by forming compounds. This low energy of noble gas atoms is associated with their outer shell electronic configuration, i.e. the stable arrangement of eight electrons (called octet). It has also been established that the two electrons in case of helium atom (called doublet) is as stable as an octet present in other noble gas atoms. The chemical stability of the octet of noble gases led chemists to assume that when atoms of other elements combine to form a molecule, the electrons in their outer shells are arranged between themselves in such a way that they achieve a stable octet of electrons (noble gas configuration) and thus a chemical bond is established between the atoms. This tendency of the atoms to attain the noble gas configuration of eight electrons in their outer shell

is known as octet rule or rule of eight and when the atoms attain the helium configuration, it is called doublet rule or rule of two. This octet rule was later called **"Electronic**

Theory of Valence".

It may be noted here that in the formation of a chemical bond, atoms interact with each other by losing, gaining or sharing of electrons so as to acquire a stable outer shell configuration of eight electrons. This means, an atom with less than eight electrons in the outer shell is chemically active and has a tendency to combine with other atoms. Accordingly, three different types of bonds may exist in the molecules/aggregates.

3.3 MOLECULES AND CHEMICAL FORMULA

A.Molecules :

A molecule is define as an electrically neutral group, may consist of two or more atoms of a single element or atoms of different elements, by chemical bonds. Some examples of molecules:Molecules are classified according to their composition are:

a)Diatomic molecule : A diatomic molecule consists of only two atoms. These may be atoms of a single element or atoms of different elements.

Example : O_2 is an example of single elements and HCl is an example of a diatomic Molecules of different elements.

b)Polyatomic molecule : A polyatomic molecule consists of more than two atoms.

Example Glucose ($C_6H_{12}O_6$) ,Ammonia (NH_3) ,water (H_2O) etc.

c)Macromolecule : A macromolecule is a very large molecule, often consisting of subunits Example: Proteins , DNA etc.

On the basis of chemical bonds molecules is classify as:

a)Ionic molecule: Ionic molecules consist of both metals and nonmetals In ionicmolecules

cation (first part of the molecule) and anion (second part of the molecule) have very different

electronegativity values resultant molecules display extreme polarity.

Example: NaCl, NaOH, CH_3COONH_4

b)Covalent molecule: Covalent molecules consist of atoms connected by covalent chemical bonds.Covalent molecules consist of nonmetals. In a pure covalent molecule, the atoms have the same electro negativity values.

Examples : H_2 , O_2 H_2O etc. **B.Chemical formula :**

A chemical formula tells us the number of atoms of each element in a compound. It contains the symbols of the atoms of the elements present in the compound as well as how many there are for each element in the form of subscripts.

Types of chemical formula:

- Empirical formula: The chemical formula which showing the simplest ratio of elements in a compound rather than the total number of atoms in the molecule.
- Molecular formula.: The chemical formula that gives the total number of atoms of each element present in a molecule.
- Structural Formula: Structural formulas identify the location of chemical bonds between the atoms of a molecule. A structural formula consists of symbols for the atoms connected by short lines that represent chemical bonds—one, two, or three lines standing

  for single, double, or triple bonds, respectively.

Rules of Writing Chemical Formula: The following rules should be adhered to write the chemical formula of a binary compounds:

- One must know the valencies of the two elements or radicals present.
- In a chemical formula, the sum of the total number of positive and negative valencies present in the compound should be zero. This can be done by finding the lowest common multiple of the two valencies.
- If present, you must always place the metal at the beginning of the formula.

Example: Write the chemical formula for magnesium chloride.
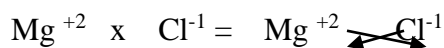
Valences of elements and radicals:

Mg = 2 (Group II) ,   Cl = -1 (Group VIIa)

The lowest common multiple of valences = 2

Mg = 2 x 1 = 2   Cl = 1 x 2 = 2

Mg^{+2} x Cl^{-1} = Mg^{+2} Cl^{-1}

Now, chemical formula for magnesium chloride is = $MgCl_2$

3.4 MOLAR MASS AND AVOGADRO'S NUMBER

Molar mass: The molar mass of a substance is the mass (in grams per mole) of 6.022×10^{23} atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

Avogadro's number :Avogadro's number number of units in one mole of any substance (defined as its molecular weight in grams), equal to 6.0221×10^{23}. The units may be electrons, atoms, ions, or molecules, depending on the nature of the substance and the character of the reactions.

3.5 IONIC BOND AND IONIC COMPOUNDS:

Ionic bond, also called electrovalent bond, type of linkage formed from the electrostatic attraction between oppositely charged ions in a chemical compound.Such bond is formed complete transfer of one or more electron from the outermost energy shell of one atom to the outermost energy shell of the other atom.In this way atoms acquire the nearest noble gases electronic configurations.In ionic bond the atom that loses the electrons becomes a positively charged ion (cation), while the one that gains them becomes a negatively charged ion (anion).The electrostatic attraction between the oppositely charged ion results in the formation of a bond between them.This is called an ionic bond.
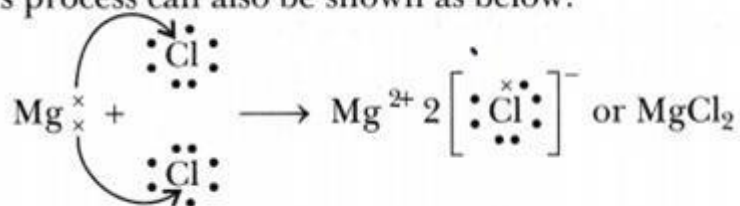
For example: **a) NaCl**

Sodium is a metal, and it can lose its one valence electron to become Na^+ ion(cation), Chlorine is a nonmetal, and it gains one electron to become an Cl^- ion (anion). By forming ions in this way, both atoms achieve a noble gas electron configuration.
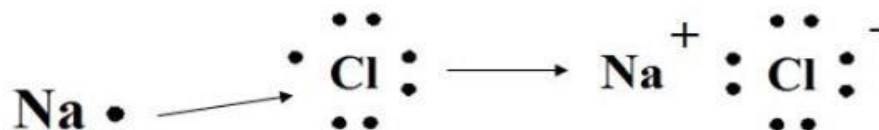
b)MgCl₂ : In MgCl₂ ionic bond is formed and this process has been done as follows.

Ionic compounds : An ionic compound usually consists of a metal and a non-metal. When lots of ions come together, they form large structures called ionic lattices. Ions in an ionic lattice arrange themselves in a regular, 3D shape with oppositely charged ions next to one another. This structure is also sometimes referred to as a crystal lattice. Like NaCl.
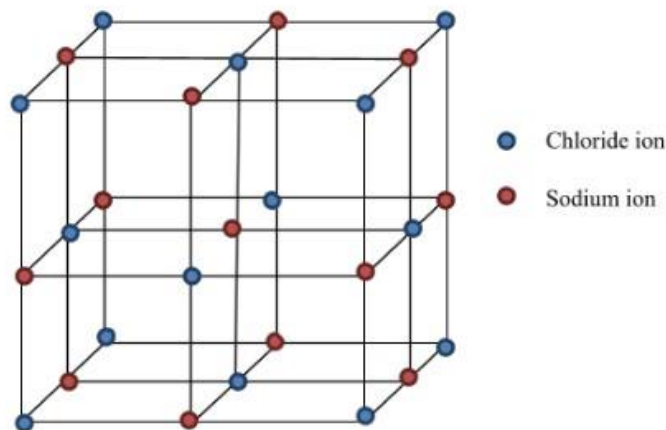
We will see that there are six chloride ions immediately surrounding a single sodium ion, so the coordination number of sodium is 6. Likewise, six sodium ions immediately surround each chloride ion, making the coordination number of chloride also equal to 6. Because the formula
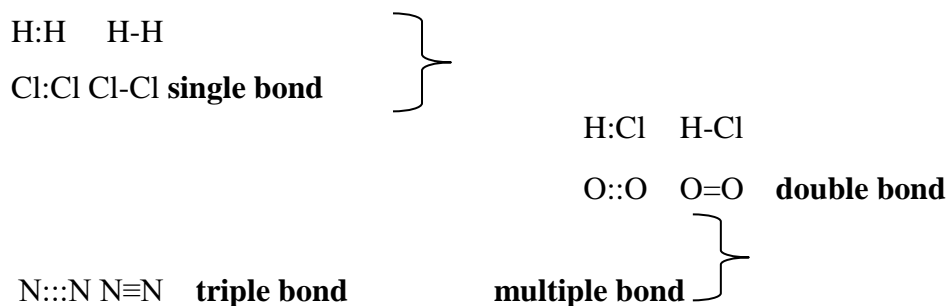
unit of sodium chloride displays a 1:1 ratio between the ions, the coordination numbers must be the same. These ionic bonds between the charged particles result in a giant structure of ions. Because the ions are held together tightly in these giant structures it takes a lot of energy to break all the bonds. As a result, ionic compounds have high melting points and boiling points.

3.6 COVALENT COMPOUND BONDING

A covalent bond is formed between the two combining atoms, generally of the electronegative non-metallic elements by the mutual sharing of one or more electron pairs (from their valence shell). Each of the two combining atoms attains stable noble gas electronic configuration, thereby enhancing the stability of the molecule. If one electron pair is shared between the two atoms, each atom contributes one electron towards the electron pair forming the bond. This electron pair is responsible for the stability of both the atoms. A covalent bond is denoted by the solid line (-) between the atoms. Depending on the number of shared electron pairs i.e. one, two, three etc. electron pairs between the combining atoms, the bond is known as a single, double, triple etc. covalent bond. For example,

H:H   H-H

Cl:Cl Cl-Cl **single bond**

H:Cl   H-Cl

O::O   O=O   **double bond**

N:::N N≡N   **triple bond**   **multiple bond**

In the molecules, the bond strength and bond length has been found in the following order:

Bond strength: triple bond > double bond > single bond

Bond length: triple bond < double bond < single bond

It may be noted that the covalent bond formation between multielectron atoms involves only the valence shell electrons that too, the unpaired electrons. Thus O-atom has two unpaired electrons in its valence shell and N-atom has three unpaired electrons thereby forming two and three bonds with themselves or other atoms.

3.6.1 Polar and non-polar covalent bond

In the examples given above, most of the bonds *viz.* single, double and triple covalent bonds, have been shown to be formed between the like atoms such as H-H, Cl-Cl, O=O and N≡N in H_2, Cl_2, O_2 and N_2, respectively. The bonded atoms in these molecules attract the bonding or shared pair of electrons by equal forces towards themselves due to equal electronegativity of the atoms. Hence the bonding pair of electron lies at the mid point of the internuclear distance (or bond distance). This type of bond is known as the non-polar covalent bond.

But if the covalent bond is formed between two unlike atoms of different elements, e.g. HCl, H_2O, NH_3 etc., the shared pair of electrons will not be equally attracted by the bonded atoms due to electronegativity difference. It shifts towards more electronegative atom and hence moves away from less electronegative atom. This develops small negative charge on more electronegative atom and equal positive charge on less electronegative atom.Such a molecule is called a polar molecule (this is different from ionic bond) and the bond present in such molecules is known as polar covalent bond. For example,

Expected mid point position of bonded pair (I) → Actual position (II)
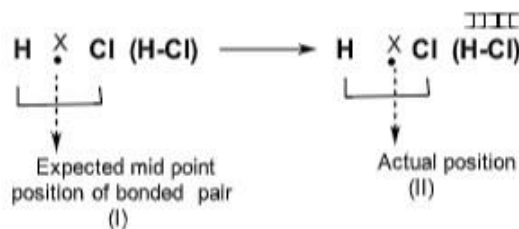
Fig 3.1

## 3.6.2 Directional characteristics of covalent bond:

The covalent bonds are directed in space. This fact is evidenced by the stereoisomerism and a wide variety of geometrical shapes shown by the covalent compounds. It is also possible to measure the actual bond angles between covalent bonds in the molecules because of the directional nature of bonds. An important fact about the covalent bonds is that these are formed by the overlapping of pure as well as hybridised atomic orbitals. All these atomic orbitals except the pure s-orbitals, are oriented in the particular directions which determine the direction of covalent bonds i.e. the direction in which the overlapping orbitals have the greatest electron density. From this discussion we can conclude that it is the directional nature of p, d and f orbitals which accounts for the directional nature of the covalent bond. For example, the three porbitals are directed along the three axes x,y and z and the bonds formed by their overlapping are also directed towards the three

axes. Though the s-orbitals are spherically symmetrical around the nucleus, their overlapping along the molecular axis gives a bond in that direction.

Let us discuss the modes of overlapping of pure and some of the hybridised atomic orbitals: **i)s-s overlapping:**

This type of overlapping occurs between the s-orbitals of the combining atoms thereby giving The s-s covalent bond. . s-s covalent bond. in the direction of molecular or internuclear axis
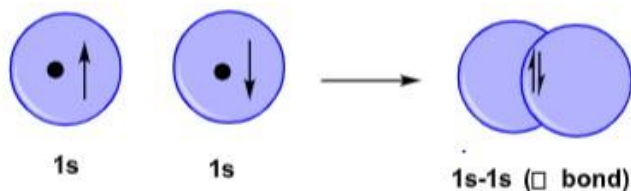
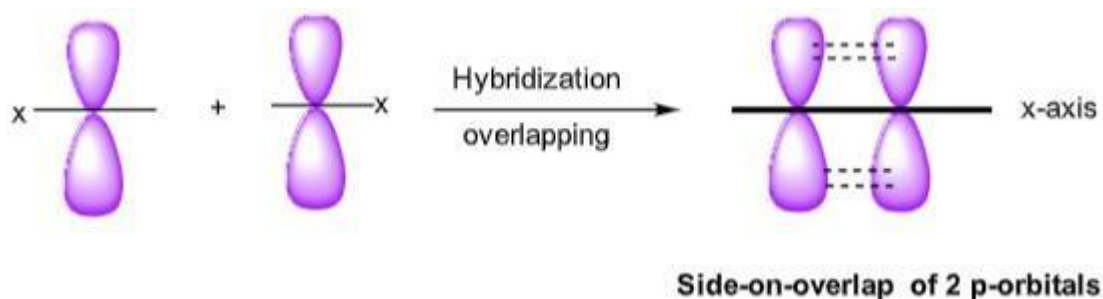*Fig 3.2 ovrelapping of two s-orbitals along molecular axis*

ii) s-p overlapping:

The overlapping taking place between the s-orbital of one atom and p-orbital of another atom iscalled s-p overlapping. The resulting bond is the s-p covalent bond formed in the direction ofthe orientation of p-orbital taking part in overlapping.
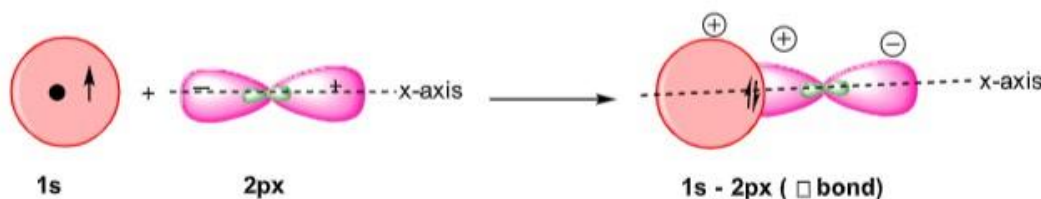
*Fig 3.3 overlapping of s and p orbitals along molecular axis* **iii)p-p overlapping:**

When the p-orbital of one atom overlaps with the p-orbital of another atom, this process is called p-p overlapping and the bond so formed is known as p-p covalent bond. The necessary condition for this type of overlapping is that the p-orbitals must be of the same type, i.e. p_x and p_x, p_y and p_y and p_z and p_z. The p_x-p_y or p_x-p_z type of overlapping does not occur.

Side-on-overlap of 2 p-orbitals

Fig 3.4 overlapping of two p-orbitals along molecular axis

If an atom possesses two or three half filled orbitals, they can simultaneously overlap with another similar atom (or other atoms as well) thereby forming multiple bonds (both σ and π), for example oxygen molecule.Similarly bonding in N_2 can be explained
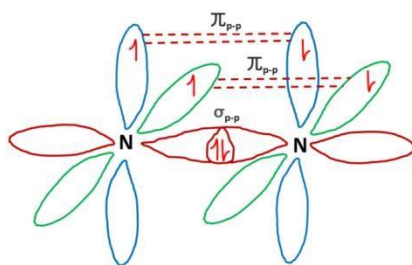
Fig 3.5 overlapping of orbitals forming σ and πbonds

iv)Overlapping of the hybrid orbitals with pure atomic orbitals:

The s and p-orbitals may overlap with hybrid orbitals to give the directional covalent bonds such as s-sp(B_eH_2), s-sp^2(BH$_3$,C_2H_4), s-sp^3 (CH$_4$ and higher alkanes), p-sp (B$_e$Cl$_2$), p-sp^2 (BCl$_3$), p-sp^3 (CCl$_4$), p-sp^{3}d (PCl$_5$), p-sp^{3}d^2 (SF$_6$) p-sp^{3}d^3(IF$_7$) etc. bonds in the directions of hybrid orbitals. d and f - orbitals in non-metallic elements (which mostly form covalent compounds) do not generally take part in overlapping as such to form covalent bonds but d- orbitals may participate in hybridisation, e.g. in PCl$_5$, SF$_6$, higher intehalogens etc. and form covalent bonds by the overlapping of hybrid orbitals with atomic orbitals in the directions of hybrid orbitals.

**v)** Overlapping of the hybrid orbitals among themselves. This type of overlapping mainly occurs among the organic compounds, e.g. sp-sp(C_2H_2), sp^2-sp^2(C_2H_4), sp^3-sp^3(C_2H_6) etc. Here only the overlapping of hybrid orbitals with themselves has been given.

3.6.3 Sigma (σ) and pi (π) covalent bonds:

σ Covalent bonds

The covalent bond formed between the two atoms by axial or head on overlapping of pure or hybrid atomic orbitals belonging to valence shells of the atoms is called a σ bond. Pure s-orbitals of the atoms on overlapping with s or p atomic orbitals or hybrid orbitals of other atoms always form σ bonds. Pure p-orbitals of the atom when overlap with s and p-orbitals (of the same symmetry) or hybrid orbitals of other atoms also form σ bonds. d and f- orbitals by themselves seldom take part in σ bond formation through the d-orbitals are sometimes involved in hybridisation and thus form a σ bonds, e.g. PCl_5, SF_6, IF_7 etc. The overlapping of hybrid orbitals between two atoms always gives σ bond.

(i)   Pure atomic orbital – pure atomic orbital overlapping
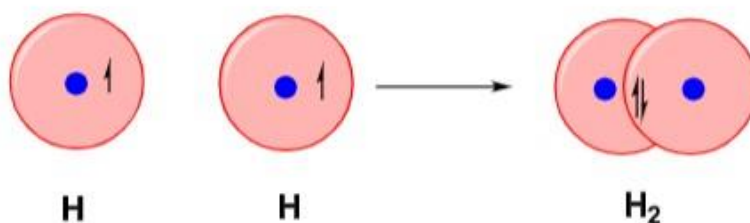
Fig 3.6(a) formation of σbond by atomic orbitals

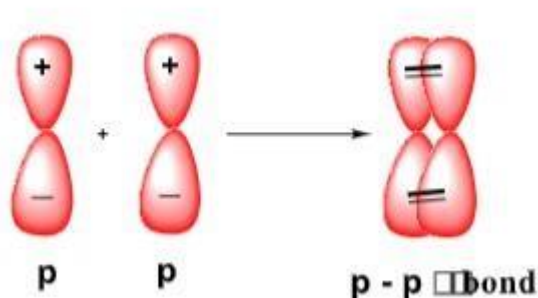**(ii)   Hybrid atomic orbital – hybrid atomic orbital overlapping**
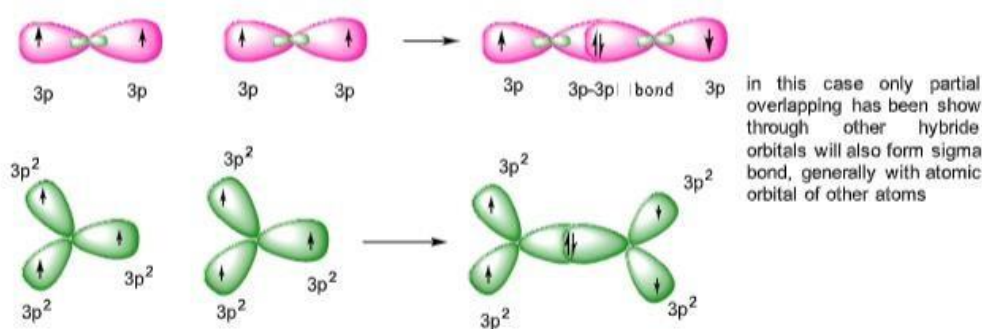
Fig 3.6(b) formation of σbond by hybrid orbitals

In this case only partial overlapping has been shown though other hybrid orbitals will also form σ bonds, generally with atomic orbitals of other atoms.Similarly sp^3-sp^3σ bond formation may also be shown.

π (pi) Covalent bond

A covalent bond formed between two atoms by side to side or lateral (perpendicular to the molecular axis) overlapping of only p-atomic orbitals or sometimes p and d- orbitals belonging to the valence shell of the atoms is called a π bond. If in a molecule, a particular atom uses one of its p-orbitals for σbond formation then rest of the two p-orbitals are used to form the πbonds by lateral overlapping. For example, if x axis is taken as the molecular axis, then πbond is formed by p_y - p_y or p_z-p_z overlapping as happens in the oxygen and nitrogen molecules.

p   p   p - p $\square$bond

Fig3.7 formation of πbond by lateral overlapping of atomic orbitals   Fo rσ and π bonds, the following points are important:

i)A σbond is formed by axial overlapping of either pure or hybrid atomic orbitals of the two combining atoms while a πbond results from the lateral overlapping of the pure atomic orbitals.

ii)A σbond is stronger than a πbond due to greater extent of overlapping of orbitals along the inter nuclear axis than in lateral overlapping.

iii)A σbonds determine the direction of the covalent bond and bond length, πbonds have no effect on the direction of the bond. However, their presence shortens the bond length.

iv)There is free rotation of the atoms about a σbond because the electron cloud overlaps symmetrically along the internuclear axis while this is not possible about a πbond because the electron clouds overlap above and below the plane of the atoms.

v)A σ bond has its free existence between any two atoms in a molecule while πbond is formed between the atoms only when σ bond already exists.

3.7 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The valance bond theory also called the atomic orbital theory can explain the geometrical shape of many molecules/ions of both transition and non-transition elements by employing the concept of hybridisation. But many molecules/ions remain unexplained in terms of their geometry by this method. To overcome this shortcoming, a modification of VBT was developed by Gillespie and Nyholm which can predict the shapes of many species which are left uncovered by the concept of simple hybridisation. According to this theory "The shape or the geometry of a polyatomic molecule/ion of non-transition (mostly non-metallic) element depends upon the number and nature of the electron pairs contained in the valence shell of the central atom." Thus the electrons already present in the valence shell plus the additional electrons acquired by the central atom as a result of bonding with other atoms are called its valence shell electrons. These electrons may be present as bonding or non-bonding electron pairs in the central atom which arrange themselves in such a way that there is a minimum repulsion between them and the molecule has minimum energy and maximum stability. Since there can be only one orientation of orbitals corresponding to minimum energy, hence the molecule attains a definite shape/geometry.

The following rules have been proposed by Gillespie and Nyholm to explain the shape of some inorganic molecule/ions-

i)If the central atom of a molecule/ion contains only the bond pairs of electron in the valence shell, the geometrical shape of the molecule/ion is said to be regular (or undistorted) e.g. linear, trigonal planar, tetrahedral, octahedral etc., respectively. This fact is evidenced by the examples given above in the chapter of hybridisation.

ii) When the valence shell of the central atom in a molecule/ion contains the bonding electron pairs and non-bonded electron pairs (called lone pairs), the molecule/ion has distorted or irregular geometrical shape due to the alteration in bond angles which is caused by the presence of lone pairs on the central atom.

This happens because of the following fact. Since the lone pair of electrons is under the influence of only one nucleus (of central atom), i.e. mono centric, these electrons occupy a broader orbital with a greater electron density radially distributed closer to that nucleus than bonding pair of electrons which is under the influence of two nuclei of bonded atoms i.e. bicentric. Its location between the atoms depends on the electro-   negativities of the combining atoms. Thus lone pairs experience more freedom than the bonded pairs and hence exert more repulsion on any adjacent

electron pair than a bond pair does on the same adjacent electron pair. The repulsion among the electron pairs follows the sequence as:

l.p.-l.p. repulsion>l.p.-b.p. repulsion>b.p.-b.p. repulsion

maximum   intermediate   minimum
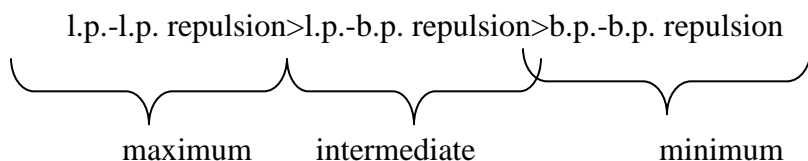
 Because of this fact, if the central atom in a molecule/ion contains both lone pairs (l.ps.) and bonded pairs (b.ps.), there occurs a contraction in the bond angle (which is formed between two adjacent b.ps.). More the number of l.ps. on the central atom, greater is the contraction caused in the bond angle. This statement is supported by the bond angles observed in CH_4, NH_3 and H_2O:

molecules	CH_4	NH_3	H_2O
Type of hybridisation involved	sp^3	sp^3	sp3
No. of l.ps. on the central atom	0	1	2
Bond angle	109.5^0	107.3^0	104.5^0
Contraction in the bond angle	-	$\approx 2^0$	$\approx 5^0$

iii) $\angle BAB$ in AB_2 type molecules decreases with increasing electronegativity of the atom B where A is a central atom. This is because as the electronegativity of the attached atom B increases, the b.p. of electrons moves away from the central atom and experiences less repulsion from its l.ps. and enhanced distance between two bond pairs also causes less repulsion between them resulting in the contraction in bond angle.

For example,   (i) $PI_3(\approx 102^0)>PBr_3(\approx 101.5^0)>PCl_3(\approx 100^0)$

(ii) $AsI_3(\approx 101^0)>As Br_3(\approx 100.5^0)> AsCl_3(\approx 98.5^0)$

iv)The repulsion between the electron pairs in filled shells is larger than that between electron pairs in incompletely filled shells. As an example, let us compare $\angle HOH$ and $\angle HSH$ in H_2O and H_2S molecules. It has been observed that$\angle HOH$ $(104.5^0)>>\angle HSH$ (92.2^0). In both the molecules, the central atoms O and S contain eight electrons in their valence shells, six of their own and two from H-atoms. Thus the valence shell of O-atom (with 2s and 2p orbitals only) is completely filled but that of S-atom is incompletely filled due to the availability of 3d-orbitals

(which remain vacant) in addition to 3s and 3p-orbitals. The total capacity of the valence shell of S-atom is to accommodate a maximum of 18 electrons (from $2n^2$ rule).

v)The bond angle involving the multiple bonds are generally larger than those involving only single bonds. However, the geometrical shape of the molecule is not affected by multiple bonds.

Limitations:

The VSEPR Theory suffers from certain limitations which are as follows:

i)This theory cannot explain the shapes of very polar molecules and those having an inert pair of electrons.

ii)The shapes of the molecules which have extensive delocalised πelectron systems are not explained by this theory. iii)This theory does not cover certain transition metal complexes.

The VSEPR Theory in combination with the concept of hybridisation has been successfully used to discuss and explain the geometrical shapes of most of the covalent inorganic molecules/ions.

Here we shall discuss the type of hybridisation and mode of bonding in certain inorganic molecule/ions in addition to those given in the syllabus of VSEPR theory.

A. Shape of SnCl₂ molecule (sp² hybridisation)

The central atom, Sn, has the ground state valence shell configuration as given below:

Sn_g: $5s^2 5p_x^1 p_y^1 p_z^0$ $\rightarrow$ sp^2 hybridization
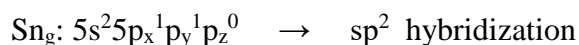
This atom undergoes partial hybridisation mixing up together the paired 5s and unpaird $5p_x$ and $5p_y$ -orbitals, leaving behind the empty p_z -orbital, to form three sp^2 hybrid orbitals one of which is occupied by the electron pair coming from the 5s-orbital. The process of hybridisation and overlapping of hybrid orbitals with atomic orbitals of Cl-atoms have been shown below:
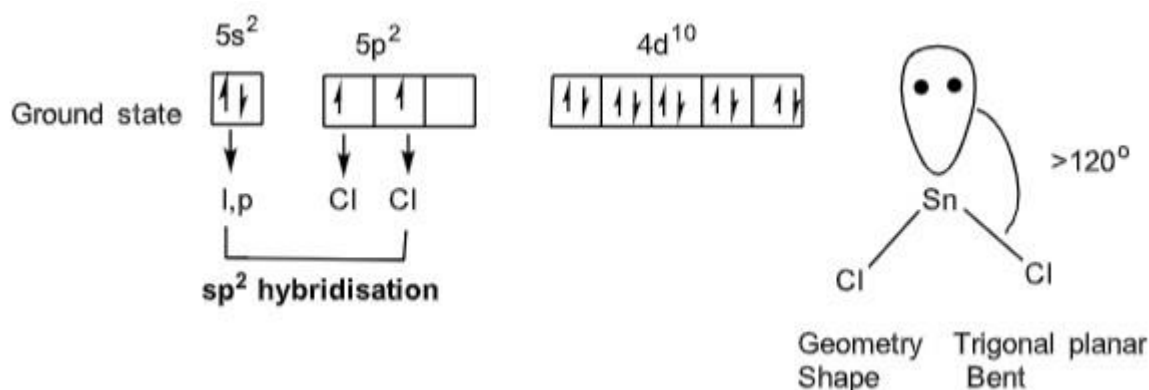
*Fig 3.8 Formation of hybrid orbitals and their overlapping with 3p-orbitals of Cl atoms to give SnCl₂ molecule*

Two unpaired hybrid orbitals of Sn atom overlap with unpaired p-orbitals of approaching Clatoms and give SnCl₂molecule which contains one lone pair of electrons on Sn-atom. Because of the

greater repulsion of lone pair on bond pairs, the $\angle$Cl SnCl is less than 120^0, the expected angle in case of sp^2 hybridisation. The molecule thus attains angular or bent shape.

B. Shape of NH₃ Molecule (sp³ hybridisation)

In NH_3 molecule, the central atom N has following ground state valence shell configuration:

$N_g : 2s^2p_x{}^1p_y{}^1p_z{}^1 \quad \rightarrow \quad sp^3$ hybridization
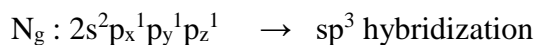
All these atomic orbitals participate in hybridisation and give four equivalent sp^3 hybrid orbitals. One of them contains an electron pair (lone pair) and three half filled hybrid orbitals then overlap with 1s orbitals of three H-atoms to form σcovalent bonds (N-H bond).
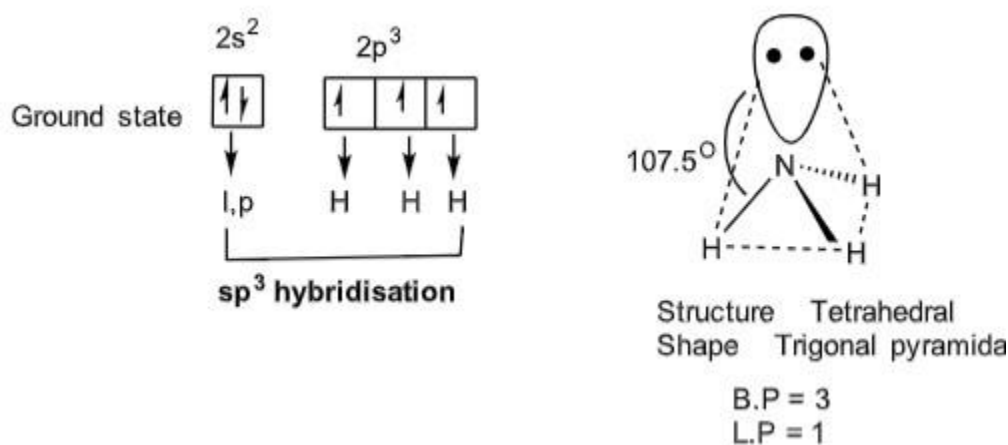

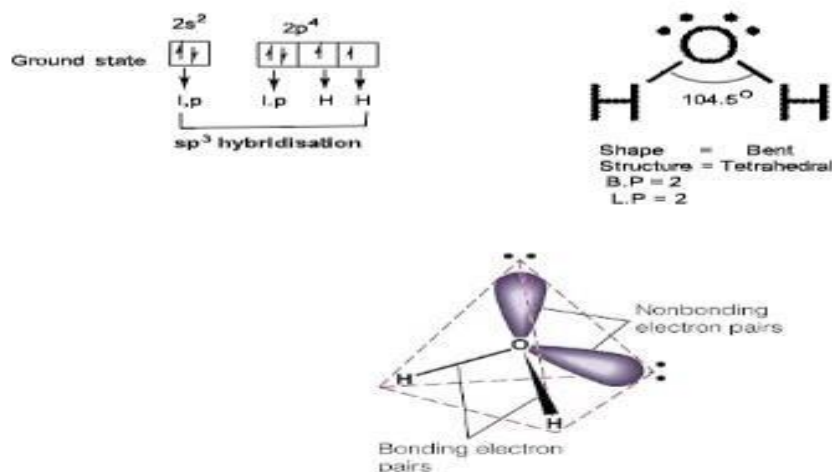*Fig 3.9 Formation of hybrid orbitals and their overlapping with 1s orbitals of 3H atoms to give NH₃ molecule*

From the figure, it is evident that one lone pair of electrons is present in NH_3 molecule which exerts more repulsion on bonded pairs than that operating between the bonding pairs of electrons. The net result is that the NH_3 molecule attains trigonal pyramidal shape with the bond angle of 107.3^0, a deviation of about 2^0 from the tetrahedral angle of 109.5^0.

C. Shape of H₂O Molecule (sp³ hybridisation)

The ground state valence shell configuration of the central atom O of H_2O molecule is:

$O_g: 2s^2p_x{}^2p_y{}^1p_z{}^1 \quad \rightarrow \quad sp^3$ hybridization
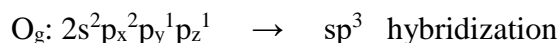
All these atomic orbitals undergo hybridisation and give rise to four equivalent sp^3 hybrid orbitals. Two of these hybrid orbitals are half filled and remaining two contain lone pairs of electrons. The unpaired hybrid orbitals than overlap with 1s orbitals of two H-atoms to form σcovalent bonds (O-H bonds).

Fig 3.10Formation of hybrid orbitals and their overlapping with 1s orbitals of two H-atoms to give H₂O molecule

There are two lone pairs of electrons present in H_2O molecule which exert strong repulsion on each other and move away towards the bonded pairs of electrons. This brings the bonded pairs closer to each other thereby causing contraction in the bond angle. H_2O molecule thus attains a V-shaped geometry with the bond angle of 104.5^0, a deviation of a bond 5^0 from the tetrahedral angle of 109.5^0

D. **Shape of H₃O⁺ Ion (sp³ hybridisation)**

Hydronium ion (H_3O^+) is formed by the combination of H_2O molecule and H^+ ion in which H_2O molecule donates one of its lone pairs of electrons to H^+ ion and it accepts that lone pair of electrons in its vacant 1s orbital.

Actually, filled sp^3 hybrid orbital of O-atom in H_2O molecule overlaps with empty s-orbital of H^+ ion as follows thereby forming a coordinate covalent bond:
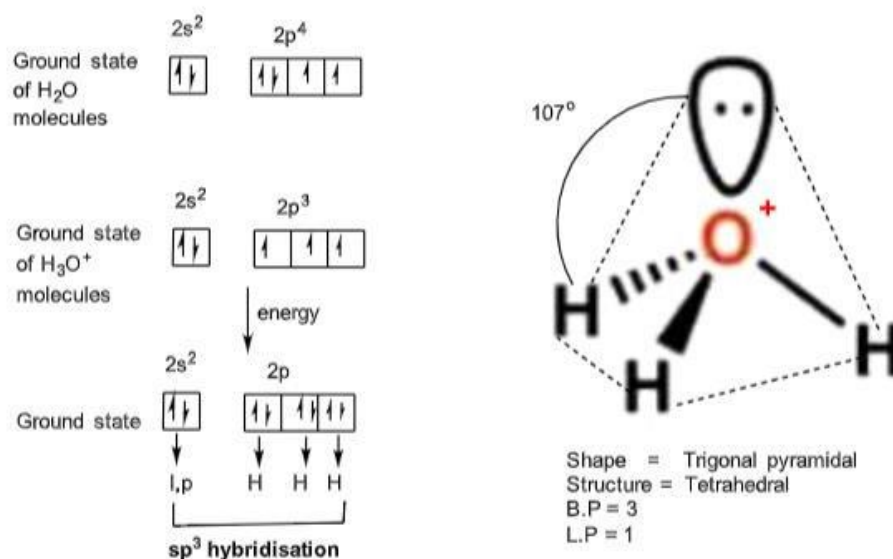
Fig 3.11 Overlapping of filled sp³ hybrid orbital of O-atom in H₂O and empty 1s orbital of H⁺ ion to form H₃O⁺ ion

This ion has trigonal pyramidal shape like that of NH_3 molecule with one lone pair of electrons on O-atom.

E. Shape of SF₄ molecule (sp³d hybridisation)

In this molecule the central S-atom is in its first excitation state in which one of its p_x electrons is promoted to the next empty dz^2 orbital. The electronic configuration in the ground and first excited state has been shown below:

S_g: $3s_2p_{x2}p_{y1}p_{z1}$ $\longrightarrow$ S_{1ex} : $3s_2p_{x1}p_{y1}p_{z1}$ $(dz_2)_1$ $\longrightarrow$ sp₃d
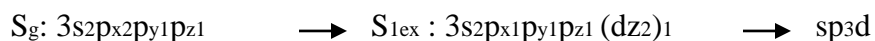
All these atomic orbitals of S_{ex} central atom get hybridised to give five sp³d hybrid orbitals directed toward the corners of a trigonal bipyramid, one of these hybrid orbitls contains an electron pair (b.p.) and the next four orbitals have unpaired electrons which overlap with the porbitals of four F-atom to form SF₄ molecule.
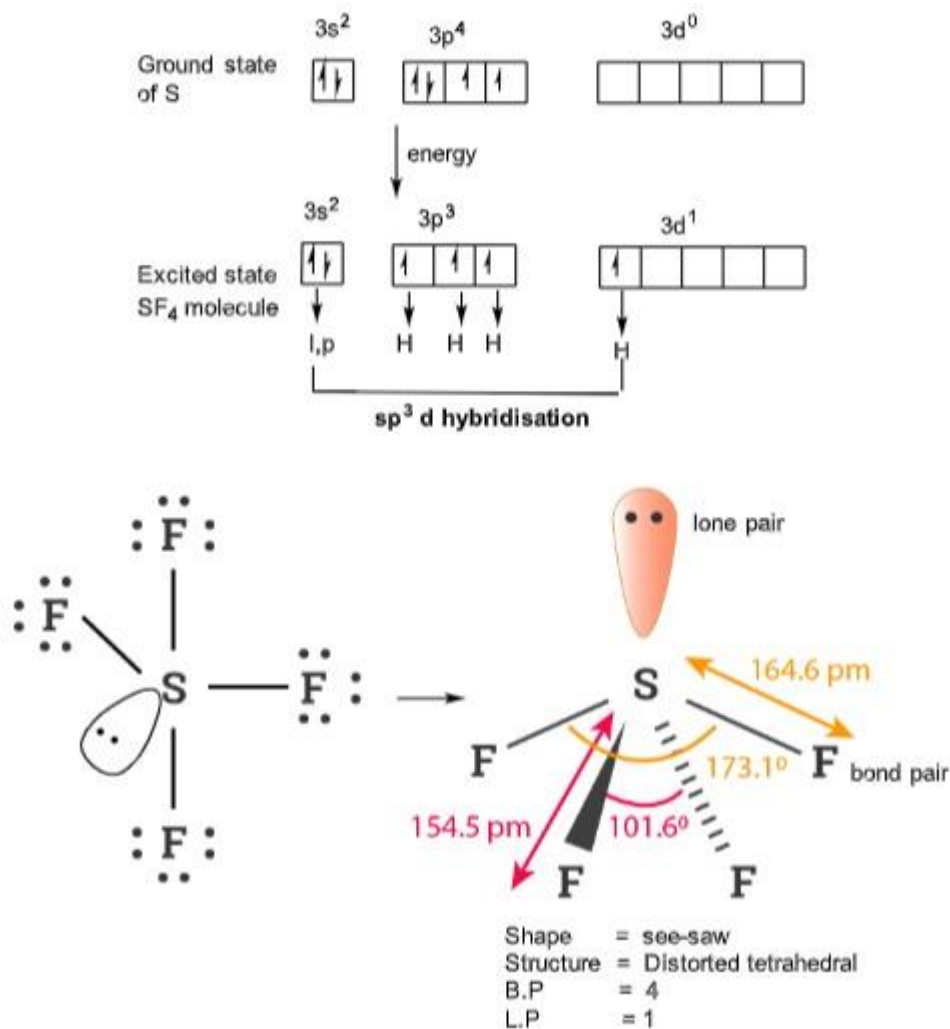
Fig 3.12 Formation of five hybrid orbitals of S$_{ex}$ atom and their overlapping with p-orbitals of four F-atom to give SF$_4$ molecule

This molecule attains a see-saw shape because of the presence of one lone pair of electron (sometimes also called distorted tetrahedral) and lone pair lies at one of the basal positions (the molecule has 1 lone pair and 4 bonded pairs)

F. Shape of ClF$_3$ molecule (sp^{3}d hybridisation)

Cl is the central atom in this molecule with valence shell electronic configuration in ground and first excited state as given below wherein one electron from a filled p-orbital say p$_y$ is promoted to a vacant d-orbital (*viz.* dz^2) of the same shell:

Cl$_g$: 3s$_2$p$_{x2}$p$_{y2}$p$_{z1}$ $\longrightarrow$ Cl$_{1stex}$: 3s$_2$p$_{x2}$p$_{y1}$p$_{z1}$ (dz$_2$)$_1$ $\longrightarrow$ sp$_3$d

All the orbitals of the valence shell of Cl_{ex}^{st} atom are mixed up together to produce five sp^3d hybrid orbitals. Two of the hybrid orbitals have lone pairs of electrons and three have unpaired electrons which then overlap with unpaired p-orbitals of three F-atoms to form σ covalent bonds. The lone pairs are said to occupy the equilateral positions and the molecule attains T-shaped structure with the bond angle of 87.6^0 instead of 90^0 due to the distortion caused by lone pairs The T-shaped structure has been confirmed by the experimental evidences. The whole act of hybridisation, overlapping and bond formation can be shown as below (molecule has 2 lone pairs and 3 bonded pairs):
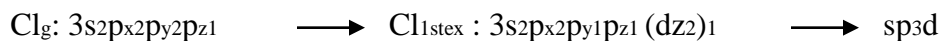

Fig 3.13 Formation of five hybrid orbitals of $Cl_i^{st}_{ex}$ atom and their overlapping with p-orbitals of three F-atoms to give ClF₃ molecule
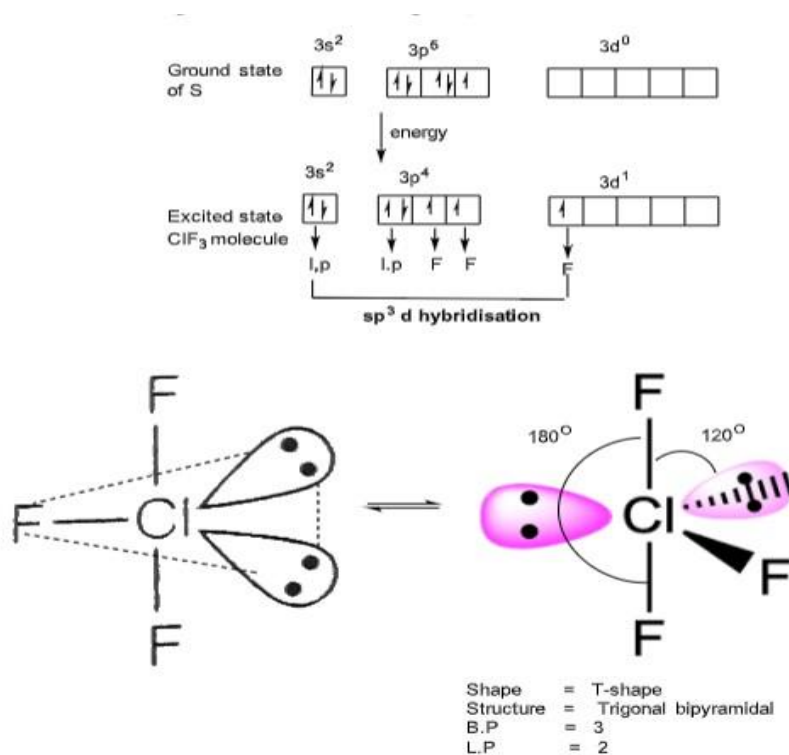
The mode of hybridisation shape and bonding in BrF_3 and ICl_3 molecules can also be explained on the similar grounds as in the case of ClF_3.

G. Shape of ICl₂⁻ Ion (sp³d hybridisation)

In ICl_2^- ion, the central atom I (iodine) has the ground state electronic configuration in its valence shell as shown below:

I_g: $5s^2 p_x^2 p_y^2 p_z^1 (d_{z^2})^0$

All these atomic orbitals including a vacant d_{z^2} orbital participate in hybridisation to produce five sp^3d hybrid orbitals of which three orbitals contain lone pairs, one hybrid orbital is half filled which overlaps with half filled p-orbitals of Cl-atom to give normal σbond and one hybrid orbital remains vacant and overlaps with the filled orbital of Cl^- ion to give a coordinate covalent σbond (dative bond). The lone pairs occupy the equatorial positions and the bonded pairs are situated in axial positions. The ion has 3 lone pairs and 2 bonded pairs as shown below and has almost linear shape:

Shape   = Trigonal Bipyramidal
Structure = Linear
B.P   = 2
L.P   = 3
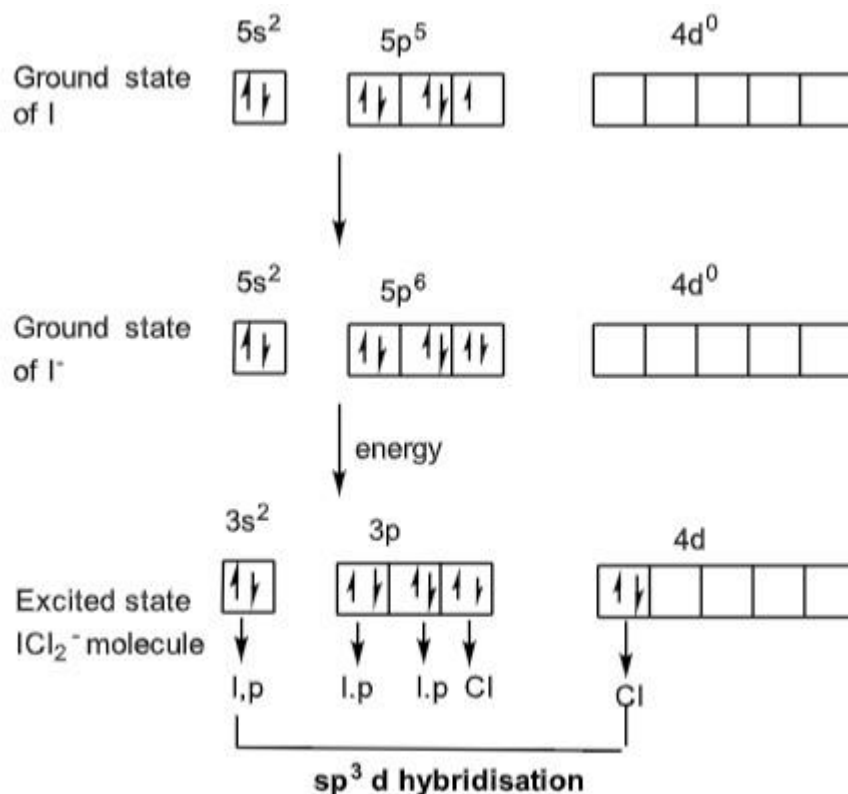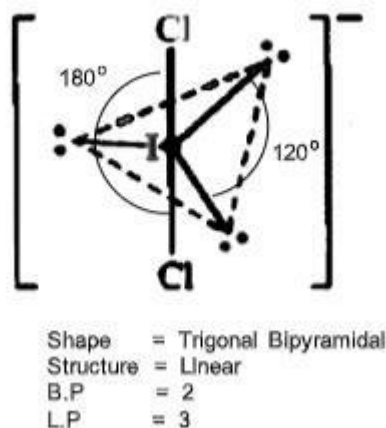
Fig 3.14 Formation of five sp³d hybrid orbitals ofcentral atom, I and overlapping of one of these hybrid orbitals with p-orbital of Cl atom and that of filled p-orbital of Cl⁻ion with vacant hybrid orbital of I atom

H. Shape of NO_3^- ion (sp² hybridisation)

The central N-atom in this ion is sp^2 hybridised leaving a pure p_z orbital behind. These sp^2hybridised orbitals then overlap with the orbitals of one O atom and one O⁻ion to form two normal σbonds and one dative σ bond as follows:
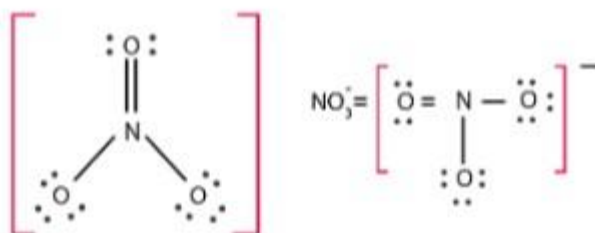
Bond angle   = 120°
Hybridization = sp²
Geometry   = Trigonal planar

Fig 3.15 Formation of two normalσbonds, one dative σ bond and one π bond   between
        N central atom and oxygen atoms/ion

I. Shape of SO_4^{2-} ion (sp³ hybridisation)

S atom has 6 electron its valence shell and in this ion all the valence electrons of S are present in unpaired state i.e. S_{2ex} state. Out of six, four orbitals are hybridised as follows: S_g : $3s_2p_{x2}p_{y1}p_{z1}$

S_{2ndex} : $3s_1p_{x1}p_{y1}p_{z1}$ $(d_{x2-y2})_1(d_{z2})_1$ $\longrightarrow$ sp_3

The SO_4^{2-} ion can be shown as follows
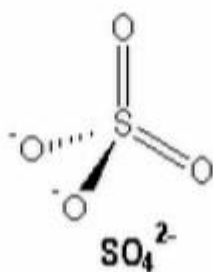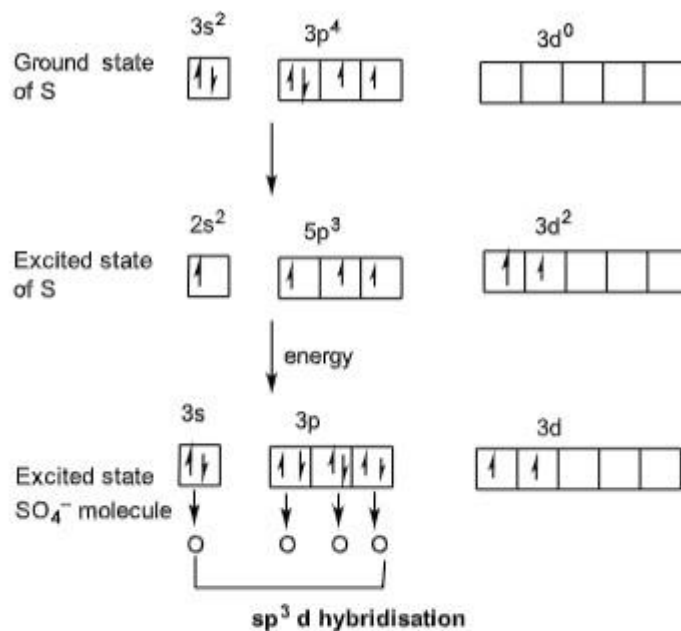
Fig 3.16 SO_4^{2-} ion

For details please refer to sp^3 hybridization & CH_4 molecule.

It has tetradedral shape like CH_4 molecule but has two single and two double bonds (σ and π). On the similar grounds the type of hybridisation and shape of XeF_2, XeF_4, $XeOF_4$ and XeF_6 molecules can be discussed. It is to be kept in mind that F-atom is monovalent, O-atom is bivalent (forms one σ and one π-bond with central atom) and central atom requires only that number of hybrid orbitals

which can form σbonds with approaching atoms and these hybrid orbitals are generally unpaired or half filled. Hence in the above molecules partial hybridisation may take place.

X_eF : sp^3d 3 lone pairs + 2 bonded pairs and linear in shape

X_eF_4: sp^3d^2 2 lone pairs + 4 bonded paires and square planar

X_eOF_4 : sp^3d^2 1 lone pair + 5 bonded pairs +1 πbond and is square pyramidal

X_eF_6 : sp^3d^3 1 lone pair + 6 bonded pairs and pentagonal pyramidal
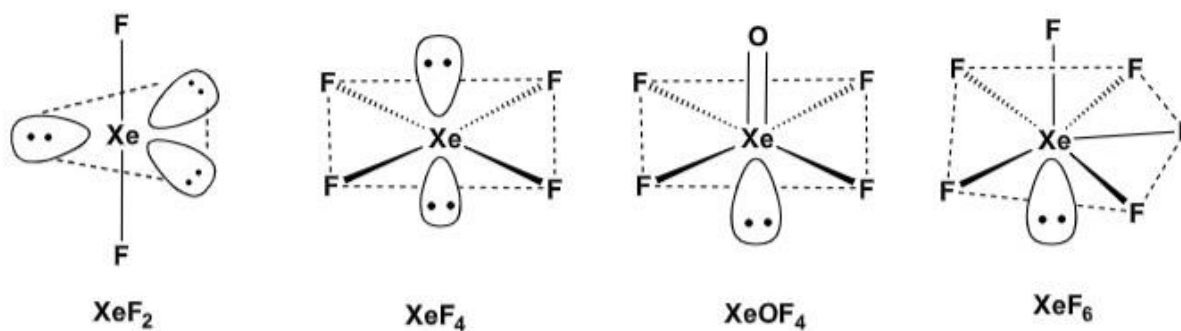
Fig 3.17 Shapes of XeF₂, XeF₄, XeOF₄ and XeF₆ molecules

3.8 VALENCE BOND THEORY (VBT)

This theory was put forward by Heitler and London in 1927 to explain the nature of covalent bond. They gave a theoretical treatment of the formation of the bond in H_2 molecule and the energy changes taking place therein. Later, it was extended by Pauling and Slater in 1931 to account for the directional characteristics of the covalent bond. The main points called the postulates of this theory are given below:

i)The atoms involved in the bond formation maintain their individuality(identity) even after the bond is formed i.e. in the molecule.

ii) The bond is formed due to the overlapping of half filled atomic orbitals (or the interaction of electron waves) belonging to the valence shell of the combining atoms as these approach each other. Thus the spins of the two electrons get mutually neutralised. The electrons in the orbitals of inner shells remain undisturbed.

iii)The filled orbitals (i.e. containing two electrons) of the valence shell do not take part in the bond formation. However, if the paired electrons can be unpaired without using much energy, they are first unpaired by promoting to the orbitals of slightly higher energy and then can take part

in bonding. For example, N can form NCl_3 only retaining a lone pair while P can form both PCl_3 and PCl_5.

iv)The electrons forming the bond undergo exchange between the atoms and thus stabilize the bond.

v)The strength of the covalent bond depends on the extent to which the two atomic orbital overlap in space.

This theory is based on two main theorems which are:

a)If $\Psi_A(1)$ and $\Psi_B(2)$ are the wave functions of the orbitals containing electrons in two isolated independent atoms A and B with energies E_A and E_B, respectively then the total wave function Ψ of the system can be given as a product of wave functions of two atoms, i.e.

$$\Psi = \Psi_A(1). \Psi_B(2) \qquad ……(3.1)$$

and the energy of the system by

$$E = E_A + E_B \qquad …….(3.2)$$

Where (1) and (2) indicate two electrons belonging to atoms A and B.

b)If a system can be represented by a number of wave functions such as Ψ_1, Ψ_2, Ψ_3 ……, then the true wave function Ψ can be obtained by the process of linear combination of all these wave functions as:

$$\Psi = N(C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3 + ……) \qquad …..(3.3)$$

Where N is normalization constant and C_1, C_2, C_3…are the coefficients indicating the weight of each of Ψs. They are so adjusted as to give a state of lowest energy. The squares of the coefficients may be taken as the measure of the weight of each wave function to total wave function.

The valance bond theory was first applied to the formation of H_2 molecule. If the two H-atoms, *viz*. H_A and H_B are infinitely apart from each other, there is no interaction at all but if these are brought close together, H_A- H_B covalent bond is formed and the energy of the system is decreased. Now if the orbitals of the two H-atoms are represented in terms of wave functions Ψ_A and Ψ_B, then the wave function for the system $H_A.H_B$ can be written as

$$\Psi = \Psi_A(1). \Psi_B(2) \qquad ……(3.1 \text{ as given above})$$

Where electrons belonging to H_A and H_B are 1 and 2.

But once the bond is formed, the electrons 1 and 2 have equal freedom to get associated with either of the H-atoms. Thus due to the exchange of electrons between H-atoms,two possible covalent structures of H_2 molecule may shown as $H_A(1).H_B(2)$ and $H_A(2).H_B(1)$. The wave functions of these structures are $\Psi_A(1). \Psi_B(2)$ and $\Psi_A(2). \Psi_B(1)$ respectively. Now the true wave function for H_2 molecules can be obtained by linear combination of the wave functions for the two covalent structures. This can be done in two ways:

i)When the combination of these wave functions takes place in a symmetric way, i.e. by addition process, symmetric wave function Ψ_s is obtained:

$$\Psi_s= \Psi_A(1). \Psi_B(2) + \Psi_A(2). \Psi_B(1) \quad ……..(3.4)$$

This is also known as covalent wave function, Ψ cov. ii)When the combination of the above wave functions takes place in a asymmetric way i.e. by subtraction process, asymmetric wave function, Ψ_a, is obtained:

$$\Psi_a= \Psi_A(1). \Psi_B(2) - \Psi_A(2). \Psi_B(1) \quad ……. (3.5)$$

The value of Ψ_s does not change by exchange of electrons 1 and 2 but that of Ψ_a changes in this process. The two situations are presented graphically as follows: *(Fig 3.18)*

The curve s is for addition process and curve a is for subtraction process of the wave functions. The calculated value of r_o for the minimum energy state i.e. the bonding state is 87 pm against the experimental value of 74 pm.
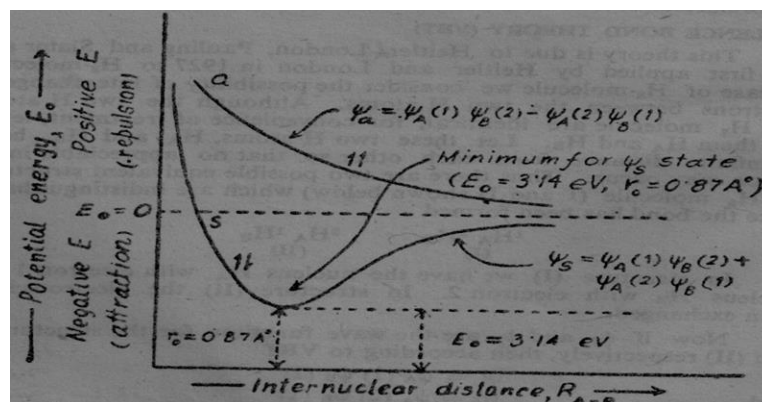

Fig 3.18

Pauling has suggested that the bond between two H-atoms in H_2 molecule is not absolutely covalent, it rather has partial ionic character. He proposed two ionic structures for H_2 molecule in which both the electrons 1and 2 are either attached to H_A or H_B as given below,

$H_A(1,2). H^+_B$ $\qquad\qquad\qquad\qquad$ $H^+_A.H_B(1,2)$

If the above wave functions for these structures are $\Psi_{(1)}$ and $\Psi_{(2)}$,
then $\Psi_{(1)}= \Psi_A(1). \Psi_A(2)$ …..(3.6) And $\Psi_{(2)}= \Psi_B(1). \Psi_B(2)$ ……(3.7)

The consideration of ionic structures as given above of H_2 molecule converts the equation 4.4 to

$\qquad$ $\Psi_S=[\Psi_A(1). \Psi_B(2) + \Psi_A(2). \Psi_B(1)] +\lambda [\Psi_{(1)}+\Psi_{(2)}]$

$\qquad$ or $\Psi_S=[\Psi_A(1). \Psi_B(2)+ \Psi_A(2). \Psi_A(1)] + \lambda[\Psi_A(1). \Psi_A(2)+ \Psi_B(1). \Psi_B(2)]$ $\quad$ ..(3.8)

$\qquad$ or $\Psi_S =\Psi_{cov.} + \Psi_{ionic}$ $\qquad\qquad\qquad\qquad\qquad$ …..(3.9)

the coefficient λ is used in equation 4.8 is a measure of the degree to which the ionic forms contribute to the bonding. Thus three important contributions to covalent bonding may be summarized as follows:

i)Delocalization of electrons over two or more nuclei

ii)Mutual screening iii)Partial ionic character.

Limitations of Valence Bond theory:

i) The formation of coordinate covalent bond (also known as dative bond) cannot be explained on the basis of this theory because according to this theory a covalent bond is formed as a result of overlapping of half filled orbitals of the combining atoms and the paired orbitals of the atoms do not take part in normal covalent bond formation.

ii) The odd electron bond formation between the atoms cannot be explained by this theory because a covalent bond is an electron pair bond means two electrons are required for a bond. iii) This theory is unable to explain the paramagnetic behaviour of oxygen molecule because paramagnetism is a property caused by the presence of unpaired electrons and in an oxygen molecule, according to VBT, two electron pair bonds are present between the oxygen atoms and hence it should be diamagnetic.

iv) In some molecules, the properties like bond length and bond angles could not be explained by assuming simple overlapping of atomic orbitals of the atoms.

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3.9 HYBRIDISATION OF ATOMIC ORBITALS

It is the theoretical model used to explain the covalent bonding in the molecules and is applied to an atom in the molecule. To explain the anomaly of expected mode of bonding (according to VBT) shown by Be, B and C in their compounds where these elements should be zerovalent, monovalent and bivalent due to the presence of 0,1 and 2 unpaired electrons in their valence shells and the observed bonding exhibited by them, i.e. these are bivalent, trivalent and tetravalent due to the availability of 2,3 and 4 unpaired electrons in their valence shells in those compounds, a hypothetical concept of hybridisation was put forward. According to this concept, before the bonding occurs in the compounds of Be, B and C, one of the 2s electrons gets promoted to the vacant 2p orbital due to the energy available from the heat of reaction when covalent bonds are formed or perhaps due to the field created by the approaching atoms, thereby making 2,3 and 4 unpaired electrons available in the valence shell of the atoms of these elements. These orbitals having unpaired electrons then mix up together or redistribute their energy to give rise a new set of orbitals equivalent in energy, identical in shape and equal to the number of atomic orbitals mixed together. This process is known as hybridisation, the atomic orbitals are said to be hybridised and the new orbitals formed are called the hybrid orbitals. The hybrid orbitals so formed then overlap with the half filled orbitals of the approaching atoms and form covalent bonds.

Salient features (or the Rules) of hybridisation

i) The atomic orbitals belonging to the valence shell of the central atom/ion of a molecule/ion with almost similar energies mix up together or hybridise to give the hybrid obitals. But the atomic orbitals of the central atom participating in the πbond formation are excluded from the hybridisation process.

ii) The number of hybrid orbitals produced is equal to the number of atomic orbitals undergoing hybridisation. The hybrid orbitals like pure atomic orbitals can accommodate a maximum of two electrons of opposite spins.

iii) If required, electron(s) may be promoted from an orbital in ground state of the central atom to the next empty higher energy orbital provided the value of n does not change as happens in the central atom of $BeCl_2$, BCl_3, CH_4, PCl_5, SF_6etc.

iv) Most of the hybrid orbitals are equivalent in energy, shape and size but may not be identical. They differ from one another in their orientation in space.

v) From the type of hybridisation, the geometry and bond angles of a molecule can be predicted. vi) In a few cases empty atomic orbitals or those with lone pairs of electrons (i.e.filled atomic orbitals) are also involved in the hybridisation process but in such cases normal covalent bond is not formed rather this process leads to the formation of coordinate covalent bond. Sometimes these filled hybrid orbitals do not form the bonds and the electron pair remains as lone pair on central atom.

vi. The hybrid orbitals are involved in the σbond formation only and π bond is not formed by them at all.

Types of hybridization:

Following are the important types of hybridisation. The central atom in a given molecule/ion can undergo any of the following possible hybridisations. **i)Sp hybridization:**

When one s and one p (oriented along molecular axis) atomic orbitals belonging to the valence shell of the central atom in a given molecule/ion mix up together to give rise two hybrid orbitals, the process is known as sp hybridisation and the new orbitals formed are called sp hybrid orbitals. This process can be shown diagrammatically as follows:
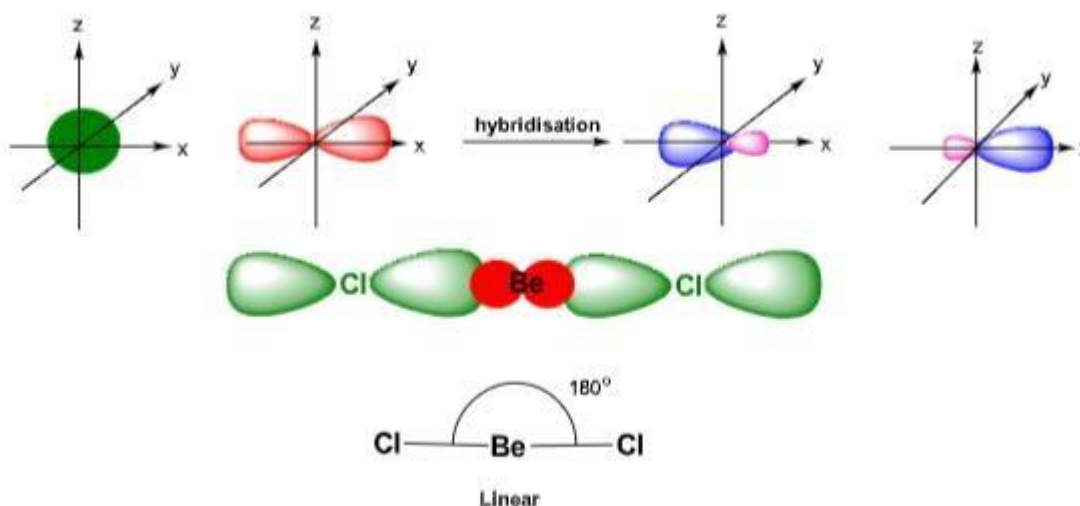
Fig 3.19(a) Formation of two collinear sp hybrid orbitals from the mixing of one s and one p atomic orbitals

Characteristics:

i)   These hybrid orbitals are equivalent in energy, shape (oval shaped) and are oriented in the opposite directions at an angle of 180^0 from each other, leading to linear geometry.

ii)   Each hybrid orbital has one large lobe and one small lobe. The larger lobe takes part in overlapping process.

iii)   These hybrid orbitals possess 50% character of s-orbital (spherical) and 50% that of p-orbital (pear shaped) and hence are oval shaped.

Examples: BeX_2 (X=H,F, Cl). Let us take BeF_2 molecule for illustration.
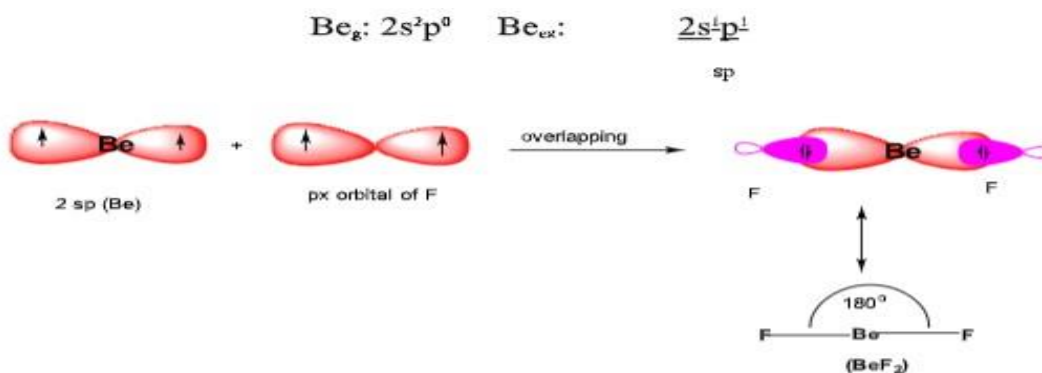
Fig 3.19 (b) formation of two σcovalent bonds by the overlapping of sp-hybrid orbitals of Be and 2p-orbitals of F-atoms **ii**

)Sp^2 hybridisation:

On mixing together one s and any two p-orbitals belonging to the valence shell of the central atom of a given molecule/ion, a set of three hybrid orbitals is obtained. This process is known as sp^2 hybridisation and the new orbitals formed are termed as sp^2 hybrid orbitals. The process can be shown as given below:

Trigonal Planar structure (BF_3)
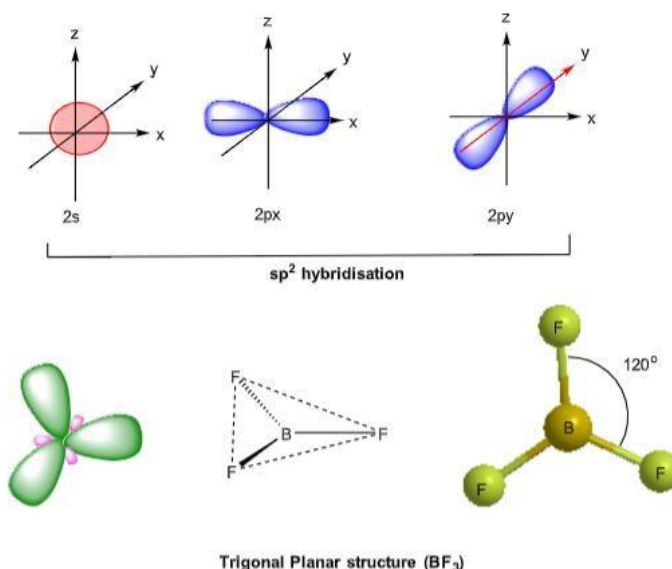
Fig 3.20(a) Formation of three trigonal planar sp² hybrid orbitals from the mixing of one s and two p atomic orbitals

Characteristics:

i) The sp^2 hybrid orbitals are equivalent in energy and shape and are oriented towards the corners of an equilateral triangle, hence inclined at an angle of 120^0 with one another, leading to trigonal planar geometry. ii) They all lie in one plane (i.e. planar).

iii) They possess 33% s- character and 66% p- character and therefore are less oval than sp- hybrid orbitals.

Examples: BX_3(X=H, F,Cl) Let us take BF_3 molecule for discussion.
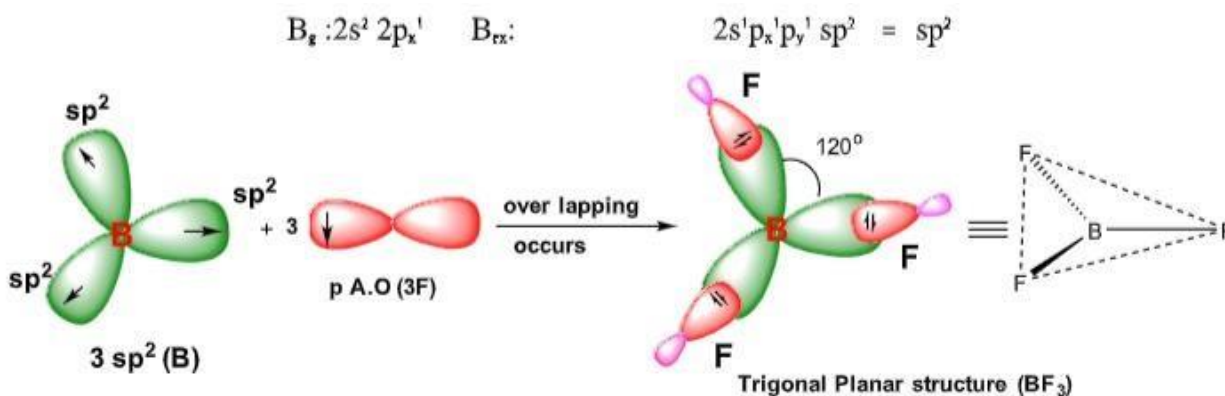
Fig 3.20(b) formation of three σ covalent bonds by the overlapping of sp² hybrid orbitals of Batoms and 2p-orbitals of 3F-atoms **iii)Sp³ hybridisation:**

In this hybridisation, one s and three p-atomic orbitals belonging to the valence shell of the central atom of a given molecule/ion mix up together and form a set of four hybrid orbitals. This mixing process is known as sp^3 hybridisation and the new orbitals formed are called sp^3 hybrid orbitals. This process has been shown below:
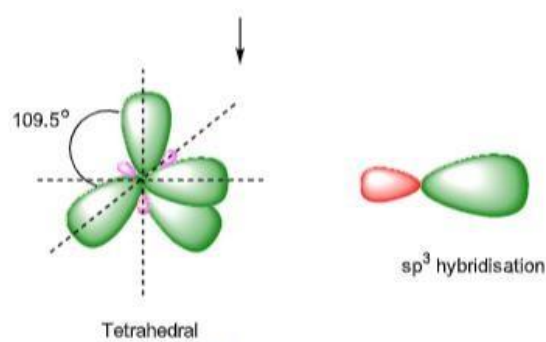
Fig 3.21(a) formation of four tetrahedral sp³ hybrid orbitals from the mixing of 1s and 3p atomic orbitals **Characteristics:**

i)   These sp^3 hybrid orbitals are equivalent in energy and shape and are oriented along the four corners of a regular tetrahedron. The bond angle between each pair of these orbitals is 109.5^0, called tetrahedral angle.

ii)   Each sp^3 hybrid orbital has 25% s- character and 75% p- character, hence their shape is closer to that of p- orbitals i.e. are pear shaped.

Examples: AX_4 where A = C, Si and X = H, F, Cl, Br, I, simplest of these is CH_4. In this molecule, C-atom is the central atom which undergoes sp^3 hybridisation as follows:

$$C_g:2s^2\ p_x^1 p_y^1 p_z^0 \qquad C_{ex}: \longrightarrow \qquad \underline{2s^1 p_x^1 p_y^1 p_z^1}$$
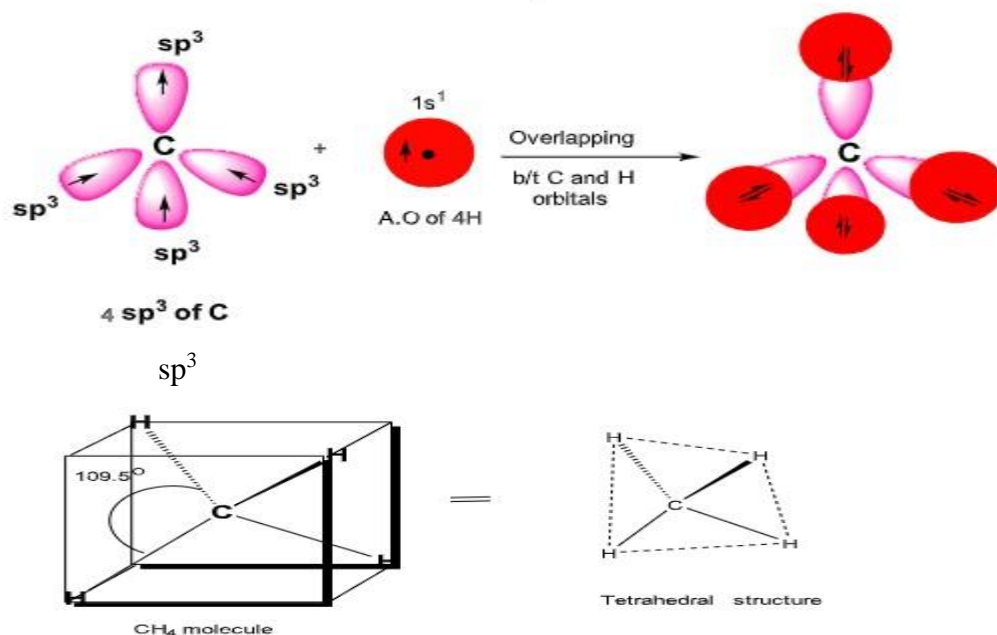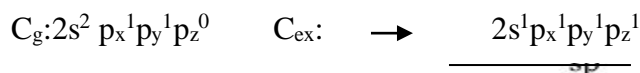
Fig 3.21 (b) formation of four σcovalent bonds by the overlapping of sp³ hybrid orbitals of Catom and 1s orbitals of four H-atoms **iv)Sp³d hybridization:**

When one s, three p and one d (generally dz^2) atomic orbitals of the valence shell of the central atom of a given molecule/ion mix up together and give rise to the formation of a set of five hybrid orbitals, the process is known as sp^3d hybridisation and the new orbitals formed are called sp^3d hybrid orbitals. The process of this type of hybridisation has been shown here:
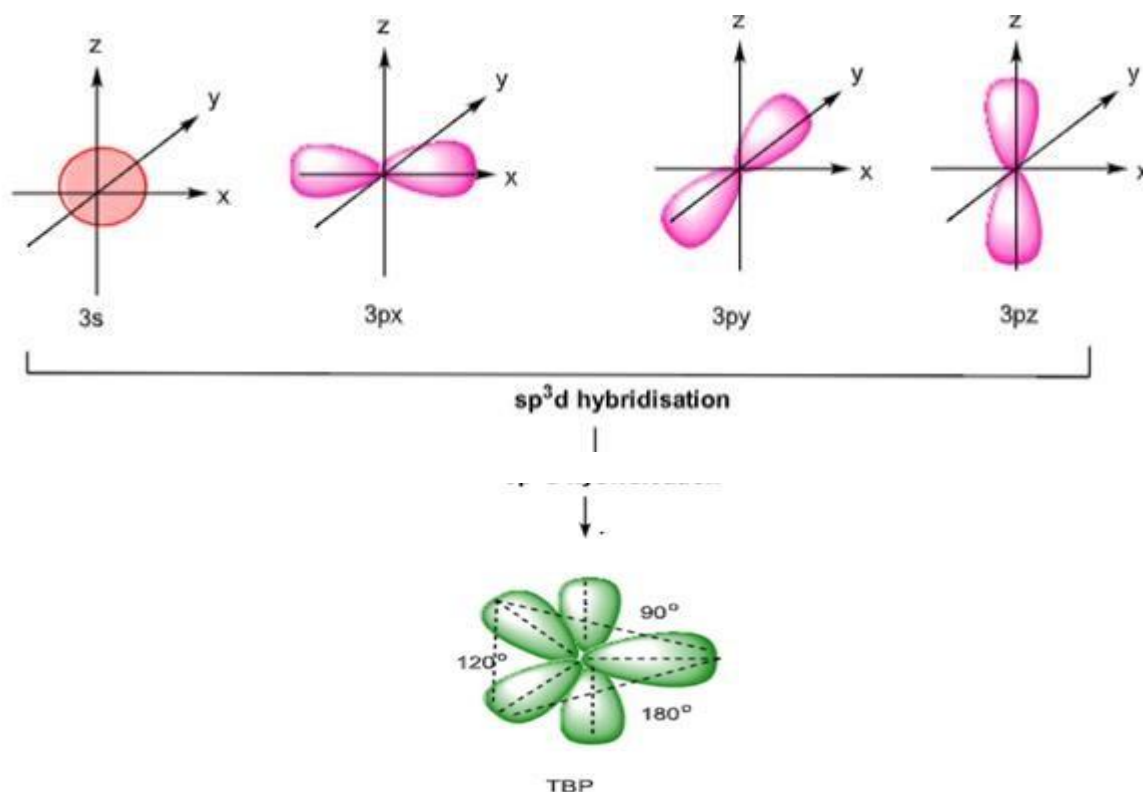
Fig 3.22 (a) formation of five trigonal tripyramidal sp^3d hybrid orbitals from the mixing of one s, three p and one d (dz^2) atomic orbitals **Characteristics:**
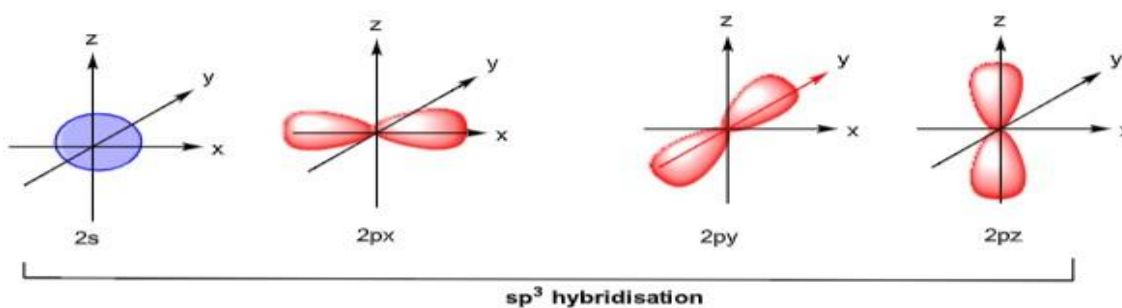
i)   The sp^3d hybrid orbitals are equivalent in energy and shape and are oriented towards the five corners of a regular trigonal bipyramid i.e. their spatial arrangement is trigonal bipyramidal.

ii)   They do not lie in one plane. Three of the five hybrid orbitals called the basal or equatorial hybrid orbitals are oriented towards the corners of an equilateral triangle forming a triangular plane while the remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of plane. The angle between each adjacent pair of basal hybrid orbitals is 120^0, that between two axial hybrid orbitals is 180^0 and that between the axial and basal hybrid orbitals is 90^0.

Examples: AX_5 molecule (A = P, As, Sb and X = F, Cl, Br). Let us discuss the hybridisation and bonding in PCl_5 molecule. p_g: $3s^2 p_{x1} p_{y1} p_{z1} \longrightarrow p_{ex}$: $3s_1 p_{x1} p_{y1} p_{z1} d_{z21}$
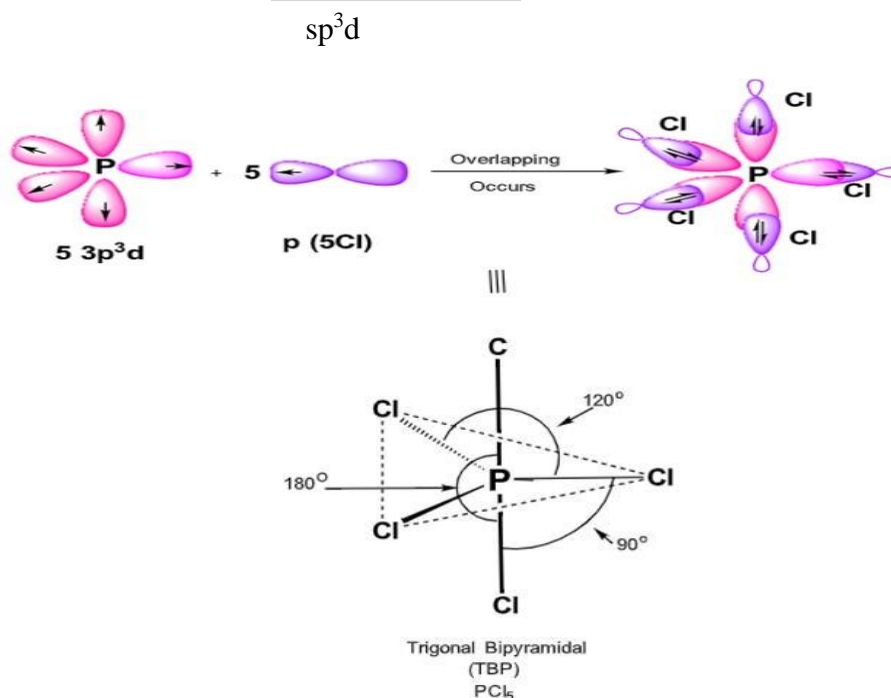
$$sp^3d$$

Fig 3.22(b) *Formation of five σcovalent bonds by the overlapping of sp^3d hybrid orbitals of P central atom and p-orbitals of five Cl-atoms* **v)Sp³d² hybridisation:**

On mixing one s-orbital, three p-orbitals and two d (generally dx^2-y^2 and dz^2) orbitals of the valence shell of central atom of the given molecule/ion, a set of six hybrid orbitals is formed. This process is known as sp^3d^2 hybridisation and the new orbitals formed are called sp^3d^2 hybrid orbitals. The formation of these orbitals is shown below:

Octahedral complex
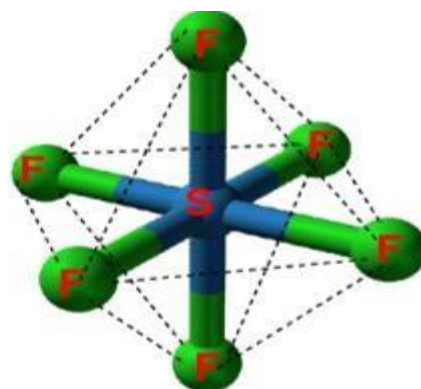
3-D modal of Octahedral complex

Fig 3.23(a) Formation of six sp³d² hybrid orbitals from the mixing of one s, three p and two datomic orbitals **Characteristics:**

i)   All the six hybrid orbitals formed are equivalent in energy and shape and are oriented along the six corners of a regular octahedron i.e. their arrangement in space is octahedral.

ii)   All the orbitals do not lie in a plane. Four hybrid orbitals of the six called basal or equatorial hybrid orbitals are lying in square plane while the remaining two called axial hybrid orbitals lie

above and below the plane on the axis passing through the centre of the square base. The angles between any adjacent pairs of hybrid orbitals (basal or axial) is 90^0.

Examples: AF_6 type molecule (A=S, Se, Te). Let us see the process of bond formation in SF_6 molecule.

$$S_g: 3s^2 p_x^2 p_y^1 p_z^1 \longrightarrow \underline{S_{ex}: s^1 p_x^1 p_y^1 p_z^1 d^1_{z2} d^1_{x2-y2}}$$
$$sp^3d^2$$

Octahedral complexes
(SF_6)
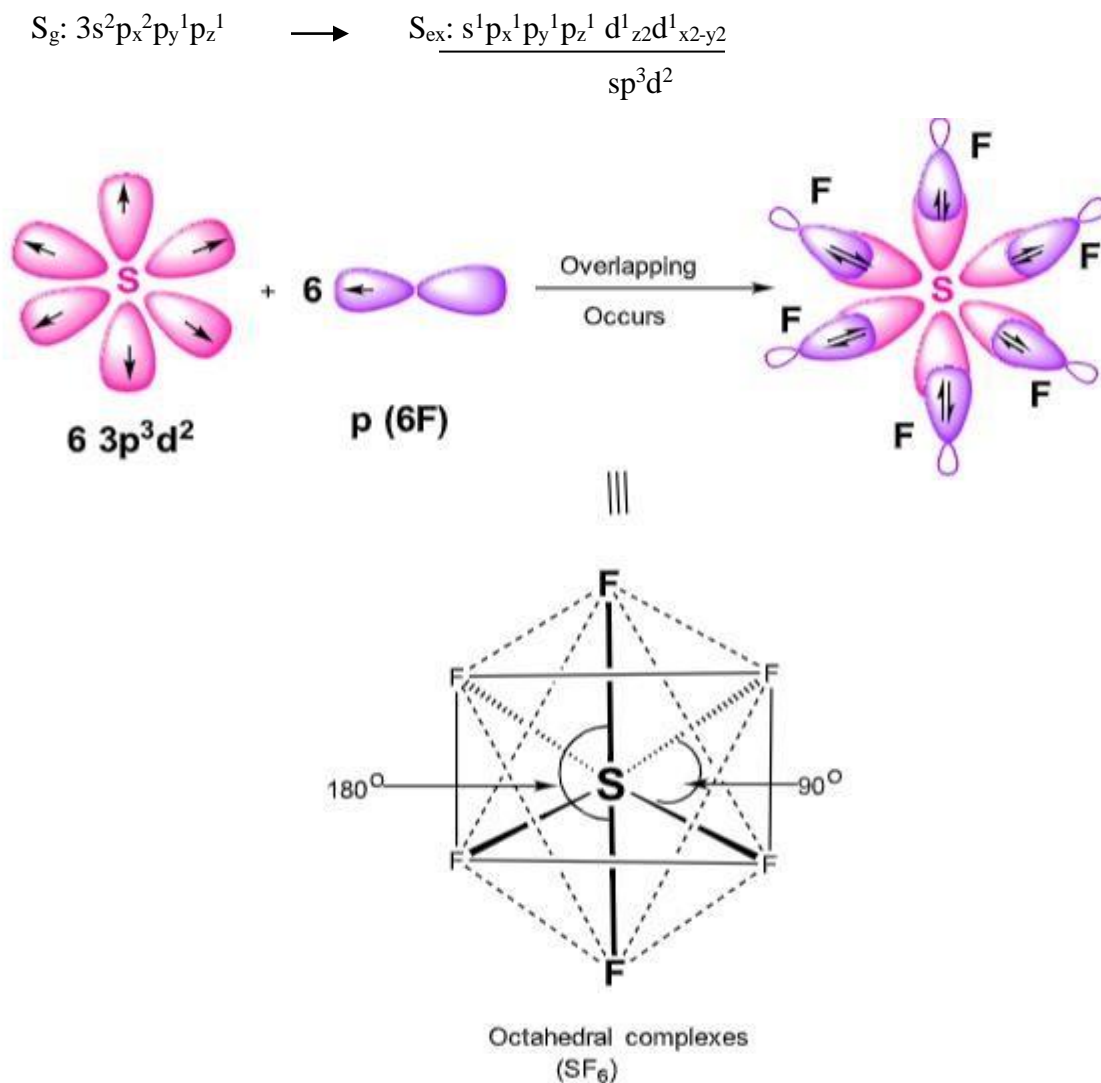
Fig 3.23 (b) Formation of six σcovalent bonds by the overlapping of sp³d² hybrid orbitals of S central atom with p-orbitals of six F atoms **vi)Sp³d³ hybridisation:**

When one s, three p and three d (generally dxy, dyz, dzx) orbitals of the valence shell of the central atom in a given molecule/ion mix up together, a set of seven new orbitals is formed. This process of mixing is called sp³d³ hybridisation and the new orbitals formed are known as sp³d³hybrid orbitals. Their formation occurs as follows:
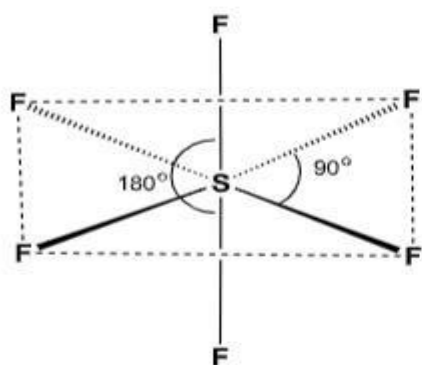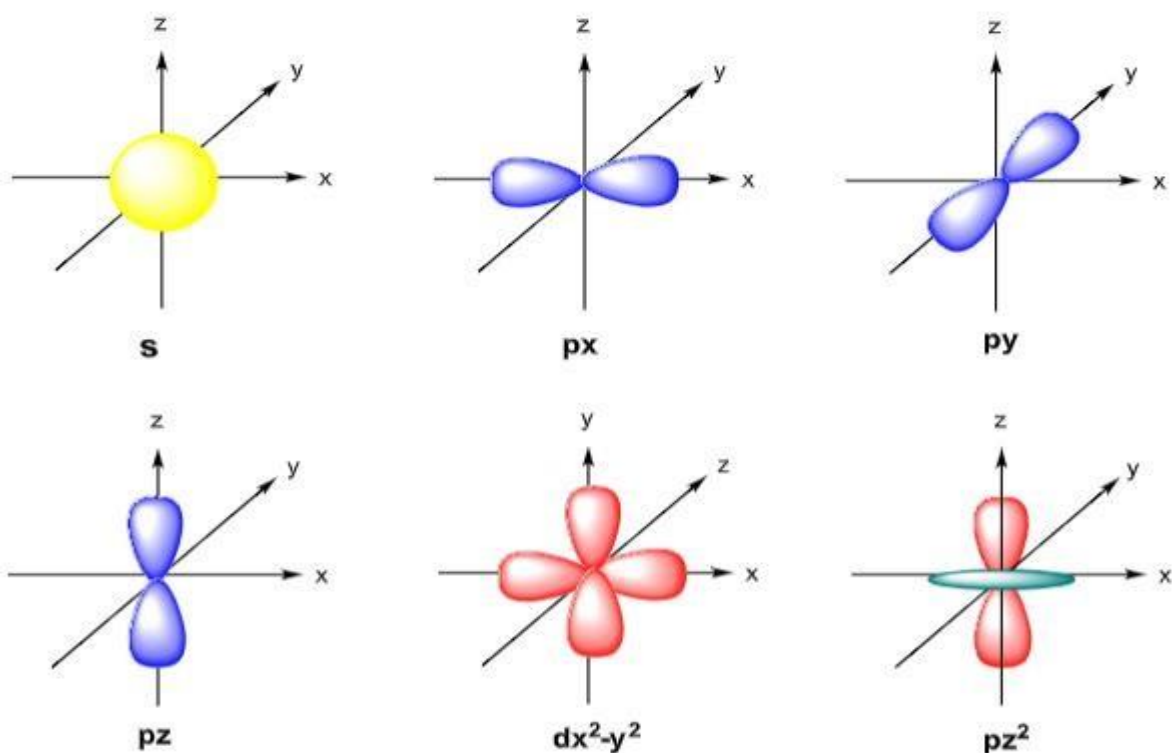
Characteristics:

i)   All the seven hybrid orbitals are equivalent in energy and shape and are oriented towards the seven corners of a regular pentagonal bipyramid i.e. their spatial arrangement is pentagonal bipyramidal.

ii)   All of them do not lie in one plane. Five of them lie in the pentagonal plane and are called basal or equatorial hybrid orbitals while remaining two called axial hybrid orbitals lie above and below the plane on the axis passing through the centre of the pentagonal plane.

iii)   The angle between any adjacent pair of basal hybrid orbitals is of 72^0 and that between an axial and a basal hybrid orbital is equal to 90^0.

   Example: IF_7 (an interhalogen compound)

   $I_g : 5s^2 p_x^2 p_y^2 p_z^1$ $I_{ex} :$ $5s^1 p_x^1 p_y^1 p_z^1 dxy^1 dyz^1 dzx^1$

$$\longrightarrow$$

$$\overline{\qquad\qquad\qquad\qquad}$$
$$sp^3d^3$$
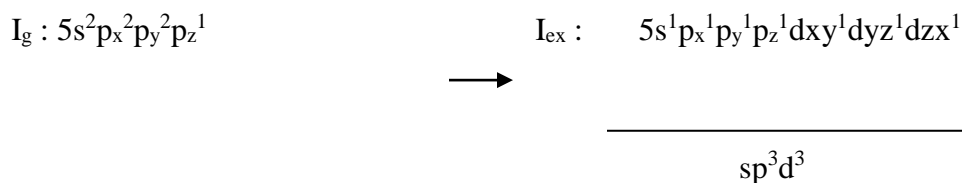
The whole act of hybridisation and bond formation in this molecule can be shows as given below
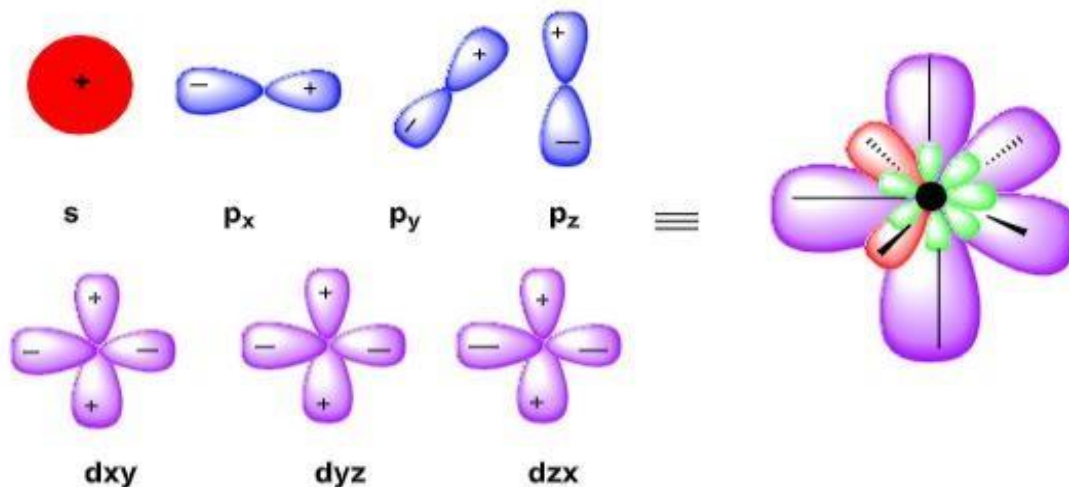
Fig 3.24 (a) Formation of seven sp^3d^3 hybrid orbitals from the mixing of one s, three p and three d-orbitals of the central atom

Pentagonal bipyramidal
(IF₇)

Pentagonal bipyramidal
(IF₇)
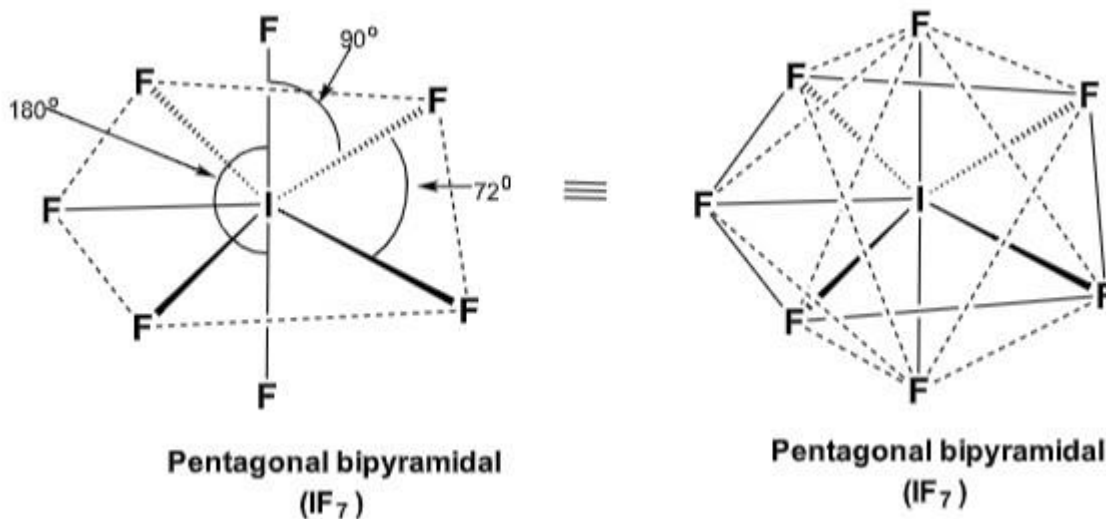
Fig 3.24(b) Formation of seven covalent bonds from the overlapping of sp^3d^3 hybrid orbitals of central I-atom and p-orbitals of seven F-atom

3.10. SUMMARY

This unit of the study material consists of a concise discussion of covalent bond based on the octet rule and deviation from the octet rule. A brief account of polar and non-polar nature of covalent bond has been given. The valence bond theory and its limitations, directional nature of covalent bond as well as pictorial representation along with the formation of sigma and pi bonds have also been discussed. The concept of hybridisation has been fruitfully discussed with examples as well as shapes of inorganic molecules and ions based on hybridisation and valence shell electron pair repulsion theory have been given in the simple way.

3.11. TERMINAL QUESTIONS

i)The d-orbital involved in sp^3d hybridisation is

(a) d_z^2 (b) dx^2y^2 (c) d_{xy} (d) d_{zx}

ii)   Which of the following compounds contains covalent bond?

(a) NaOH   (b) HCl   (c) K_2S (d) LiH

iii)   Which of the following compounds has the least tendency to form hydrogen bond?

[1]   (a) HF (b) NH_3 (c) HCl   (d) H^2O

iv)   Nitrogen atom in NH_3molecule is sp^3 hybridised.NH_3contains a lone pair of electron on

    N-   atom. What is the shape of this molecule?

     (a) Tetrahedral   (b) square plannar   (c)

Trigonal plannar   (d) Trigonal pyramidal

v)Discuss the difference between a polar and a non-polar covalent bond with examples.

vi) What do you understand by directional nature of covalent

bond? vii) Explain molar mass and Avogadro number?   viii)

Discuss the shape of H_3O^+, PCl_5, NH_3, SF^{45}. ix) Write the chemical

formula: a) Ca with Cl   b) N with O

x) XeF_2 molecule is linear though Xe atom in this molecule undergoes sp^3d hybridisation.

Explain.

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and Distributers, Daryaganj, Delhi (2013).

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York (1960).

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ANSWERS

i) a   ii) b   iii) c   iv) d

3.12 REFERENCES

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UNIT 4: ELECTRONEGATIVITY AND POLARIZATION OF COVALENT BOND

4.1 INTRODUCTION

Organic Chemistry is the subclass of chemistry that involves the study of carbon and its compounds. It is established fact now that carbon can forms unlimited number of compounds. Thus the domain of organic chemistry is continuously growing with new research finding being made around the globe. As a consequence, impact and role of organic compounds in our daily lives is expanding from medicine to agriculture and polymers to petroleum etc. Today, organic chemistry is well developed science which has great deal of scope for further developments. Therefore, plethora of information and theories are available on organic chemistry. This implies that new students of organic chemistry require a great deal of study to understand the latest developments in the field. The study of organic chemistry seems intricate; however it is very interesting and in this course begins with concise details on the concepts on structure and bonding in organic compounds as well as different types of effects in organic compounds.

4.2 OBJECTIVES

Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the organic chemistry. Topics covered in this chapter such as electro negativity and polarization of covalent bond ,different types of effects as well as hydrogen bonding and its significance are essential basics of the organic chemistry. The chapter is developed to stimulate interest of the reader into the organic chemistry and at the same time to build the deep understanding of the fundamental concepts of organic chemistry. To offer students an easy and interesting learning experience, each of the topics covered is depicted with lucid diagrams and figures also.

4.3 ELECTRO NEGATIVITY AND POLARIZATION OF COVALENT BOND

Electro negativity: A pure covalent bond is formed when electrons are shared equally between two atoms.If in two atoms electrons are shared unequally, due to difference in electronegative, the resulting bond would be a polar covalent bonds. Electronegativity determines how the shared electrons are distributed between the two atoms in a polar covalent bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+ , or a partial negative charge, indicated by δ^- , and a bond between two atoms that possess partial charges is a polar bond.

For example: Like, in HCl polar covalent bond would be formed between H and Cl.The larger the electronegative difference between H and Cl , the greater would be magnitude of δ and the higher would be polarity of the bond.

$$\overset{\delta+}{H}\!-\!\overset{\delta-}{Cl} \qquad \overset{\longrightarrow}{H \quad Cl}$$

(a)   (b)
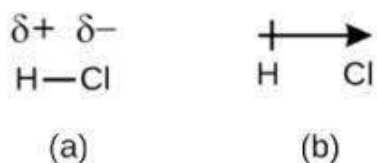
Polarization of covalent bond: The formation of bond intermediate between an ionic and a covalent bond occure through a phenomenon known as polarisation of ions.When a oppositely charged ions approach each other , the attraction between the positive charge cation and negative charge of anion and also the simultaneous repulsion between their nuclei and between their electrons results in the didtortation, deformation or polarisation of electron charge cloud of the anion.The electron charge cloud of the anion no longer remains spherical but get distorted or polarised towards the cation.The electron charge cloud of the cation also get distorted or polarised by the anion through a similar process but the polarisation of the cation is far less pronounced because of its small size.Thw polarisation of ions results in a high electron charge concentration between the two nuclei.The results in the formation of a bond which is intermediate between an ionic and a covalent bond.This type of bond is called polar covalent bond and extent of polarisation depends, evidently , on the polarising power of the cation and the polarisability of the anion.

No polarisation

Polarisation of anion

Polarisation of electron charge cloud of an anion by a cation.
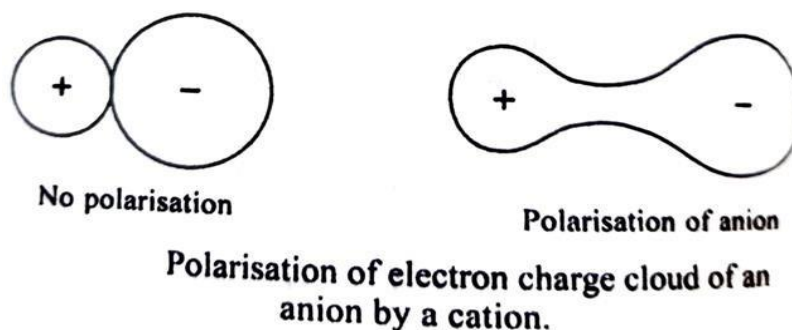
Figure : 4.1

The rule obey the polarisation are known as **Fajan's rules**. These are given below:

- Size of the Ion: Smaller the size of the cation, the larger the size of the anion, and hence greater is the covalent character of the ionic bond.
- The Charge of the Cation: Greater the charge of cation, greater is the covalent character of the ionic bond.
- Electronic Configuration: It has been found that, cations with pseudo inert gas configuration, such as, $ns^2 p^6 d^{10}$, or with inert pair configuration, such as,$(n-1)d^{10} ns^2$, have high polarizing power, while cations with noble gas configuration, such as, $ns^2 np^6$, have low polarizing power.

4.4 INDUCTIVE EFFECT

Inductive effect is the polarity produced in a molecule due to the difference in electronegativity of bonded atoms. It is an experimentally observable effect and transmits through the C-C chain in organic molecules. The electron cloud in a σ-bond is slightly pulled in by more electronegative atom. Thus more electronegative atom assumes partial negative charge ($\delta-$) and the less electronegative atom assumes partial positive charge ($\delta+$). This causes permanent polarization of the bond. Thus inductive effect is a permanent effect.
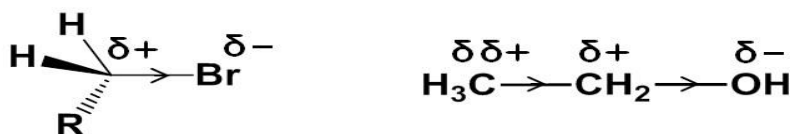
Figure 4.2: Demonstration of inductive effect operative in alkyl bromide and ethyl alcohol.

For example, bromine atom has higher electronegativity that carbon atom. Hence bromine atom in bromoalkane molecule slightly attracts the electron pair of C-Br bond and assumes $\delta-$ charge (**Figure 4.2**). As a result, adjacent carbon atom assumes a $\delta+$ charge. Practically inductive effect transmits up to two to three atoms across the C-C chain.

Inductive effect is classified as –I and +I effects. When in an organic compound carbon assumes slight positive charge due to the high electronegativity of adjacent atoms, it is termed as –I effect. The organic functional groups showing –I effects are given in their decreasing –I effect ahead:

$NR_3^+ > NO_2 > SO_2R > CN > COOH > F > Cl > Br > I > OAr > COOR > OR > COR > SH > SR > OH > NH_2 > Ar$
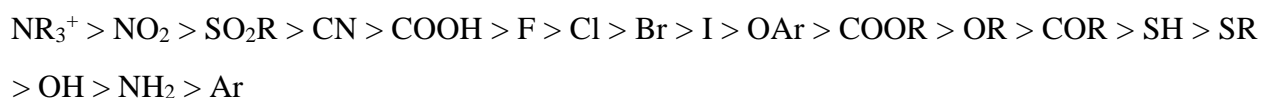
When carbon atom is bonded with electropositive atoms or groups such as methyl group it assumes slightly negative charge and the effect is called +I effect. The organic functional groups showing +I effects are given in their decreasing +I effect ahead:

$$O^- > COO^- > CR_3 > CH_3$$
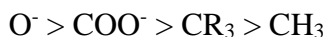
The strength of inductive effect decreases along the C-C chain such that the greater the distance from the group, weaker the effect. Inductive effect affects several properties of the organic molecules such as their acidity and basicity. It also affects the stability of carbocations and carbanions.

Effect on acidity and basicity:

Acidity of organic compounds such as carboxylic acids is the measure of how easily they release a proton. It can also be expressed in terms of stability of conjugate bases. More stable the conjugate base more will be the acidity of carboxylic acid. Hence, substituent with -I effect increase the acidity of carboxylic acid. For example, trifluoroacetic acid is stronger acid than the acetic acid (**Figure 4.3**). Similarly, basicity of amine is their affinity to accept protons. Thus, substituents with -I effect decrease the basicity of amines. For example, pyridine is stronger base than the nitropyridine (**Figure 4.3**).
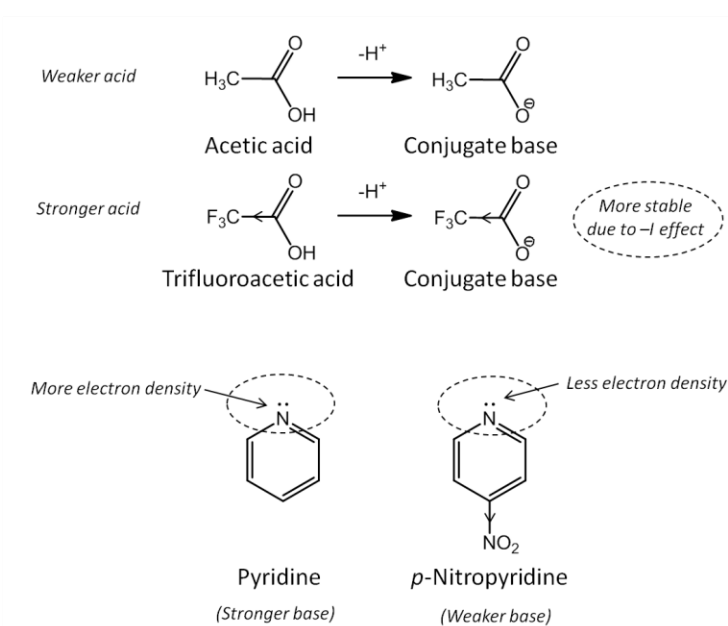
Figure 4.3. Effect of inductive effect on acidity and basicity.

Stability of carbocations and carbanions

Substituents with -I effect increase the positive charge density of carbocations, hence they decrease the stability of carbocations. On the other hand, substituents with +I effect stabilize the carbocations (**Figure 4.4**). Similarly, Substituents with -I effect decrease the negative charge density of carbanions, hence they increase the stability of carbanions. On the other hand, substituents with +I effect destabilize the carbanions.
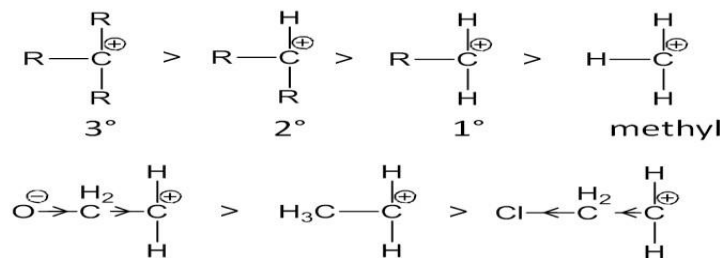
Figure 4.4: Effect of inductive effect on stability of carbocations.

4.5 MESOMERIC EFFECT:

The polarity developed between atoms of a conjugated system by the electron transfer or pi–bond electron transfer is known as the mesomeric effect. In simple terms, we can describe that the mesomeric effect occurs when π electrons move away from or towards a substituent group in a conjugated orbital system. For example:
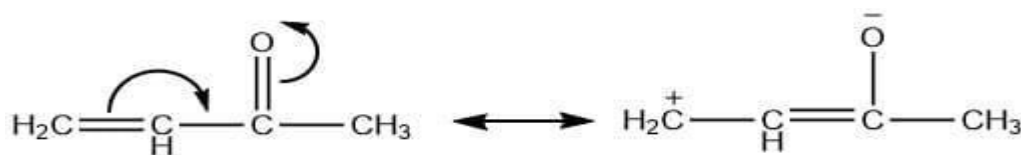
The mesomeric effect can be subdivided into two types:

    a) +M effect

    b) -M effect

a)+M effect (Positive mesomeric effect)

When the electrons or the pi electrons are transferred from a particular group towards a conjugate system, thus increasing the electron density of the conjugated system, such a phenomenon is known as the (+M) effect or positive mesomeric effect.

The +M effect causes the conjugate system to have a negative charge or the electron density to increase on the conjugate system. These conjugate complexes have a higher electrophile reactivity and a lower nucleophile reactivity.

The positive mesomeric effect can be seen in the following group in this particular order:

$-O^- > -NH_2 > -OR > -NHCOR > -OCOR > -Ph > -CH_3 > -F > -Cl > -Br > -I$
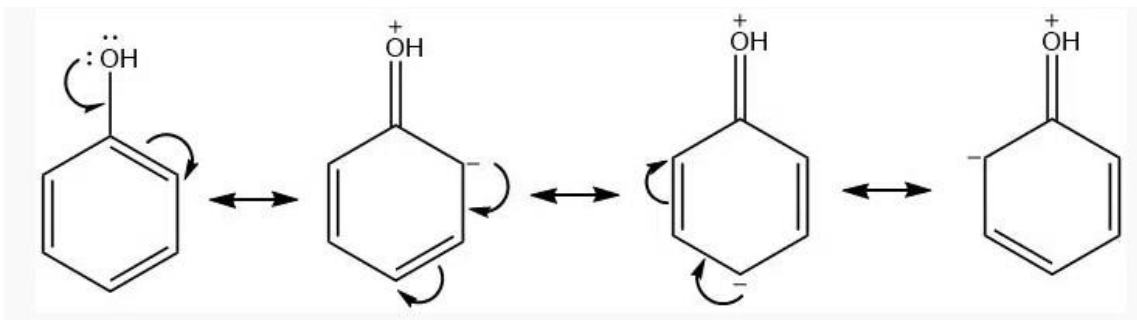
b) -M effect (negative mesomeric effect)

When the π electrons are moved from the rest of the molecule to a particular group, the electron density of the molecule/conjugated system decreases. Such an effect is called negative mesomeric effect (-M effect). It is shown by electron-withdrawing substituent.

The –M effect makes a molecule more reactive to a nucleophile by lowering the electron density in the conjugate system but also makes it less reactive to an electrophile for the same reasons.The negative mesomeric effect can be seen in the following group in this particular order:$-NO_2 > -CN > -SO_3H > -CHO > -COR > -COOCOR > -COOR > -COOH > -CONH_2 > -COO^-$

4.6 ELECTROMERIC EFFECT:

Electromeric effect is the molecular polarization produced due to the presence of a reagent. This effect is shown by compound having double or triple bonds. For example, carbonyl bond polarizes in presence of a nucleophilic reagent such as cyanide anion. However, the polarity vanishes when the reagent is removed. Thus, electromeric effect is a temporary effect. Electromeric effect can be classified into +E and -E effects based on the direction of transfer of the electron pair. When the electron pair moves towards the attacking reagent, it is termed as the +E effect. The addition of acids to alkenes is an example of the +E effect. When the electron pair

BASICS OF CHEMISTRY

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moves away from the attacking reagent, it is termed as the -E effect. The addition of cyanide ion to carbonyl compounds is an example of -E effect.
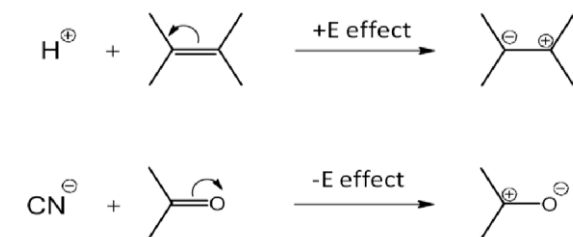
Figure 4.5: Schematic depiction of +E and -E effects.

The other effect operates not through bonds, but directly through space or solvent molecules, and is called the field effect. It is very difficult to separate inductive effect and field effect, but it   has been done in a number of cases, generally the field effect depends on the geometry of the molecule but the inductive effect depends only on the nature of bonds. For example, in isomer 1 and 2 the inductive effect of the chlorine atoms on the position of the electrons in the COOH group should be the same since the same bonds intervene; but the field effect is different because the chlorines are closer in space to the COOH in 1 than they are in 2. This effect can be confirmed by the comparison of the acidity of 1 and 2.

1
$pK_a = 6.07$

2
$pK_a = 5.67$
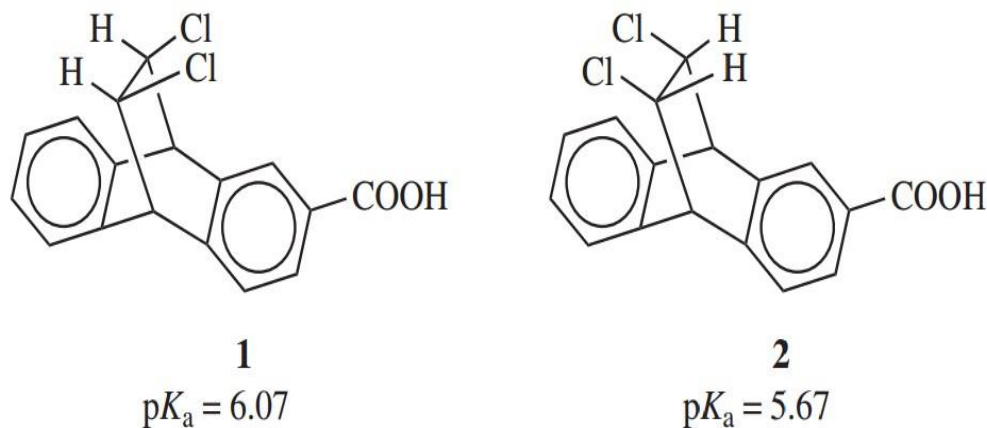
4.7 HYDROGEN BONDING

A hydrogen bond is the electrostatic attraction between two polar groups that occurs when a hydrogen (H) atom covalently bound to a highly electronegative atom such as fluorine (F) ,

nitrogen (N) , oxygen (O) experiences the electrostatic field of another highly electronegative atom nearby. In other words when hydrogen atom covalently connected to electronegative atom comes in vicinity to another electronegative atom, it acts as a bridge to join both entities. It is a weak bond formed by the weak interaction and is represented by dotted line (……).

The common examples in which hydrogen bonding exists are:
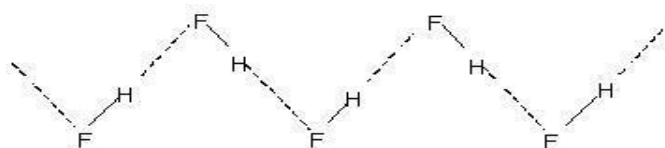
(HF)$_x$ cluster
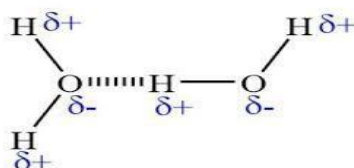
In H$_2$O molecules hydrogen bonding

Types of Hydrogen bonding

The hydrogen bonding in the compounds has been found of two types:

i)**Intermolecular hydrogen bonding :** This type of H-bonding takes place between several molecules of the same substance or different substances. This process is also known as association. The examples of this type of H-bonding are H$_2$O, NH$_3$, HF etc.

For example: Intermolecular H-bonding are given below between the same and different molecules of substances.
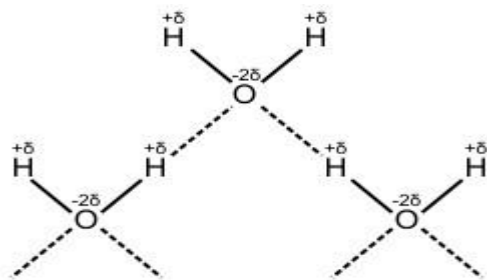
In H$_2$O molecules hydrogen bonding (same molecules)
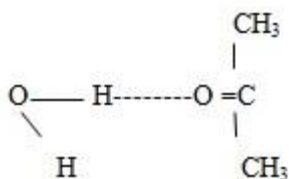
Acetone

In acetone and water hydrogen bonding (different molecules) ii)Intramolecular hydrogen bonding : This type of hydrogen bond is formed between the two atoms of the same molecule, one of the atoms being H-atom. It may lead to the linking of two groups of a molecule to form a ring structure.For example: intramolecular hydrogen bonding occurs are aromatic organicmolecules *viz.* o-nitrophenol, o-chlorophenol, salicylic acid, salicylaldehyde etc.
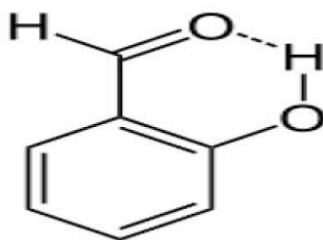
Intramolecular Hydrogen Bonding in Salicylaldehyde

Significance of Hydrogen Bonding:

1. Hydrogen bonds are important in forming the secondary structures of proteins —the helix and the pleated sheet.
2. Water has relatively high boiling point due to hydrogen bonds.
3. The structure of DNA has a double – helix structure because hydrogen bond hold together the base pairs in the middle.
4. When one molecule forms hydrogen bonds through two or more sites with another molecule to form a ring structure which is known as chelate and the process is known as chelation.

4.8 SUMMARY

This chapter provides with the concise description of fundamental concepts of the organic chemistry. The description on topics such as Electronegativity,and polarization of covalent bond on the basis of Fajan's rule . Other significantly important topics such as inductive, mesomeric electromeric effects., Introduction to the topics such as and hydrogen bonding ,its types and its significance.The main object is, stimulate the interest of reader to the advanced studies in organic chemistry.

4.9 TERMINAL QUESTION

Q.1 What is the phenomenon of polarization of covalent bond?

Q.2 What is mesomeric effect ? It should divided into how many type explain.

Q.3 What is electromeric effect? Why it is called a temporary effect?

Q.4 What do understand by hydrogen bonding? How they are divided?

Q.5 What is Inductive effect ? How they are classified?

Q.6 Discuss the stability order of alkyl carbocations with the help of inductive effect.

Q.7 Write a short note on Fajan's rules?

Q.8 Why water is liquid at room temperature while hydrogen sulfide is a gas?

Q.9 NH_3 has much higher boiling point than PH_3 why explain?

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BLOCK-II: PERIODIC PROPERTIES AND GASEOUS STATE UNIT 5: PERIODIC PROPERTIES

CONTENTS:

5.8 References for further studies

5.1INTRODUCTION

With the rapid advance of chemistry with time, the number of discovered elements increased continuously. These elements exhibited marked difference in their properties. Hence it became more and more difficult and tedious job for the scientists to study each and every element individually for its physical and chemical behaviour. Therefore, many attempts were made to arrange the elements with similar physical and chemical behaviour, at one place to make their study systematic and easier. This attempt was named the periodic classification of elements which means, the ideal arrangement of those elements which are alike in their behavior. It was thought, in the process, that there might be some relation between some fundamental characteristic of an element and its properties. Originally, this characteristic taken into account was the atomic weight, later called atomic mass. Eventually, the atomic mass was replaced by more appropriate basis, the atomic number. At the same time the periodicity in properties of the elements was also taken care of.

According to modern Periodic law, the atomic properties of the elements, *viz.* atomic and ionic radii, atomic volume, ionization potential (or energy), electron affinity or affinity energy and electro negativity and properties associated with them, viz. oxidizing and reducing properties, metallic (or electropositive) and non-metallic (or electronegative) properties are the periodic functions of their atomic number. Hence the term periodic means the recurrence of similar properties of elements after certain regular intervals, also called the periodicity. These properties have been found to depend on the electronic configuration of the elements. It means the cause of periodicity in properties of elements appears to lie in the recurrence of similar valence shell configuration of their atoms at certain regular intervals. Though, these properties apply up to some extent to all the elements of the periodic table, yet special emphasis will be laid down on the main group elements while taking the examples of the applications of the properties.

5.2 OBJECTIVE

The objective of writing the text of this unit is to give the readers information about how the elements whose number increased with time, were organised in the tabular form. The systematic classification of these elements with respect to their physical/chemical properties made the readers and the scientists comfortable and predictable in their further study. Till date, this number has gone up to 112 to whom symbols have been assigned and some more elements have been predicted and evidenced by laboratory studies. In this unit is to provide the readers an adequate knowledge of the properties of atoms of the elements which are called atomic or periodic properties. A sincere attempt has been made to provide the information regarding the size of the atoms/ions and their determination, effect of energy supplied to an atom of the elements, the behavior of the atoms towards the electrons trying to enter the region of their influence as well as those lying between the atoms as bonding pairs, variation of atomic properties of elements along the periods (horizontal rows) and down in groups (vertical columns) and some other interesting facts related to these properties.

5.3 PERIODIC TABLE AND PERIODIC LAW

The first important attempt for the arrangement of elements, i.e. their classification, was made by Dobereiner in the beginning of nineteenth century by proposing what is now known as

"Dobereiner's law of triads". According to him when various triads (i.e. containing three) of elements with similar properties were arranged in increasing order of their atomic weights, the atomic weight of the middle element of the triad was found approximately equal to the arithmetic mean of the remaining two corner elements. For example:

Li	Na	K
7	23	39

S	Se	Te
32	79	127.6

Cl	Br	I
35.5	80	127

This law of triads was not found useful because triads of all the known elements at that time could not be formed.

In the middle of nineteenth century, scientist **Duma** put forward his idea called **"Duma's homologous series"** in an attempt to classify the elements. He proposed that "the atomic weights of certain elements could be placed in homologous series like organic compounds". For example, the elements of nitrogen family were arranged as follows:

Element	Atomic Weight	Homologous series
N	14	A
P	31 (14+17)	A+B
As	75 (14+17+44)	A+B+C
Sb	119 (14+17+2x44)	A+B+2C
Bi	207 (14+17+4x44)	A+B+4C

(Here A = 14, B = 17 and C = 44).

This scheme of Duma was also not found useful in the classification of elements.

Further step in this field was takenin 1864 by John Newlands, an English chemist. He tried to correlate the chemical properties of elements with their atomic weights and proposed a law, now known as "**Newlands' law of octaves**". According to this law "**if the elements were arranged in increasing order of their atomic weights, every eighth element was found to have similar properties**". For example, as given below, the eighth element starting from Li is Na which have similar properties. Similarly, Mg is the eighth element from Be and both of them also have similar properties.

Li	Be	B	C	N	O	F
7	9	11	12	14	16	19

Na	Mg	Al	Si	P	S	Cl
23	24	27	28	31	32	35.5

However, this classification proposed by Newlands was limited to 14 elements only (given above) and his work was not accepted by scientific community. **Laws of periodic table:**

A) Mendeleev's Periodic law:

Dmitri Mendeleev, a Russian chemist, in 1869 observed that "**when the elements were arranged in the increasing order of their atomic weights, the elements with similar properties recurred (or reappeared) at regular intervals (or periods)**". From this observation, he put forward a law

known as Mendeleev's periodic law. This law states: **"The physical and chemical properties of elements are periodic functions of their atomic weights"**.

Working on this law, he arranged the elements, known at his time, in the increasing order of atomic weights and presented them in the form of a table. That was known as **Mendeleev's periodic table (please see table 5.1).**

Table 2.1: Mendeleeff's Original Periodic Table.

Group / Row	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	H=1							
	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
	K=39	Ca=40	?=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Co=59 Ni=59
	Cu=63	Zn=65 ?=68		?=72	As=75	Se=79	Br=80	
	Rb=85	Sr=87	Yt=88	Zr=90	Nb=94	Mo=96		
	Ag=108	Cd=112 In=113		Sn=118 –	Sb=122	Te=127.6	?=100	Ru=104 Rh=104 Pd=106
	Cs=133	Ba=137	Di'=138	Ce=140			I=127 –	
			Er=178	Hf=180	Ta=182	W=184		Os=195 Ir=197 Pt=198
	Au=199	Hg=200 Tl=204		Pb=207	Bi=209			
				Th=231		U=240		

Table 5.1: Mendeleev's original Periodic Table

In that table, the elements were arranged in columns (called groups) and rows (called periods). The original periodic table formed by Mendeleev had following characteristics: i)The elements were arranged in the increasing order of their atomic weights.

ii) The table contained eight vertical columns and seven horizontal rows.

i) Every column (group) contained two sub groups (subgroup A and subgroup B) except, the eighth column which contained three series of three elements (triads). iv) The columns contained the elements of similar physical and chemicalproperties.

v) First period (horizontal row) was called very short period, second and third periods were named as short periods, fourth and fifth periods were called long periods and sixth period was named very long period. Seventh period contained only a few elements (and is still incomplete). The elements of 2nd and 3rd periods were called the typical elements by Mendeleev because, these were truely the representatives of their respective groups.

vi)   Mendeleev had left empty spaces for elements unknown at his time, e.g. Sc, Ga, Ge etc. but had predicted their properties. At his time, around 65 elements were known.

Merits of Mendeleev's Periodic Table:

i)It helped in the study of elements and compounds which has become easy and systematic.

ii)The empty spaces in the Mendeleev's periodic table encouraged the scientists to work in the field of discovery of new elements since he had predicted the properties of the probable elements.

Defects of the Mendeleev's Periodic Table:

Although Mendeleev's periodic table helped a lot to study the properties of elements and correlate the elements with one another, yet there were some anomalies which existed unanswered in the Mendeleev's table. These were:

i)The position of hydrogen remained inappropriate because some of its properties resembled with alkali metals and some others with halogens. Hence it might be placed in   group I or group VII.

ii) Dissimilar elements of sub groups were placed together in groups, i.e. alkali metals and coinage metals of 1st group have altogether different properties. Similar is the case with halogens and elements of manganese family in group VII (sub groupA and B elements).

iii)Certain elements with higher atomic weights were placed before those with lower atomic weights, e.g.

Cobalt   Nickel (elements of group VIII, triad I)
58.93   58.69

Tellurium   Iodine (elements of group VI and VII)
127.60 126.90

iv)The Table did not show any correlation between chemical properties and   electronic configuration of elements.

 v) No information regarding the position of isotopes and isobars was available from the   table.

Modified form of Mendeleev's Periodic Table:

Mendeleev did not imagine the discovery of inert elements, therefore no place was left by him in his periodic table for these elements. After the discovery of inert gases (later called the noble gases),a new group was added to accommodate these elements to his Periodic Table which is called zero group. Similarly, the lanthanides and actinides could not find the proper place in his periodic table. Later including these and other elements which were discovered after Mendeleeff, a modified table was prepared which has been given (**Table 5.2**).

Group →	I		II		III		IV		V		VI		VII		VIII	0
Periods↓	A	B	A	B	A	B	A	B	A	B	A	B	A	B		
1	H															He
2	Li		Be			B		C		N		O		F		Ne
3	Na		Mg			Al		Si		P		S		Cl		Ar
4	K		Ca		Sc		Ti		V		Cr		Mn		Fe Co Ni	Kr
		Cu		Zn		Ga		Ge		As		Se		Br		
5	Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru Rh Pd	Xe
		Ag		Cd		In		Sn		Sb		Te		I		
6	Cs		Ba		La*		Hf		Ta		W		Re		Os Ir Pt	Rn
		Au		Hg		Tl		Pb		Bi		Po		At		
7	Fr		Ra		Ac**											

Lanthanide series* (along with langhanum)	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide series** (along with actinium)	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Table 5.2 Modified form of the Mendeleev periodic table based on atomic weight.

This table has following characteristics:

(i) This table contains nine vertical columns or groups including the zero group.

(ii) Except the elements of zero group and eighth group, all the groups have been divided into A and B sub groups. The elements of subgroup A have been kept on left side and those of B on the right side of the group. Elements of a subgroup have more similarities than those placed in the other sub group of the same group. For example, elements of subgroup I A (*viz.,* Li, Na, K, Rb, Cs, etc.) have almost similar properties but differ from subgroup IB elements (*viz.,* Cu, Ag, Au).

(iii) The atomic weights of the elements increase regularly on moving from top to bottom in a column and, in general, in a period with few exceptions.

(iv) The number of horizontal rows has been kept the same but the nomenclature of periods (given in point v of Mendeleev's original periodic table) has been changed in the modified table. The first three periods, in this case, are known as short periods containing 2,8 and 8 elements and the last four are called the long periods though the number of elements is 18 in the fourth and fifth periods and 32 in the sixth period. Seventh period is still incomplete. It may be noted here that there is regular variation in the properties of elements from left to right in a period.

(v) By the year 1900, some 30 more elements had been added to the list of elements. These along with those discovered later have been given in the table.

B) Lothar Meyer's arrangement:

German chemist Lothar Meger, in 1870 proposed independently a more extensive tabulation of the elements based on regular periodic recurrence of properties. He calculated the atomic volumes of the known elements i.e. volume occupied by one mole of the elements (in cm^3) in the solid state. Thus

$$\text{Atomic volume} = \frac{\text{mass of one mole}}{\text{density}}$$

When he plotted these atomic volumes against the corresponding atomic masses, a curve with sharp peaks and broad minima was obtained. This idea could not get wide acceptance and was not taken for further work by scientific community.

C) Modern Periodic law (Moseley's Periodic Law).

This is also called Moseley's periodic law. Henry Moseley, a British physicist, in 1911-12, discovered a new property of the elements called **atomic number** which is equal to the total number of protons in the nucleus of the atom of an element (this is also equal to the number of electrons in the atom). He correlated this property with the physical and chemical properties of the elements. This led Moseley to predict that most of the defects of Mendeleeff's periodic table could be removed if the classification of the elements is done on the basis of atomic number rather than the atomic weight. He, thus, modified the periodic law and stated that **"the properties of the elements are the periodic functions of their atomic numbers".** Meaning thereby, if the elements are arranged in the increasing order of their atomic numbers, the recurrence of properties of the

elements takes place at regular intervals. The elements with similar properties fall in the same vertical columns (or groups) and are called elements of that family.

Modern or Long form of Periodic Table:

This table is also known as Bohr's periodic table and is based on the atomic number, which is a fundamental property of the elements, and Moseley's periodic law. This table helps us to understand the cause of periodicity of properties, i.e. recurrence of similar properties at certain regular intervals viz., 2,8,18, and 32 which are referred to as magic numbers. This is because the atomic number of elements in a group increases by magic numbers at various steps. This is said to be attributed to the electronic arrangement in the atoms of elements.

The modern periodic table has 18 vertical columns called groups or families and 7 horizontal rows called periods. This has been given in (**Table 5.3**).

Table 5.3 Modern or long form of the periodic table.

The detailed discussion of the modern periodic table is given below:

Groups:

In terms of the electronic configuration/arrangement in atoms of the elements, a group consists of elements whose atoms have the same outer most shell electronic configuration (except some of the higher homologues of iron triad). According to IUPAC (International Union of Pure and Applied Chemistry), the groups are numbered as 1,2,3……17,18. Also there is yet another system in practice among the authors in chemistry according to which groups are named as IA, IB, IIA,

IIB, IIIA, IIIB. ………..VIIA, VIIB, VIII and zero group in place of numbering the groups from 1 to 18. In the **table 2.3**, both the systems of numbering the groups have been given. At the same time, the elements have been allocated the blocks in the table *viz.,* groups 1 or (IA) and 2 or (IIA) have been placed in s-block, the groups 13 or (IIIA), 14 or (IVA)……….17 or (VIIA) and 18 or (zero group) have been included in p-block. These elements of s and p-block (total 8 columns) are collectively called **main group elements.** The elements placed in s-block and p-block except the elements of groups 18 (zero group) are also known as **representative elements** and zero group elements are called inert or noble gases. The elements of the groups 3 or (IIIB), 4 or (IVB),……..7 or (VIIB), 8 to 10 or (VIII),11 or (IB) and 12 or (IIB) (total ten vertical columns) have been placed in d-block (also called transition elements). There are 28 elements arranged separately in two horizontal rows at the bottom of the main body of the periodic table, each row containing 14 elements. These have been included in f-block also known as innertransition elements or rare earth metals. First row of the elements is called 4f-block elements or lanthanides because they all are having almost similar properties and follow the element lanthanum. The second row is the 5f-block elements or actinides as they fall after actinium and also have almost similar properties.

The transition elements have been placed between s-and p-block elements and inner transition elements within transition elements.

Periods:

The modern periodic table has seven periods. Each period begins with alkali metal (except first one) and ends at a noble gas. The elements in the periods have also been arranged in the increasing order of their atomic numbers and it increases by one unit at each step. The first three periods are known as short periods:

The elements of first period are H_1 and He_2 only (2 elements) The second period contains the elements from Li_3 to Ne_{10} (8 elements) and the third period includes the from Na_{11} to Ar_{18}(8 elements). The next three periods are collectively called long periods and include the elements as follows:

Fourth period: potassium   (K, Z= 19) to krypton (Kr, Z = 36)   (18 elements)

Fifth period: rubidium   (Rb, Z = 37) to xenon (Xe, Z = 54)   (18 elements)

Sixth period: caesium   (Cs, Z = 55) to radon (Rn, Z = 86)   (32 elements).
Seventh period: francium   (Fr, Z = 87) to copernicium (Cn, Z = 112)   (26elements, incomplete)

The seventh period will be completed at $Z = 118$ (a noble gas) but at present it is in complete. All the elements of this period are radioactive.

The elements of third period except Ar (Na_{11} - Cl_{17}) are called typical elements.

The typical feature of the long form of periodic table is that the elements of 4th, 5th and 6th periods which fall under main group elements are sometimes called the **"normal elements"** because they resemble the elements of 2nd and 3rd periods below which they are placed. The 6th period also includes 14 elements ($Z = 58$ to 71) which follow lanthanum (La_{57}) and hence are known as lanthanones or lanthanides. The 7th Period contains another series of 14 elements ($Z = 90$ to 103) following actinium (Ac_{89}), therefore these elements are called actinones or actinides. The elements beyond uranium (U, $Z = 92$) *viz.,* $Z = 93$ to 103 (neptunium to lawrencium) are known as trans-uranic elements and have been prepared artificially in the laboratory.

Lanthanides:	Ce_{58}	14 elements	Lu_{71}
Actinides:	Th_{90}	14 elements	Lr_{103}

In general, all the elements of the long form of periodic table have been divided into four categories:

i)Representative elements:

These are the main group elements including the groups 1,2,13…….17 which have either ns^1 or ns^2 and $ns^2 p^x$ (x = 1-5) outer shell electronic configuration where n is the highest value of principal quantum number. All these elements have been placed in subgroups A of the periodic table.

ii)Noble gases:

These also fall within main group elements and include group 18 (or zero) elements. These all have completely filled s- or s- and p-subshells of outer most or ultimate shell with highest n value, i.e. ns^2 or $ns^2 p^6$ (ns^2 for He). These have also been placed in subgroup A of periodic table.

iii)Transition metals:

These are the elements of groups 3 to 12 and in general have incomplete d-subshell of the penultimate shell and filled s-subshell of ultimate shell with highest n-value. But the elements of some of the groups also have incompletely filled s-subshell of the ultimate shell in addition to

incompletely filled d-subshell of the penultimate shell. All these elements have been placed in subgroups B of the periodic table. **iv)Innertransition elements:**

These elements are said to belong to group 3 or (IIIB) due to close similarity in their chemical properties with those placed in group 3. These elements genrally have incompletely filled (n-1) d and (n-2) f-subshells.

According to their electronic configuration and the type of subshell to which the last of differentiating electron enters in the atom of the elements, the elements in the modern periodic table have been classified into four blocks i.e. s, p,d and f-block elements. **i) s-Block elements:**

All these elements are metals and solid except H and He which are gases. These are the elements in which the last electron enters the s-subshell. The elements of group 1 (alkali metals, *viz.,* Li, Na, K, Rb, Cs, Fr) and group 2 (alkaline earth metals, *viz.,* Be, Mg, Ca, Sr, Ba, Ra) belong to this block in addition to hydrogen (H) and helium (He). The general valence shell electronic configuration of these elements is ns^x (x = 1 or 2) where n is the number of valence shell or number of period which the element belongs to. **ii) p-Block elements:**

These elements in which the differentiating electron enters the orbitals of p-subshell of the valence or outer most shell are called p-block elements. The elements of groups 13 to 18 (except He with configuration $1s^2$) belong to this block. The group number and the elements contained in them are shown here:

Group 13	:	B,	Al,	Ga,	In,	Tl
Group 14	:	C,	Si,	Ge,	Sn,	Pb
Group 15	:	N,	P,	As,	Sb,	Bi
Group 16	:	O,	S,	Se,	Te,	Po
Group 17	:	F,	Cl,	Br,	I,	At
Group 18	:	Ne,	Ar,	Kr,	Xe,	Rn

The general valence shell electronic configuration of these elements in $ns^2 np^x$ (x=1 to 6) and n is the number of shell. The elements of this block exist in all the three states of matter *viz.* solid, liquid and gas. Most of them are non- metals and the rest are metals and metalloids (or semimetals).

iii) d-Block elements:

The elements in which the last electron enters the orbitals of (n-1) d subshell, (i.e. the subshell of penultimate shell) and d-orbitals are, thus, being progressively filled are known as d-block elements. These elements are also termed as **transition elements** and have been placed in the

middle between s-block and p-block elements in the periodic table. Thus, these elements serve as a bridge or transition between highly electropositive s-block and highly electronegative p-block elements thereby being responsible for gradual change in the properties along a period. Hence the name, transition elements has been given to them. These include the elements of group 3 to group 12 (ten columns). These have further been categorised into 3d, 4d, 5d and 6d series depending on the shell number whose d-orbitals are being filled. Each of these series contains ten elements as given below:

3d series: scandium (Sc, Z = 21) to zinc (Zn, Z = 30)

4d series: yttrium (Y, Z = 39) to cadmium (Cd, Z = 48)

5d series: lanthanum (La, Z = 57), hafnium (Hf, Z = 72) to mercury (Hg, Z = 80)

6d series: actinium (Ac, Z = 89), rutherfordium (Rf, Z = 104) to copernicium (Cn, Z = 112)

The general valence shell electronic configuration of these elements is $(n-1)\,d^x\,ns^{1 \text{or} 2}$ (x = 1 to 10). All these elements are metalsand solid except Hg (a liquid).

iv)f-Block elements:

In these elements, the last or differentiating electron, in general, enters the orbitals of (n-2) fsubshell, i.e. the subshell of antipenultimate shell. All these elements are metals and solids. These elements are also called **inner transition elements** because they have incomplete fsubshell as well as incomplete d-subshell and fall within d-block elements. These elements have been divided into two series of 14 elements each, as follows:

4f-series elements (lanthanides): cerium (Ce, Z = 58) to lutetium (Lu, Z = 71)

5f- series elements (actinides): thorium (Th, Z = 90) to lawrencium (Lr, Z = 103)

The general valence shell electronic configuration of these elements is $(n-2)\,f^{0-14}\,(n-1)d^{0-2}ns^2$.

It has been noticed that for s and p-block elements, the outermost shell itself is the valence shell. For d-block elements, two subshells *viz.,*(n- 1)d and n-s subshells taken together form the valence shell. For f-block elements, three subshells *viz.,* (n-2)f (n-1)d and n-s subshells jointly form the valence shell. This is due to nearly similar energy of these subshells. A valence shell is that shell of the atoms of the elements, from which the electrons are used for bond formation or chemical combination.

For long form of the periodic table, it may be noted that the s-block elements (group 1and2) have been placed in the extreme left portion of the table and the p-block elements arekept in the extreme right portion. The middle portion includes d-block elements. At the bottom, f-block elements have been placed separately in two series/rows.

Merits and demerits of modern periodic table

By taking the atomic number as the basis for the classification of the elements in the modern periodic table, most of the demerits of Mendeleev periodic table have been removed.

i) The main characteristic of the modern or long form of the periodic table is that the classification of the elements has been made on the basis of their atomic number which gives an information regarding the valence shell electronic configurations of the elements. If we know the electronic configuration or the atomic number of an element, we can find out its position in the periodic table, i.e. to which group and period that element belongs. For example, for an element the valence-shell electronic configuration is $3s^23p^5$. This gives us the information that 3 is the value of n, i.e. the period and there are 7 electrons in the valence shell, means the elements belongs to VIIA group. Therefore, the element is a member of VIIA group (group 17) and 3rd period.

ii)The subgroups have been placed separately in the modern periodic table thereby making it easy to have the information regarding the properties of the elements.

iii)The modern periodic table still has the drawback regarding the position of hydrogen which shows some properties similar to those of the group 1 elements (i.e. alkali metals) and some with the group 17 elements (i.e. halogens). Also the lanthanides and the actinides have not yet been included in the main body of the periodic table.

properties.

5.4 PERIODIC RELATIONSHIP AMONG THE ELEMENTS

Periodicity of properties

In the modern periodic table, the term periodicity of properties implies that the elements of similar properties reappear at a certain regular intervals of atomic numbers. On examining the properties of elements, it has been found that the elements of the same group have similar properties. These

numbers at which this repetition occurs, are 2,8,18 and 32, i.e. we have to pass these numbers to come across an element of similar properties in a group. These numbers are referred to as magic numbers as stated earlier.

Cause of periodicity

When we look into the electronic configuration of the elements, we find that all the elements belonging to a particular group have similar outer or valence shell electronic configuration. For example, elements of group 1 (IA) have ns^1, those of group 3(IIIB) have $(n-1)d^1ns^2$, the elements of group 13 (IIIA) have ns^2p^1 and those of group 17 (VIIA) have ns^2p^1 valence shell electronic configuration. Because of similar valence shell electronic configuration/arrangement, the elements of a particular group have similar.

5.5*. PERIODIC PROPERTIES*

of their radii. Atomic radii, in general, are used for the distance between the nucleus and electron cloud of the outer most shell of the atoms. Since it is impossible to isolated an individual atom or ion and at the same time, the electron cloud, according to wave mechanical concept, is said to come closer to the nucleus at one moment and to go away from it at the other moment, i.e. it does not remain at constant distance from the nucleus, hence it is rather impossible to measure this distance by any means. These quantities are, however, generally derived indirectly from the measured distance between the nuclei of two bonded atoms in a gaseous molecule, generally known as inter nuclear distance (or bond distance) or between the nuclei of two neighbouring ions in crystalline solids called inter ionic distance.

The experimental techniques like Infrared or microwave spectroscopy, X-ray diffraction, electron diffraction etc. are used to determine the internuclear distance in covalent molecules and interionic distance in ionic substances. These determinations become essential to correlate certain physical properties of elements with them because density, melting point, boiling point etc. are related to the size of atoms.

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[1] **.5.1 Atomic and Ionic Radii:**

These terms correspond to the size of the atoms and ions which are represented by the magnitude

Classification of Atomic Radii

For the purpose of feasibility, the atomic radii of the elements have been explained in three operational categories, as follows:Atomic radii:

A. Covalent radii
B. Metallic or crystal radii
C. van der Waals' radii **A. Covalent radii**

Covalent molecules may be formed by two similar (A_2 type) or two dissimilar atoms (AB type).

Hence, covalent radius of an atom is conveniently defined as "**half of the distance between the nuclei of two atoms of the same element bonded together in a molecule by a single covalent bond**". Thus, for the atom A in A_2 type molecule in which two A atoms are linked by a single bond, covalent radius, denoted by r_A, is given as:

$$d_{A-A} \quad = \quad r_A + r_A = 2r_A \qquad\qquad ....(5.1)$$

$$\text{or } r_A = \quad \frac{dA-A}{2} \qquad\qquad .... (5.2)$$

where d_{A-A} is the internuclear distance between two A atoms in A_2 molecules; r_A in equation 3.2 is known as single bond covalent radius of atom A and is used for a gaseous diatomic molecule. For example, internuclear distance (d_{H-H}) in H_2 molecule is 0.74 Å. The covalent radius of H –

atom, $r_H \quad = \frac{dH-H}{2} = \frac{74}{2}$ pm = 0.37Å. Similarly, the internuclear distance (d_{Cl-Cl}) atom (r_{Cl}) may be calculated as: (Å = 10^{-8} cm)

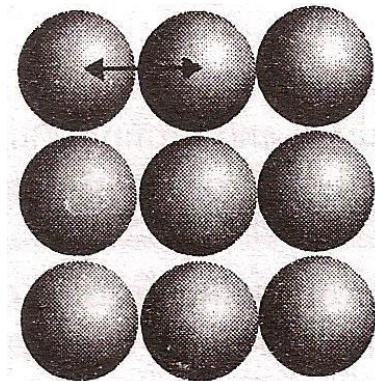$$r_{Cl} \quad = \quad \frac{dCl-Cl}{2} = \frac{1.98}{2} \text{ pm} = 0.99\text{Å}.$$

For atoms bonded together to form and extensive three dimensional network, atomic radius in simply "**half of the distance between the nuclei of two neighbouring atoms**" i.e.

$$r_{cov} \quad = \quad \frac{\text{inter nuclear distance}}{2}$$
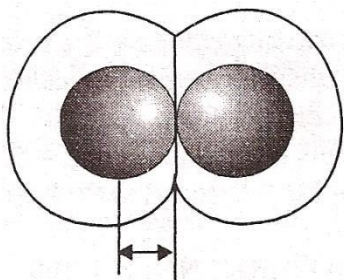
Fig. 5.1 Diatomic molecule

(covlalent radius)

Fig. 5.2 Bulk of atoms

(internuclear distance)

In hetero nuclear molecules (e.g. AB type), the single bond covalent radius can be calculated as given below;

a)When the atoms A and B bonded together by purely covalent bond and the electronegativities of these two atoms are almost same, the internuclear distance is equal to the sum of radii of A and B;

$$d_{A-B} = r_A + r_B \text{ (when } \chi_A = \chi_B) \qquad \dots\dots\dots\dots\dots.(5.3)$$

The internuclear distance, $d_{A\text{-}B}$, can be measured by experimental method and if r_A or r_B (any one) is known, the other unknown term (r_A or r_B) can be calculated by using the equation 3.3.

The value of r_A or r_B may be obtained from $r_A = \dfrac{dA - A}{2}$ or $r_B = \dfrac{dB - B}{2}$.

b)If the electronegativities of the two combining atoms are not the same ($\chi_A \neq \chi_B$), then the experimental value of $d_{A\text{-}B}$ has been found less than the calculated value obtained as a sum of covalent radii r_A and r_B of the heteroatomic molecule. For example,   i)In $(CH_3)_3$ N molecule,

   $(d_{N\text{-}C})$ exp $= 1.47$ Å   and $(d_{N\text{-}C})_{cal.} = r_N + r_C$

$= 0.75+0.77 = 1.52$ Å ii)In HF molecule, $(d_{H\text{-}F})_{exp} = 0.92$ Å   and $(d_{H\text{-}F})_{cal.} = r_H + r_F =$

$0.37+0.72 = 1.09$ Å

 This shortening of $d_{A\text{-}B}$ bond length may be due to the following factor:

a)The higher ionic character of the bond between A and B atoms with larger difference in electronegativities of the hetero atoms. In such a case more electronegative atom attracts the shared pair of electrons towards itself thereby developing slight negative charge on that atom due to accumulation of electrons closer to it and positive charge of equal magnitude on the other atom. This development of opposite charges brings the atoms closer to each other. That is why the experimental value of $d_{A\text{-}B}$ is less than the calculated value. Some correction measures have been suggested in such cases.

In order to compensate this, the following correction has been suggested:

$$d_{A\text{-}B} \quad = \quad r_{A} + r_{B} - 0.09\ (\chi_B - \chi_A) \qquad \text{……...} \quad (5.4)$$

(schoemaker and Stevenson)

Still, if the discrepancy remains, another correction measure may be applied (Porterfield):

$$d_{A\text{-}B} \quad = \quad r_{A} + r_{B} - 0.07\ (\chi_B - \chi_A)^{2} \qquad \text{……............} \quad (5.5)$$

b)The other factors in some cases, may be multiplicity of bonds and effective nuclear charge which cause reduction in the length of covalent bonds and as a consequence in covalent radii. For

example, it has been found that single bond covalent radius> double bond covalent radius> triple bond covalent radius. This is because the formation of multiple bonds brings the combining atoms closer to each other and the bond length is reduced.

Table 5.4: Covalent radii (single bond radii) for hydrogen and some p-block (non-metallic and metalloid) elements except noble gases (in Å)

Group number	s-block		p-block				
	1	2	13	14	15	16	17
Elements with covalent radii	H	-	B	C	N	O	F
	0.37	-	0.82	0.77	0.75	0.73	0.72
	-	-	-	Si	P	S	Cl
			-	1.11	1.06	1.02	0.99
				Ge	As	Se	Br
				1.22	1.20	1.16	1.14
				-	Sb	Te	I
					1.40	1.36	1.33

Among the s-and p-block elements, only the non-metallic elements and metalloids have been taken to tabulate the covalent radii because the formation of covalent bond, in general, is the exclusive property of the non-metals and metalloids. Noble gases have also been excluded from the table because these, except a few, do not participate in covalent bond formation.

Factors affecting the magnitude of covalent radii

There are many factors which influence the magnitude of covalent radii. Some of them are:

(i) **Effective nuclear charge ($Z_{eff.}$)**

As the value of Z_{eff} increases, the force of attraction between the nucleus and outermost shell electrons also increases thereby decreasing the covalent radii of the elements, i.e. $r_{cov.} \alpha \dfrac{1}{Z_{eff}}$

(ii) **Principal quantum number (n)**

This gives the number of shells present in the atoms of the elements. As the value of principal quantum number increases the outermost electrons get farther away from the nucleus and covalent radius also increases provided other factors remain the same, i.e. $r_{cov.} \propto n$

(iii) **Multiplicity of Bonds**

With the increase in the number of bonds between the atoms, these come closer to each other thereby decreasing the covalent radii i.e. $r_{cov.} \propto \overline{multiplicity\ of\ bonds}[1]$

B. Metallic or Crystal Radii

These terms are taken synonymous to covalent radii of metal atoms, though metals generally do not form covalent compounds except hydrides and organo- metallic compounds. Further, metals are assumed to be closely packed spheres in the crystals in which their outer boundaries touch one another. Thus metallic or crystal radius may be theoretically defined as **"half of the distance between the nuclei of any two adjacent metal atoms in close-packed metallic crystal"** For example, the internuclear distance between any two adjacent sodium atoms in a crystal of sodium metal in 3.80 Å. Hence crystal or metallic radius of sodium metal is $3\frac{80}{2} = 1.90$ Å
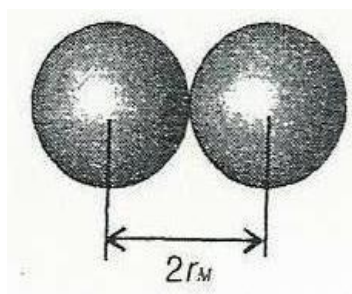
Fig. 5.3 Metallic radius

In practice, in the metallic phase, atomic volumes of metal atoms can be determined from their atomic masses and respective densities. Thus, atomic volume $= \frac{mass}{density}$. From these data, metallic radii can be obtained. It has been found that the covalent radii of metal atoms determined in metal hydrides and organimatallic compounds and metallic radii determined from atomic volumes in metallic phase have almost similar values though not exactly equal. Hence,the term metallic covalent radii can be used. The metallic radii have slightly higher (10%) value than metallic covalent radii because individual bond in metals is weaker and longer than the covalent bond.

Group number	1	2	13	14	15	16
Elements with metallic radii	Li	Be	-	-	-	-
	1.55	1.12	-	-	-	-
	Na	Mg	Al	-	-	-
	1.90	1.60	1.43	-	-	-
	K	Ca	Ga	-	-	-
	2.35	1.97	1.41	-	-	-
	Rb	Sr	In	Sn	-	-
	2.48	2.15	1.66	1.62	-	-
	Cs	Ba	Tl	Pb	Bi	Po
	2.67	2.22	1.71	1.75	1.70	1.76

Table 5.5 Metallic radii of main group metals (in Å)

C. van der Waals' radii

In solid state, the nonmetallic elements usually exist as aggregations of molecules. Although the bonding within a nonmetal molecule is more or less covalent in character yet the binding force between the molecules is van der Waals' force. Thus each molecule assumes equilibrium position within the crystalline solid. It is to be noted that these forces are absent if the substances are in the gaseous state. van der Waals' radius can be defined as" **half of the distance between the nuclei of two non-bonded but adjacent atoms belonging to two neighbouring molecules**". These radii have higher values by 90-100% in lighter elements and 70-80% in heavier elements than covalent radii because of non-bonded type of binding force between the molecules. The values of van der Waals' radii are obtained from X-ray studies of various non-metallic elements in the solid state. On comparing the covalent radii and van der Waals' radii of the nonmetallic elements, it is noted that the van der Waals' radii have higher values. Please refer to **Table 5.6** and **Table 5.7**

Group number	1	15	16	17	18

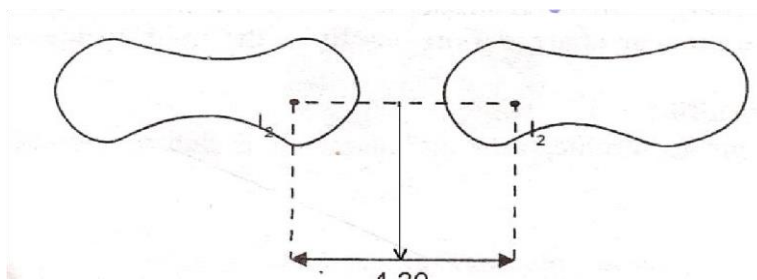| Elements with van der Waal's radii	H				He
	1.20				1.20
		N	O	F	Ne
		1.50	1.40	1.35	1.60
		P	S	Cl	Ar
		1.90	1.85	1.80	1.91
		As	Se	Br	Kr
		2.00	2.00	1.95	2.00
		Sb	Te	I	Xe
		2.20	2.20	2.15	2.00

Table 5.7

Fig. 5.4 van der Waals' radii

Periodic trends of atomic radii a)Variation in a period

The atomic radii (*viz*. covalent radii, metallic radii and van der Waals' radii) and hence the atomic size, in general, decrease on moving from left to right in a period. This is because the atomic number in a period increases by one unit at each step but the electrons in all the elements in a period enter the same outer or valence shell. Hence, there operates an increased force for attraction between these outer electrons and the nuclear charge. As a result, the atomic radius or atomic size

decreases regularly except the noble gases. For example, we can take the elements of second period and hydrogen. The term covalent radius does not apply to the noble gases. van der Waals' radii are applicable to all nonmetallic elements including noble gases but the values for noble gases are exceptionally high due to larger repulsion among the monoatomic species with large number of electron. One Å unit is equal to 10^{-10}m

| Elements	H	C	N	O	F	Ne
Covalent radii (in Å)	0.37	0.77	0.75	0.73	0.72	-
van der Waals' radii (in Å)	1.20	-	1.50	1.40	1.35	1.60

b)Variation in a group

On going down a group, the atomic sizes of elements increase continuously both in metals and non metals as is evident from the table of covalent radii, metallic radii and van der Waals' radii except the metals of third transition series whose atomic sizes are almost similar to those of second transition series metals. At the same time lanthanide series and actinide series of metals have deceasing trend in their metallic radii.

The regular increasing trend in atomic sizes among the main group elements is due to the introduction of new shell at each step in a group which produces larger effect than that produced by the increase in effective nuclear charge.

Ionic radii

Though, it is very difficult to define ionic radius, yet an approximate definition can be given as "**the effective distance between the nucleus of an ion and the point up to which the nucleus exerts its attractive influence on the electron cloud of the ion**". Because it is rather impossible to determine the outer boundary of an ion, therefore if the ions in an ionic crystal are taken as spheres whose outer boundaries are touching one another, the interionic distance (or internuclear distance) may be supposed to be the sum of the radii of the two ions (an additive property).
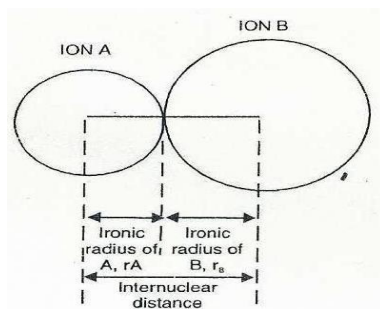
Fig. 5.5 The ionic radius

X-ray analysis of ionic crystals is used for measuring the eqiulibrium distance between the nuclei of the two adjacent ions called interionic distance in taking the ions as spheres. This distance in taken as the sum of the ionic radii of the two ions. e.g.

$$d_{C^+ - A^-} = r_{C^+} + r_{A^-} \qquad\qquad .... \quad (5.6)$$

This equation can be used to find out the ionic radius of a cation or an anion. The interionic distance $d_{C^+A^-}$ can be measured by experimental method and if the radius of any one ion is calculated by some other method, the radius of antother ion can be obtained by using the above equation. For example, the inter nuclear distance between sodium and chloride ions ($d_{Na^+Cl^-}$) in NaCl crystal is 2.76Å and radius of sodium ion (r_{Na^+}) is 0.95 Å. From these values we can calculate the radius of chloride ion (r_{Cl^-}) as follows:

$$d_{Na^+Cl^-} = r_{Na^+} + r_{Cl^-}$$

Putting the values of $d_{Na^+Cl^-}$ and r_{Na^+}, we get 2.75 Å = 0.95 Å + r_{Cl^-} $\quad \therefore$

$r_{Cl^-} = 2.76 - 0.95$Å $= 1.81$Å

Periodic trends of ionic radii

Periodic variation of ionic radii can be easily visualised in main group elements though it is, in general, applied for transition elements.

a)Variation in a period

Since atomic size decreases along a period from left to right, the cationic or anionic size also decreases in the same direction. For transition elements this trend is observed if they are in the same oxidation state.

b)Variation in a group

As we move down a group of main group elements, the cationic or anionic size increases regularly provided the elements are in the same oxidation state. Similar trend, in general, is observed for transition elements though the change in cationic size is very small or negligible between second and third transition series elements. Reverse trend has been observed in case of lanthanides and actinides where ionic size decreases in the series.

Some important facts regarding ionic radii are given below:

i)Ionic radii of isoelectronic species

The isoelectronic species are the cations, anions and atoms of different elements having same number of electrons and same electronic configuration. For example, a common isoelectronic series with ten electrons, i.e. $1s^2\,2s^2\,2p^6$ configuration is given here with their radii;

Ion/atom	C^{4-}	N^{3-}	O^{2-}	F^-	Ne	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Atomic numbers	6	7	8	9	10	11	12	13	14
Radius (Å units)	2.60	1.71	1.42	1.36	-	0.95	0.65	0.50	0.41

It is evident from this table that, as the atomic number (or nuclear charge) of the parent atoms from which the ions have been derived, increases the ionic radius decreases. This is because with the increase in the nuclear charge, the attractive force between the nucleus and the outer electrons also increases thereby the electrons come closer to the nucleus and consequently the size of the ions decreases.

i)A cation is smaller in size than its parent atom because a cation is formed by the removal of electron (s) from the neutral atom; hence the number of electrons becomes less than the number of protons (nuclear charge). As a result, the electrons are strongly pulled by the nucleus thereby causing a contraction in the size of the cation. Therefore, the cation is smaller in size than its parent atom.

ii)An anion is larger is size than its parent atom. This is because, an anion is formed by the addition of extra electron (s) in a neutral atom. Thus the number of electrons becomes greater than that of protons (nuclear charge) and the electrons are loosely held by the nucleus. As a result, the anionic size becomes larger than the size of the parent atom.

iii)For the cations or the anions of the same element in different oxidation states, the cationic size decreases but the anionic size increases with the increasing oxidation states, i.e. for anions: r_{A^-} $<r_{A2^-}< r_{A3^-} <r_{A4^-}$ …….etc. and for cations $r_{C^+}> r_{C^{2+}} >r_{C^{3+}}>$……etc. (C = cation, A = anion)

Factors affecting ionic radii

The main factors that affect ionic radii are as follows:

a)Crystal coordination number (CCN)

With the increase in the crystal coordination number, the interionic distance also increases thereby increasing the ionic radii, For example, the radius of Cl⁻ ion (r_{Cl^-}) in CsCl crystal (C.C.N. = 8) is slightly higher than its radius in NaCl Crystal (CCN =6). This is because with the higher CCN, the number of ions surrounding a particular ion is greater, causing less attraction between the oppositely charged ions than that with lower CCN i.e. $r_{ion} \alpha$ CCN **b)Radius ratio (R_r)**

Radius ratio ($R_r = \frac{rc^+}{rA^-}$) also affects the magnitude of ionic radius. If the R_r is larger due to large cation and small anion, the anion-anion repulsion is less and the interionic distance becomes shorter than the sum of the ionic radii (i,e. $d_{C+A-} <r_C+r_{A^-}$) but if R_r is smaller due to small cation and large anion, the anion-anion repulsion is more and interionic distance is greater than the sum of the ionic radii (i.e. . $d_{C+A-} > r_C+ r_{A^-}$)

c)Covalent character of Ionic Bond

Ionic radii decrease as the covalent character in ionic bond increases. $r_{ion} \alpha \frac{1}{covalent\ character}$.

5.5.2 Ionization energy (IE):

This term is related with the removal of electron (s) from the neutral atom and converting it into a positive ion (or cation). If the energy is supplied to an atom, its electron (s) may be promoted to a higher energy level and if this energy is sufficient enough, the electron (s) may completely be removed from it giving a cation. Thus "**the minimum amount of energy required to remove a loosely bound electron from an isolated gaseous atom of an element in its ground state is called its ionization energy**". In the definition, gaseous atoms are specified because an atom in gas phase is uninfluenced by its neighbours and there is no intermolecular forces to take into account while measuring ionization energy. This can be shown as follows:

$$C(g) + (IE)_1 \longrightarrow C^+ (g) + e \text{ (energy absorbed, endothermic process)}$$
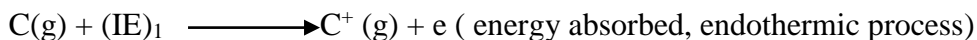
In this process, if one electron is removed, it is termed as the first ionization energy, $(IE)_1$. For many electron atom, if more electrons are removed from an atom, the ejection of electrons occurs one by one in steps depending on the amount of energy absorbed/supplied. Thus corresponding to the removal of second electron, the energy is known as second ionization energy, $(IE)_2$ and if third electron is removed, the corresponding energy which has to be supplied is called third ionization energy, $(IE)_3$ and so on. Alternatively, these are also known as successive ionization energies. The sequence of ionization energies in their increasing order may be given as:

$$(IE)_1 \ll (IE)_2 \lll (IE)_3 \ \ldots\ldots\ldots\ldots.(IE)_n.$$

This is because when an electron is removed from a neutral atom to give a cation, the number of the remaining electrons of the cation becomes less than the nuclear charge and greater attractive force operates between these electrons and nucleus causing contraction in the size of cation. Therefore, more energy is required to remove another electron from the cation, i.e. $(IE)_1 \ll (IE)_2.$ Due to the similar reason, still higher amount of energy is required to remove yet another electron, i.e. $(IE)_2 \lll (IE)_3$ and so on.

An alternative explanation for this observation may be given. Since, the magnitude of ionization energy is a measure of tightness with which an electron is held in the atom, hence higher the ionization energy, more tightly the electron is held in the atom and more difficult it is to remove it. The ionization energy is expressed in the units of kilojoules per mole (kJ/mole) or kilo calories per mole (k Cal/mole)

It has been observed that among the elements of the periodic table, the alkali metals have the least and the noble gases have the highest ionization energy values in the respective periods. Helium has the highest value and caesium possesses the lowest value of first ionization energy among all the main group elements.

Atomic Number (Z)	Element	$(IE)_1$	$(IE)_2$	$(IE)_3$ ……
1	H	1312	-	-
2	He	2373	5251	-
3	Li	520	7300	11850
4	Be	899	1757	14850
5	B	801	2430	3660
6	C	1086	2350	4620
7	N	1400	2860	4580
8	O	1314	3390	5300
9	F	1680	3370	6050
10	Ne	2080	3950	6120

Table 5.8: The successive ionization energy values (in kJ/ mole) of the first ten element

Factors affecting the magnitude of ionization energy

i)Atomic Size (or The Principal Quantum Number)

As the principal quantum number for the outer electrons increases, the atomic size also increases and the ionization energy of the elements decreases and vice versa, i.e. IE $\alpha \; \overline{\frac{1}{n \; or \; r \; atom}}$. This can be seen in a group. **ii)Nuclear charge**

As the nuclear charge increases, other factors remaining the same, more and more attractive force operates between the nucleus and outer electron(s). Thus more energy is required for the removal of electron(s) and as a consequence, the ionization energy goes on increasing. This is observed along the periods, in general, IE α nuclear charge.

(iii) Penetrating power of valence electrons

In a given shell, the penetrating power of the electrons decreases in the order   s > p > d >f, therefore, ns electrons are more firmly held by the nucleus (due to highest penetrating power) than np – electrons followed by d and f electrons (due to their scattered orientation).

Accordingly, the ionization energy decreases as follows: ns >np >nd >nf i.e. IE α penetrating power.

iv) Shielding effect of inner electrons

In poly electron atom, the valence electrons are attracted by the nucleus and at the same time repelled by the inner shell electrons. As a result, the outer most electron experiences less attraction from the nucleus because inner electrons act as screen or shield between outer electrons and nucleus. This effect produced by inner electrons is called the shielding effect. Within a given shell, this effect decreases in the order: s>p>d>f. Thus, an increase in the number of inner or intervening electrons causes more shielding effect thereby decreasing the attractive force between the nucleus and outer electrons. Consequently the ionization energy also

decreases, i.e. IE α $\dfrac{1}{shielding\ effect}$

v)Stable electronic configuration

 According to Hund's rule, half filled (*viz.*ns^1, np^3, nd^5 etc.) or completely filled orbitals (*viz.*ns^2, np^6, nd^{10} etc.) are more stable than the partially filled orbitals. Hence more energy is required to remove the electron (s) from such orbitals. This means that the ionization energy of an atom having half filled or completely filled orbitals in its ground state is relatively higher than expected normally from its position in the periodic table. The relative stablility order of such orbitals has been found as $d^5< p^3< d^{10} \ll p^6$. For example, the ionization energies for Be ($2s^2$) and N ($2s^2\ 2p^3$) in the second period and Mg and P, the higher homologues of Be an N, in the third period are slighty higher than expected values. This is becauseof the extra stability of the electronic configuration of these elements, High values of ionization energy for noble gas elements is also due to stable $ns^2\ np^6$ (He - ns^2) configuration in the vacance shell, i.e. IE∝ stable configuration.

To gain the necessary energy for the removal of electrons from an atom, a potential difference has to be applied across the sample of element. This potential difference giving the necessary energy is called the ionization potential.

Priodic trends

i) Variation along a period

On going from left to right in a period, there is, in general, an increase in the ionization energy values of the elements due to the effect of reduction in the atomic radii and increase in the nuclear charge by one unit at each step but the outer shell remaining the same (n is constant for the elements of a period). Thus, the electrons in these elements are being successively filled to the same shell. Such electrons shield each other poorly from the increasing nuclear charge. As a result, Z_{eff} increases which cause an increase in ionization energy.

There are some exceptions to this trend. Let us consider the elements of secound period i.e. Li_3 to Ne_{10} for which the expected order of ionization energy is Li< Be < B < C< N< O< F < Ne. The experimental values, however, show that Be and N have higher IEvalues than those of the nextelements, i.e. B and O. This anomaly can be explained on the basis of their stable electronic configurations, i.e. Be (ns^2)> B $(ns^2 np^1)$ and N $(ns^2 np^3)$ > O $(ns^2 np^4)$ (please refer to the IE table of elements). This is evident from the ionization energy values of the above elements that it is easier to remove the last and loosely bound electron from B or O-atoms as compared to that from Be or N-atom and thus elements (B and O) have lower first ionization energy values than Be and N.

The elements of the transition series show irregular trends of ionization energies along their periods due to shielding effects and electronic configurations.

ii) Variation in a group

On going from top to bottom in a group of elements, the nuclear charge increases regularly. This must cause an increase in the IEvalues of the elements. At the same time, the atomic size also increases due to the introduction of a new shell at every next element in the group. This causes a decrease in the IE values of the elements. The effect of increased size is more than that due to increased nuclear charge. The net result is the continuous fall in the values of ionization energy down the group.

Alternatively, this trend may also be explained by the fact given here. As we move down a group, the number of inner shell electrons called intervening electrons increases. As a result there in more shielding effect caused by the inner electrons on the outer electrons. This decreases the ionization energy values of the elements in a group.

There are some exceptions also. The first ionization energy of $Ga_{31,}$ an element of fourth period is slightly higher than that of Al_{13}, the element of third period [(IE)$_1$ of Al = 577.6 kJ/mole and (IE)$_1$ of Ga= 578.8 kJ/mole]This is perhaps due to the poor shielding effect of $3d^{10}$ electrons. Also, the third row of transition elements shows higher value of ionization energy as compared to second row elements. This is due to the decrease in size of these elements as a result of insertion of lanthanides in 6th period (Lanthenide contraction).

Application of ionization energy

i)Prediction of electropositive character

The electropositive character of the elements is related to the ease with which the electron (s) could be removed from the atom of the elements. More electropositive is the elements, more easily the electron (s) can be removed. As we move down a group, the ionization energy of the elements decreases regularly and hence the electropositive character also increases accordingly. Across a period, the ionization energy of the elements, in general, increases means the electropositive character decreases from left to right. Alkali metals placed at the extreme left portion of the periodic table, are the most electropositive elements with low values of ionization energy.

ii)Prediction of metallic and non-metallic character

The elements with low ionization energy are more metallic in nature because they can lose electrons easily. Hence metallic character increases from top tobottom in the groups and decreases along the period from left to right. The elements showing the opposite trend in ionization energy and periodic variation to that of metals are called the non-metal.

iii)Prediction of reducing power of an element

Lower the value of ionization energy of an element, greater is its reducing power. The alkali metals with the lowest ionization energy values are the strongest reducing agents among all the elements.
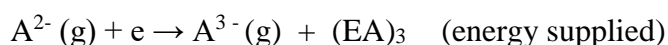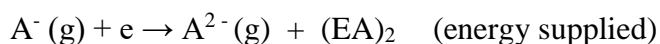
5.5.3 Electron affinity (or affinity energy) (EA).

This term is related with the formation of an anion from a neutral atom of an element by the addition of electron (s). Thus, this is the tendency of the atom to gain the additional electron (s).

The electron affinity (EA) of an element can be defined as the "**amount of energy released when an electron is added to the outer shell of an isolated gaseous atom of the element to produce the gaseous anion**".

This can be shown as: A (g) + e $\rightarrow$ A⁻(g) – (EA)₁ (electron affinity energy released).

Evidently, this is an exothermic process. The expression actually shows the first electron affinity. Once the uninegative anion has been formed by accepting one electron by the neutral atom, addition of another electron (s) in this ion becomes more difficult due to repulsive force operating between the anion and the incoming electron. To overcome this repulsive force, extra energy has to be supplied to the electron which must actually be more than the energy released during the addition of electron, i.e. the energy supplied to electron > energy released during the addition of electron. The net energy change is the energy absorbed (supplied) by the electron, hence the addition of second or third etc. electron to the anion is an endothermic process:

$$A^- (g) + e \rightarrow A^{2-} (g) \; + \; (EA)_2 \quad \text{(energy supplied)}$$

$$A^{2-} (g) + e \rightarrow A^{3-} (g) \; + \; (EA)_3 \quad \text{(energy supplied)}$$

The electron affinity values for the elements of second period are given below:

Element	Li	Be	B	C	N	O	F
(EA)₁ in kJ/mole	60	≤ 0	27	122	≤ 0	141	328

The electron affinity values of Be and N are shown zero because it is very difficult to add an extra electron to the outer shells of these elements due to extra stability of the electronic configuration.

The electron affinity values of halogens are very high because of the $ns^2 \, np^5$ outer shell electronic configuration and very strong tendency to accept the incoming electron thereby getting converted into the negative ions with noble gas configuration, i.e. $ns^2 \, np^6$. Though the first element of halogen group, is expected to have the highest value of EA,but its EAvalue is less than that of Cl. This is due to the smaller size and greater electron-electron repulsion in F-atom which opposes the entry of the incoming electron. The EA values of the noble gases are almost zero due to no

tendency of accepting the additional electron because of stable $ns^2 np^6$ configuration. EA values of halogens and noble gas elements are given below (in k J/mole):

Element	F	Cl	Br	I	At	He	Ne	Ar	Kr	Xe	Rn
$(E_A)_1$ value	328	349	325	295	280	≤ 0	≤ 0	≤ 0	≤ 0	≤ 0	≤ 0

Factors affecting the electron affinity

All the factors which affect the ionization energy also affect the electron affinity. The main factors among them are discussed here:

i)Atomic size

Smaller the atomic size, stronger is the attraction of nucleus for the incoming electron and hence greater is its electron affinity and vice versa, i. e. $EA \propto \frac{1}{atomic\ size}$ (as is seen along a period)

ii)Effective nuclear charge (Z_{eff})

Greater is the effective nuclear change of the elements, stronger is the attraction between it and the electron to be added to the atom. Thus with the increase in Z_{eff}, other factors remaining the same, electron affinity of the elements also increases, i.e. $EA \propto Z_{eff}$ (as is seen along a period). **iii)Stable electronic configuration**

The atoms of the elements with stable electronic configuration do not show any tendency to accommodate the incoming electron (s). Hence the EA values for such elements is almost zero. For example, the elements of 2nd group with ns^2 outer electronic configuration have zero EA values. The elements of 15th group with $ns^2 np^3$ outer electronic configuration have zero or very low EA values. The noble gases with $ns^2 np^6$ stable configuration in the outer shell also have zero EA values i.e. do not have any affinity for the electron (s) to be added to them.

The electron affinity of an element can be determined by using the Born-Haber cycle. **Periodic trends of electron affinity**

i) Variation along the periods

In general, with few exceptions, the electron affinity values of the elements go on increasing on moving from left to right in a period, i.e. from alkali metals to halogens. This is because atomic

size decreases and the effective nuclear charge increases along a period. Both these factors increase the force of attraction between the nucleus and the incoming electron which is added easily to the outer shell of the host atom. Exceptions are the elements of 2nd, 15th and 18th groups.

ii)Variation in the groups

The electron affinity values go on decreasing when we move from top to bottom down in a group. On descending a group, the atomic size and the nuclear charge both increase regularly. The increasing atomic size tends to decrease the EAvalues while increasing nuclear charge causes an increase in these values. The net result is that the effect produced by the progressive increase in size more than compensates the effect produced by progressive increase in nuclear charge and hence EA values decrease regularly down the group.

5.5.4 Electronegativity (X, chi)

In a homoatomic molecule, the bonding pair of electrons lies at the middle of internuclear space. But this is not true for a hetroatomic molecule. As a result polarity is developed on the hetero atoms of the molecule due to the shifting of the bonding pair of electrons towards one particular atom. For example, in H_2 or Cl_2 molecules, the bonded pair of electrons lies at the middle of two nuclei, i.e. is equally attracted by both the atoms. But in HF or like molecules, the bonded pair of electrons is attracted with stronger force by F atom (in HF) and thus, is shifted towards it from its expected middle position. This causes the development of slight negative change on F and equal positive change on H atom, therefore HF is a polar molecule.

This means an atom in a heteroatomic molecule with stronger affinity for bonding electrons is able to pull them towards itself and takes them away from the atom with weaker affinity for them. In the above example *(viz.* HF) F is said to have stronger affinity for bonded electrons as compared to that of hydrogen atom.To explain this tendency in heteroatomic molecules, Linus Pauling, in 1932, introduced the concept of electronegativity. According to him "**electronegativity is the relative tendency or power of an atom of an element in the heteroatomic molecules to attract the shared pair of electrons towards itself**".

Methods of evaluating electronegativity

Various chemists have defined and proposed the methods for evaluating electronegativity. These are known as electronegativity scales.

i)Pauling's Scale

Pauling's definition of electronegativity has been given in the beginning. He used thermodynamic data to calculate the electronegativity of different elements. He considered the formation of AB molecule by the combination of A_2 and B_2 molecules.

$$A_2 + B_2 = 2\ AB$$

$$\text{Or } \frac{1}{2}A_2 + \frac{1}{2}B_2 = AB \qquad\qquad \ldots\ldots\ldots (5.7)$$
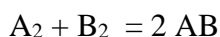
This reaction may also be written as

$\frac{1}{2}(A - A) + \frac{1}{2}(B - B) = A - B$ because A_2, B_2 and AB are covalent molecules. This is an exothermic reaction, means the formation of A-B molecules is accompanied by the release of energy, i.e. the bond dissociation energy of A-B covalent bond (E_{A-B}) is always higher than the mean of the bond dissociation energy of

A-A (E_{A-A}) and B-B (E_{B-B}) covalent bonds and $E_{A-B} > \frac{1}{2}(E_{A-A} + E_{B-B})$

Pauling proposed that the difference in the E_{A-B} and mean of E_{A-A} and E_{B-B} is related to the difference in electro negativities of A (χ_A) and B (χ_B)

$$\therefore \Delta = E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) = 23\ (\chi_B - \chi_A)^2 \text{ (where } \chi_B > \chi_A,) \qquad \ldots\ldots\ldots\ldots(5.8)$$

Thus, $\Delta = 23\ (\chi_B - \chi_A)^2$

Or $\chi_B - \chi_A = 0.208\ \sqrt{\Delta}$ \qquad\qquad $\ldots\ldots\ldots (5.9)$

In place of arithmetic mean, he later used the geometric mean of E_{A-A} and E_{B-B} and expressed the equation as:

$$\Delta' = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = 30(\chi_B - \chi_A)^2 \qquad \ldots\ldots\ldots\ldots(5.10)$$

$$\therefore \Delta' = 30\ (\chi_B - \chi_A)^2$$

$$\therefore \chi_B - \chi_A = 0.182\ \sqrt{\Delta'} \qquad\qquad \ldots\ldots\ldots\ldots.(5.11)$$

Here χ_A and χ_B are the electronegativities of the atoms A and B. The factors 0.208 and 0.182 arise from the conversion of Δ measured in kCal/ mole into electron volts.

	s-block			p-block elements			
1	2	13	14	15	16	17	18
H							He
2.1							0
Li	Be	B	C	N	O	F	Ne
1.0	1.5	2.0	2.5	3.0	3.5	4.0	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.9	1.2	1.5	1.8	2.1	2.5	3.0	0
K	Ca	Ga	Ge	As	Se	Br	Kr
0.8	1.2	1.6	1.8	2.0	2.4	2.8	0
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.7	1.8	1.9	2.1	2.5	0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
0.7	1.9	1.8	1.8	1.9	2.0	2.2	0
Fr	Ra						
0.7	1.9						

Table 5.9: Electronegativity values of s and p-block elements as determined by Pauling (on F = 4.0 scale)

From this table it can be noted that the variation in the values of electronegativity is more pronounced among the non-metals.

ii) Allred and Rochow's Scale

Allred and Rochow proposed that the electronegativity of an element (say A) can be calculated by using the following equation:

$$(\chi_A)_{AR} = \frac{0.359 \, xZeff}{r^2} + 0.744 \qquad \ldots\ldots\ldots\ldots \qquad (5.12)$$

where $(\chi_A)_{AR}$ = electronegativity of the element A on Allred and Rochow's scale, Z_{eff} = effective nuclear charge $(Z - \sigma)$ at the periphery of the element A,

r is radius of the atom of element A in Å.

Putting the value of Z_{eff}, the equation can be rewritten as

$$(\chi_A)_{AR} = \frac{0.359 \, x(Z-\sigma)}{r^2} + 0.744 \qquad\qquad (5.13)$$

The electronegativity values obtained by this method agree closely to those obtained by Pauling's approach. These values for the elements of first three periods are given below: **Table 5.10: Electrongativity values of s and p-block elements belonging to first three   periods on Allred and Rochow's scale**

Group	1	2	13	14	15	16	17	18
	H 2.20							He 3.2
	Li 0.97	Be 1.47	B 2.01	C 2.50	N 3.07	O 3.50	F 4.10	NA 5.1
	Na 1.01	Mg 1.23	Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83	Ar 3.3
	K 0.91	Ca 1.04	Ca 1.82	Ge 2.02	As 2.20	Se 2.48	Br 2.74	Kr 3.1
	Rb 0.89	Sr 0.99	In 1.78	Sn 1.72	Sb 1.82	Te 2.01	D 2.21	Xe 2.4
	Cs 0.86	Ba 0.97	Tl 1.44	Pb 1.55	Bi 1.67	Po 1.76	At 1.90	Rn -

According to this scale, the inert elements also possess electronegativity. As per the definition given by Pauling, this scale seems to be arbitrary but it has its own importance.

iii)Mulliken's scale

It is based on the ionization energy and electron affinity of an atom of an element. According to Mulliken "**the average of ionization energy (IE) and electron affinity (EA) of the atom of an element is a measure of its electronegaivity**".

Thus, the electronegativity $= \dfrac{I_E + E_A}{2}$ .... (5.14) He proposed two relations for obtaining the electronegativity:

a)When the energies are measured in electron volts (eV), then

$$\chi_A \quad = \quad 0.374 \; \frac{(I_E + E_A)}{2} + 0.17$$

$$= \quad 0.187 \; \frac{(I_E + E_A)}{2} + 0.17 \qquad \text{................ (5.15)}$$

b)When the energies are expressed in kJ/mole, then

$$\chi_A \quad = \frac{I_E + E_A}{540} \qquad \text{.............. (5.16)}$$

All these terms χ_A, IEand EA are for the atom A.

Factors affecting the magnitude of electronegativity

Various factors which affect the magnitude of the electronegativity of an element qualitatively are as follows:

i)Atomic size

It has been observed that the smaller atom has greater tendency to attract the shared pair of electrons towards itself and hence has greater electronegativity. Thus electronegativity α

$$\frac{1}{Atomicsize}$$

ii)Charge on the atom (or oxidation state of the element)

Higher the amount of positive charge on the atom of an element means higher positive oxidation state, smaller is the size and more is the electronegativity, i.e. electronegativity α positive oxidation state (or charge).

iii) Effective nuclear charge (Z_{eff})

With the increase in the magnitude of Z_{eff} of an element, the electronegativity of that element also increases. This factor may effectively be used to explain the variation of electronegativity in a group or along a period. Thus, electronegativity α Z_{eff}. **iv) Ionization energy and electron affinity**

According to Mulliken's scale, electronegativity of an element depends on its ionizations energy and electron affinity, Thus, the atoms of the elements which have higher values of ionization energy and electron affinity also have higher values of electronegativity, i.e. electronegativity α IEand EA.

v)Type of hybridization of the central atom in a molecule

It has been observed that electronegativity of an atom having hybrid orbital with greater scharacter is high because the electronic charge in hybrid orbitals of an atom in a molecule which has greater

s-character remains closer to the nucleus of that atom. For example, the s- character in sp^3, sp^2, and sp hybrid orbitals of CH_4, C_2H_4 and C_2H_2 is 25%, 33% and 50%, respectively. Accordingly, the s-character of hybrid orbitals gives more electronegativity to C atom. Hence the electronegativity of carbon atom in these molecules is in the following increasing order:

$CH_4 < C_2H_4 < C_2H_2$
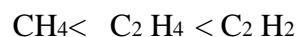
Periodic trends of electronegativity

i)Variation in the groups of main group elements

On going down a group of main group elements, the electronegativity values go on decreasing due to increasing atomic size and decreasing Z_{eff} of the elements. At the same time, the electropositive character of the elements also increases causing a reduction in electronegativity values of the elements as well as their ionization energies and electron affinities.

ii)Variation along a period

On moving from left to right across a period of main group elements i.e. from alkali metals to halogens, electronegativity values increase with increasing atomic number. This happens secause Z_{eff} increases, electropositive character decreases, atomic size of the elements also decreases thereby increasing electronegativity. Ionization energy and electron affinity, in general, also increase along a period.

Applications of Electronegativity : On the basis of electronegativity, certain facts in chemistry can be explained which are given below:

i)To predict the nature of bonds

With the help of the electronegativity difference $\chi_B - \chi_A$ (where $\chi_B < \chi_A$) between two atoms A and B, we can predict whether A-B bond would be non-polar covalent bond, polar covalent bond or ionic bond. If $\chi_B - \chi_A = 0$, i.e. either the atoms A and B are same or if different have almost similar electronegativity values, the bond is non- polar covalent bond. When $\chi_B - \chi_A$ is relatively small, e.g. O- H, Cl-H etc. the bond formed between the atoms is polar covalent bond. When $\chi_B - \chi_A$ is very large, complete transfer of an electron from atom A to atom B takes place and the resulting bond between the atoms is purely ionic.

The percent ionic character present in the polar covalent bond can be calculated. For a polar covalent molecule A^{S+}-B^{S-}, Pauling has correlated the percent ionic character of a covalent bond with the electronegativity difference between the combining atoms as is given below:

$(\chi_B - \chi_A)$	0.6	1.0	1.7	2	3
Percent ionic character	9	22	51	63	91

He used the equation:

Amount of ionic character in A-B bond $= [1-e^{0.25(\chi_B - \chi_A)}]$ %   ………(5.17)

Further, Hannay and Smith gave the following equation to calculate the ionic character.

Ionic Character in A - B bond $= [16 (\chi_B - \chi_A) + 3.5 (\chi_B - \chi_A)^2]$ % $(\chi_B > \chi_A)$….(5.18) **ii)To**

calculate the bond length

In a heterodiatomic molecule of AB type, the bond length d_{A-B} can be calculated provided the molecule has ionic character and the values of atomic radii r_A and r_B as well as the electronegatitvities χ_A and χ_B are known. This can be done by using the Schoemaker and Stevenson equation, *viz.* $d_{A-B} = r_A + r_B - 9 (\chi_B - \chi_A) (\chi_B > \chi_A)$ …………..(5.19) **iii) To predict the trends in acid-base character**

a)The acidic character of the oxides has been bound to increase from left to right along a period because of decreasing $\chi_0 - \chi_B$ values (χ_0 and χ_B are electro- negativities of oxygen and other atom), e.g.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2	Cl_2O_7
χ_B	0.9	1.2	1.5	1.8	2.1	2.5	3
$\chi_0 - \chi_B$	2.6	2.3	2.0	1.7	1.4	1.0	0.5
Nature	strongly basic	basic	ampoteric	weakly acidic	acidic	strongly acidic	strongly acidic

   $(\chi_0 = 3.5)$

b)The acidic character of hydrides of the elements of the same period goes on increasing from left to right across a period. For example, the acidic nature of CH_4, NH_3, H_2O and HF molecules, the hydrides of the elements of second period, increases in the order: CH_4, $< NH_3$, $< H_2O <$ HF because of the increasing electronegativity of the central atom and increasing elelctronegativity difference between the central atom and hydreogen atom i.e.

$\chi_{central atom} - \chi_H$

c)The acidic character of oxyacids of the elements of the same group and in the same oxidation state, e.g. $HClO_4$, HB_rO_4 and HIO_4 decreases as the electronegativity of central halogen atom decreases as we move down the group form Cl to I (χ_{Cl} = 3.0) and χ_I = 2.5 on Pauling's scale).

i)To explain the diagonal relationship

It has been found that the elements of second period of the periodic table show similarities in properties with the elements lying diagonally opposite on right hand side in the third period This property is called diagonal relationship. These elements are shown below:

Elements of 2nd period Li   Be   B   C   N   O   F

Elements of 3rd period   Na   Mg   Al   Si   P   S   Cl
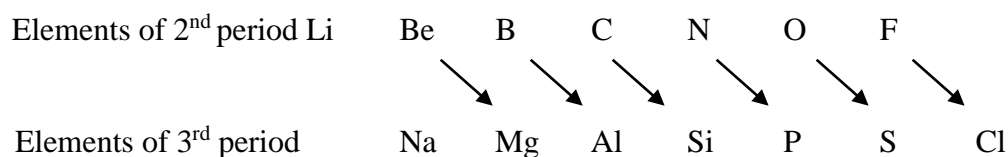
This similarity in properties can be explained by various facts and one of them is the concept of electronegativity. The electronegativites of the diagonally opposite elements are almost the same and hence show similar properties.

5.6 SUMMARY

This unit contains a comprehensive text on the history of the periodic table i.e. how the historical attempts were taken to develop a classification of elements system in a manner which could facilitate their study, during the time of Dobereiner, Duma and Newlands. The laws of periodic table and on the basis of these laws, the attempts to classify elements have also been exhaustively discussed. In the light of these laws, the elements, arranged in the tabular form, have been given, *viz*. Mendeleeff's pefiodic table, Modified form of Mendeleeff's periodic table (both on the basis of atomic weights) and modern periodic table on the basis of atomic number. In addition to this, the elements have also been classified in the blocks (with general characteristics of each block). A concise description of the periodicity of properties and its cause have been discussed.

The text of this unit contains a concise and comprehensive discussion of various periodic properties such as atomic and ionic radii, ionization energy, electron affinity and electronegativity, factors affecting these properties, periodic trends (or variation) of the properties, the methods of their determinations and their applications wherever necessary and available. The periodic properties are the basis of the physical and chemical properties of the elements which can be predicted keeping in view the above properties.

5.6 TERMINAL QUESTIONS

Q.1..Write a concise note on Dobereiner's law of triads.

Q.2. Discuss in short, the Newland's law of octaves.

Q.3. State the Mendeleeff's periodic law.

Q.4. Give a brief discussion of Mendeleeff's periodic table.

Q.5. State and explain the merits and demerits of Mendeleff's periodic talbe.

Q.6. Give a brief account of modern periodic law.

Q.7. Discuss the main features of modern periodic table.

Q.8. What are the transition elements and why are they called so?

Q.9. Write a brief note on inner transition elements.

Q.10. What is the cause of periodicity of properties in the elements in periodic table?

Q.11. What are the p-block elements?

Q.12 "Arrange the following ions in the increasing of their size

 a) Na_+, Mg_{2+}, Al_{3+}, F_-, O_{2-}, N_{3-} b) C_{4-}, N_{3-} ,O_{2-}, F_-

Q.13.Which atom or ion in the following pairs has smaller size and why ?

 a) Na, Na $^+$ b)Be, Mg c) Fe^2,Fe^3 **Q.14**.Explain

giving appropriate reasons:

 a)The Cl^- ion is larger in size than Cl atom.

 b)The atomic radius decreases with the increasing atomic numbers in a period.

Q.15.Arrange the following in the decreasing order of their ionization energy: Be, B, N, O and F.

Q.16.Arrange then Be, B, N, O and F in the increasing order of their electron affinities.

Q.17.EA values of the halogens are the highest in each period. Explain.

Q.18. The noble gases have very high values of ionization energy but their electron affinity values are almost zero. Why?

Q.19. Which of the following elements has the highest values of electron affinity and why?

a.Na, Cl, Si, Ar

b.(i)$1s^2$, $2s^2$, $2p^1$ (ii) $1s^2$, $2s^2$, $2p^6$, $3s^1$ (iii) $1s^2$, $2s^2$, $2p^5$ (iv) $1s^2$, $2s^2$, $2p^3$ **Q.20.**Distinguish between electron affinity and electronegativity.

Q.21. Which element among the following has the highest value of electro negativity and the highest value of electron affinity? F, Cl, O, Br, and I.

Q.22. Which one of the following oxides is basic, amphoteric, and acidic in nature?

a. MgO   b. Al_2O_3 c. P_4O_{10}

Q.23. How does electron affinity depend on effective nuclear charge?

Q.24. The group and the period assigned to the element with $3d^1 4s^2$ valence shell configuration are:

   (a) IIIB & 3   (b) IIIB & 4 (c) IIIA & 3   (d)   IIIA & 4

Q.25. Nepturium (Z = 93) is an elements of

   (a) 4f- series (b) 4d- series   (c)   5f -series   (d)   5d -series.

Q.26. Seaborgium (Z = 106) is a member of

   (a) 6d- series (b) 5d-series   (c)   4d-series   (d)   3d-series.

ANSWERS:

A.12. a) $Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$ **b)** $F^- < O^{2-} < N^{3-} < C^{4-}$

All of the above are isoelectronic ions whose ionic size decreases with increasing nuclear charge (atomic number) of the parent atom.

A.13.a) Na^+ has smaller size because this has been derived from Na atom by removing its outermost electron. This causes greater attraction between the nucleus and the remaining electrons and contraction in the size occurs.

   b)Be has smaller size because both Be and Mg belong to the same group. Down a group the size of the atom of the elements increases.

c)Fe^{3+} ion has smaller size because both Fe^{2+} and Fe^{3+} are the ions of Fe. As the oxidation state increases, the ionic size decreases (for the ions of the same element). **A.14.**

a)Please see some important facts regarding ionic radii no. 3.

b)Please see variation of atomic radius in a period.

[1]**A.15.** The decreasing order of the ionization energy is

$$F > N > O > Be > B.$$

A.16. The increasing order of the electron affinity is

$$Be < N < B < O < F$$

A.19. **a.** Among the given elements Cl with $3s^2\ 3p^5$ outer shell configuration has the greatest tendency to accept the incoming electron and hence has the highest value   of electron affinity.

b. (iii) With $2s^2\ 2p^5$ configuration in the outer shell has the highest value of electron affinity among the given elements,

A.21. Among the given elements F has the highest values of electronegativity. (Pauling's scale) and Cl has the highest value of electron affinity.

A.22. Basic oxide: MgO ,   Amphoteric oxide: Al_2O_3 ,   Acidic oxide: P^4O_{10}

A.24 b

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A.25 c

A.26 a

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UNIT 6: GASEOUS STATE

CONTENTS

6.1 INTRODUCTION

Amongst the three common states of matter, the gaseous state is simplest. The laws of gaseous behaviour are more uniform and are better understood. Basically this unit we learnt about Pressure volume relationship- Boyle's law, the temperature volume relationship – Charle's law as well as relation between both laws on the bases of Ideal gas equation.There was no theoretical background to justify them. In the nineteenth century, however, Kronig, Clausius, Maxwell and Boltzmann developed a theory known as kinetic molecular theory of gases, which provided sound theoretical basis for the various gas laws.

The solid, liquid, and gas are three forms of matter. These forms of matter differ considerably in their properties. Pressure, volume, temperature, amount of substance, specific heat, etc., are some of the measurable properties of gases. The amount, volume, pressure, and temperature are the most important properties as these four independent variables describe the state of the gas. The interdependence of these variables leads to different gas laws.

Some important characteristic properties of gases are given below.

1. Gases occupy all available space i.e. the shape and volume of the container in which they are filled.

2. When compared to liquids and solids gases show very low density.

3. The molecules in a gaseous element scatter by forces in all direction due to the negligible force of attraction between them. Therefore the molecules exert pressure in all directions.

4. The intermolecular force between molecules of gaseous elements is negligible. Hence these forces between the molecules in gas makes it the most compressible state of matter.

5. The molecules in gaseous elements exert pressure on the walls of the container and take the shape of the container in which contains this gas.

6. When a gas confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

We all know that acids and bases play an essential and important role in our everyday life.. A substance can be classified as an acid or a base depending on certain properties. There are several theories to define and classify acids and bases that include Arrhenius theory, Bronsted-Lowry acid/base concept, and Lewis acid-base concept. The strength of acids and bases can be determined by measuring pH values of solutions. Every theory of acid and base shows some advantages and some limitations to overcome; the drawback of each theory.This unit will throw light on different theories of acids/bases, their drawbacks and relative strengths of acids and bases.

6.2 OBJECTIVES

All matter exists in three common state of matter; these common states are solid, liquid and gas. A particle level representation of gaseous, liquid and solid states .

The smallest structural unit of all chemical substances in these states is molecule. How the molecules are arranged in a solid, liquid and gas, is the fundamental question before a chemist. It is the 'molecular model' of matter in these states which determine their physical behaviour.The gaseous state is the simplest of all the three physical states of matter.Gases show maximum regularity in their behaviour irrespective of their chemical nature.Even the gases having very different chemical properties obey certain laws known as gas laws.Gases are characterised by certain quantitative relations between mass, pressure, volume, and temperature.

With respect to acid and base concept the main goal of this Unit is to broaden your understanding about the following issues: Definitions of acids and bases, Different theories of acids and bases,Acid and base strength.

6.3 PRESSURE OF A GAS

 The pressure of a gas may be defined as the force exerted by the gas per unit area of the wall of the containing vessel. An atmosphere is made of the layers of gases surrounding a planet or other celestial body. The pressure exerted air (present in the atmosphere) on the surface of the earth is called atmospheric pressure.It is measured with the help of simple apparatus known as **barometers.** It is shown in Figure 6.1
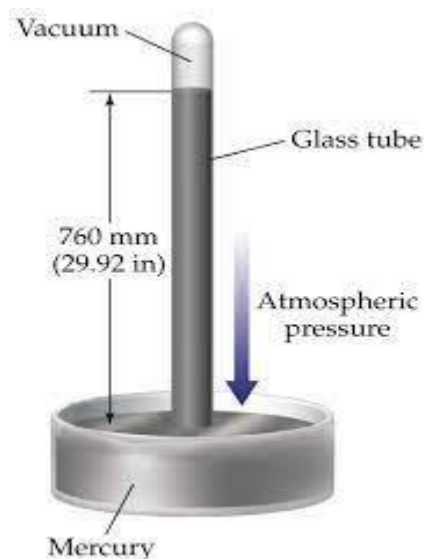
Figure 6.1

It can very easily be constructed. A glass tube of about 80 cm in length and closed at one end, is filled with mercury. The mercury level drops in the tube and after sometime becomes steady. At this stage the downward pressure exerted by the column of mercury in the tube is exactly balanced by the atmospheric pressure. The height of the mercury column h in the tube thus corresponds to the atmospheric pressure. This height h is approximately 76 cm / 760mm. If the atmospheric pressure increase , the height in the column rises and when the atmospheric pressure decrease , the height of mercury column also decreases correspondingly. Therefore, the height of the mercury column in the tube can be taken as a measure of atmospheric pressure.

Suppose, m is the mass of mercury column in the tube and A is the area of cross section of the tube . If P pressure exerted by the mercury column , then ,

$$P = \frac{Force}{Area} = \frac{Mass \times Acceleration}{A} = \frac{mg}{A} \quad .... \quad .6.1$$

Where, g is the acceleration due to gravity . If V is the volume of mercury in the tube and d is the density of mercury , m mass is given by, $\quad m = V d = A h d \quad$ (Volume = area of cross section x height) $\quad$ value of m put in equation 6.1

$$P = \frac{mg}{A} = \frac{Ahdg}{A} = h d g$$

$$P = h d g \qquad ....6.2$$

With the help of this equation, the height h shown by barometer can be converted into the atmospheric pressure in proper units.

Unit of pressure : SI unit of pressure is **Pascal (Pa).**

$$1 \text{ atm} = 101.325 \times 103 \text{ Nm}^{-2} = 101.325 \times 10^3 \text{ Pa}$$

$$= 101.325 \text{ k Pa}$$

The other units of pressure is **torr** and **bar** are also common in use.

$$1 \text{ torr} = 1 \text{mm Hg}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

6.4 PRUSSURE VOLUME RELATIONSHIP- BOYLE'S LAW:

In 1662 Robert A.Boyle's studied the behaviour of gases at constant temperature "According to them the volume of gas is inversely proportional to the pressure exerted by the gas".In other word " The volume of a given mass of a gas is inversely proportional to its pressure provided the temperature remains constant".

 Mathematically , Boyle's law may be expressed as:

$$V \; \alpha \; \frac{1}{P} \; (\text{ at constant temperature and for a given mass of the gas})$$

$$V = k \; \frac{1}{P}$$

Where, k = Proportionality constant

or,   PV = k = Constant

  Boyle's law can also be stated as follows :

The product of pressure and volume for a given mass of a gas is constant at a conatant temperature.

Suppose at temperature T, V_1 is the volume of a given mass of a gas at pressure P_1 and

V_2 is the volume of the same masss of gas at pressure P_2 , then we have form:

$$P_1 V_1 = P_2 V_2 = \text{Constant (at constant temperature T)}$$

For a fixed amount of gas at constant temperature, the pressure v/s volume curve can be represented as:
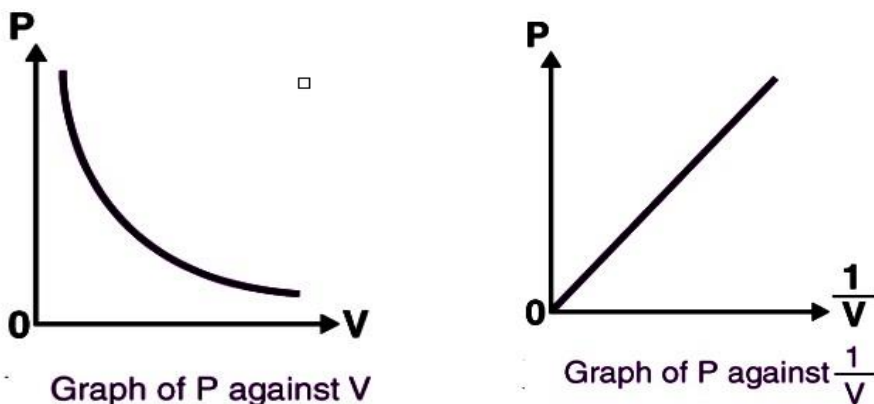
Figure 6.2

Example: What will be the minimum pressure required to compress 500 L of air at 1 bar to 200 L at 30 °C.

Solution: Initial volume = V_1 = 500 L,   Initial pressure = P_1 = 1 bar,

Final volume = V_2 = 200 L ,   Temperature constant   Final Pressure = P_2 =?

At constant temperature by Boyle's law

$$P_1V_1 = P_2V_2$$

$$\therefore P_2 = P_1V_1 / V_2$$

$$\therefore P_2 = 1 \text{ bar} \times 500 \text{ L} / 200 \text{L}$$

$$\therefore P_2 = 2.5 \text{ bar}$$

Hence minimum pressure required = 2.5 bar

1.5 THE TEMPERATURE VOLUME RELATIONSHIP – CHARLES' LAW

French physicist Jacques Charles (1746-1823) studied the effect of temperature on the volume of a gas at constant pressure. According to this law "At constant pressure, the volume of a fixed mass of gas is directly proportional to its absolute temperature.(i.e. temperature on Kelvin scale)

Mathematically, Charles' law may be expressed as:

$$V \; \alpha \; T \quad \text{(at constant pressure and for a given mass of the gas)}$$

$$V = k \, T$$

Where, k = Proportionality constant

or $\qquad \dfrac{V}{T} = k$

If V_1 is the volume of a certain mass of a gas at absolute temperature T_1 and a particular pressure , and V_2 is the volume of the same of the same gas at temperature T_2 at the same pressure, then according to Charles' law,

$$\dfrac{V1}{T1} = \dfrac{V2}{T2} \qquad \text{(at constant pressure P)}$$

For a fixed amount of gas at constant pressure, the temperature v/s volume curve can be represented as:
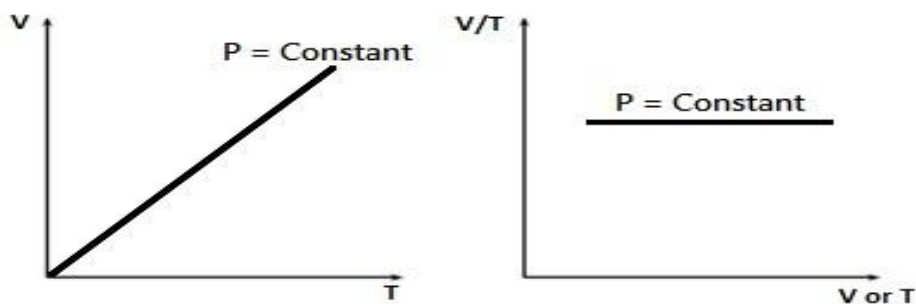
Figure 6.3

Example: A sample of a gas occupies 10 dm^3 at 127 °C and 1 bar pressure. The gas is

Cooled to – 73 °C at the same pressure. What will be the volume of the gas?

Solution: Initial temperature = T_1 = 127 °C = 127 + 273 = 400 K,

Initial volume = V_1 =10 dm^3,

Final temperature = T_2 = − 73 °C = − 73 + 273 = 200 K

Final volume = V_2 = ?

By Charles' Law

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

$$\therefore V_2 = (T_2/T_1) \text{ x}$$

$$\therefore V_2 = (200/400) \text{ x } 10 \text{ dm}^3 = 5 \text{ dm}^3$$

The new volume of the gas is 5 dm^3

6.5.1Absolute scale of temperature: With the help of Charles' law invent a new scale of temperature which is absolute. It is absolute in th sense that 0 on this scale does not depend upon any particular property of any particular substance. This new scale is referred to as the absolute scale or Kelvin scale.

According to Charles' law , Quantitatively , the volume of a gas decrease by 1/ 273 of its volume at 0^{0}C for each 1^{0}C fall in temperature. Thus we have:

$$V_t = V_0 \left(1 + \frac{t}{273} \right.$$

If we put t = -273 ^{0}C in the above equation, we have

$$\text{Volume at } -273°C = V_0 \left(\frac{273 - 273}{273} \right) = 0$$

This implies that if the temperature of a gas is reduced to -273 ^{0}C ,its volume will be reduced to zero. Hence it is clear that lowest possible temperature for a gas is -273 ^{0}C.This lowest possible temperature at which all gases are supposed to occupy zero volume is called Absolute zero of temperature. This scale was first suggested by scientist Lord Kelvin. Therefore, this scale is also known as **Kelvin scale of Temperature**.

Temperature on Kelvin scale are indicated simply by writing the letter "K". By convenation , the degree sign (^{0}) is not used while expressing temperature on this scale. Thus , -273.15 ^{0}C = 0 K

The relationship between Kelvin scale and Celsius scale is

Temperature in Kelvin scale (K) = Temperature on Celsius scale (^{0}C) + 273.15

For example: Convert 1^0C to Kelvin scale.

$$1^0C = 1 + 273.15 = 274.15 \text{ K}$$

In general, $t^0C = (t + 273.15)$ K

6.6 AVOGADRO'S LAW :

Avogadro's law states that "equal volumes of all gases, at the same temperature and pressure, have the same number of molecules."

For a given mass of an ideal gas, the volume and amount (moles) of the gas are directly proportional if the temperature and pressure are constant.

Mathematically, This law can be written as:

V α Number of molecules (at constant temperature and pressure)

or, V α n or, V =
k n where, k is Proportionality
constant.

If V_1 is the volume of a certain mass of a gas at constant temperature and pressure the number of molecules is n_1, and for V_2 volume the number of molecules become n_2, than we have, according to Avogadro law,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

The equation shows that, as the number of moles of gas increases, the volume of the gas also increases in proportion. Similarly, if the number of moles of gas is decreased, then the volume also decreases.
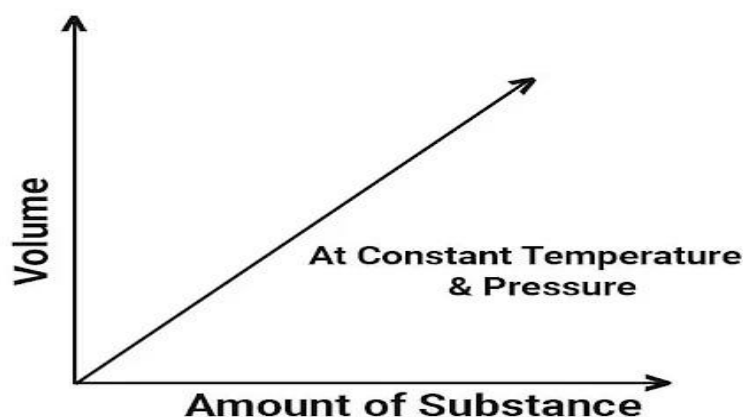
Figure 6.4

Example: 5.00 L of a gas is known to contain 0.965 mol. If the amount of gas is increased to 1.80 mol, what new volume will result (at an unchanged temperature and pressure)?

Solution: According to Avogadro's law:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$V_1 = 5.00$ L $n_1 = 0.965$ mol

$V_2 = ?$ $n_2 = 1.80$ L

$$V_1 n_2 = V_2 n_1$$

$$(5.00 \text{ L}) (1.80 \text{ mol}) = (x) (0.965 \text{ mol})$$

x = 9.33 L

6.7 IDEAL GAS EQUATION :

Boyle's law , Charles' law ,and Avogadro's law can be combined together to obtain a very important equation known as ideal gas equation. This equation correlates pressure, temperature, volume, and number of moles of gas. This equation can be derived as follows:

According to Boyle's law,

$$V \alpha \frac{1}{P}(\text{ at constant temperature and for a given mass of the gas})$$

According to Charles' law,

$$V \propto T \quad \text{(at constant pressure and for a given mass of the gas)}$$

According to Avogadro's law,

$$V \propto n \quad (\text{at constant temperature and pressure}) \text{ Combining}$$

three equations, we get,

$$V \propto \frac{1}{P} \quad \propto T \quad \propto n$$

$$V \propto \frac{nT}{P}$$

$$V = \frac{RnT}{P}$$

On rearranging above equation we get,

$$V = n R T$$

Where, R is the universal gas constant, and the value of R become,

R= 8.31 k Pa dm^{3}K^{-1} or 8.31J K^{-1}mol $^{-1}$ or ,   R =

0.082 litre atm K^{-1}mol $^{-1}$ or ,   R = 8.31 x 10^7 ergs K^{-}

^{1}mol $^{-1}$ or ,   R = 82.01 atm cm^3 K^{-1}mol $^{-1}$

OR,   R = 1.987 cal K^{-1}mol $^{-1}$

When a gas is described under two different conditions, the ideal gas equation must be applied twice - to an initial condition 1 and a final condition 2. This is: Initial condition (1) P_1V_1

= n R T$_1$ or, $\frac{P1V1}{nT1} = R$

Final condition (2) $P_2V_2 = n R T_2$

$$\frac{P2V2}{nT2} = R$$

The two equations are equal to each other since each is equal to the same constant R Therefore, we have:

$$\frac{P1V1}{T1} = \frac{P2V2}{T2}$$

The equation is called the **general gas equation**. The equation is particularly useful when one or two of the gas properties are held constant between the two conditions.

Standard Conditions of Temperature and Pressure (STP):

Scientists have chosen a particular set of conditions to use as a reference:

Temperature : 0°C (273.15 K)

Pressure   : 1bar =100kPa=105Pa

Volume   : 22.71 L at STP and 22.41 L at 0°C and 1 atmosphere,

Example: A certain quantity of a gas measured 500ml at a temperature of 15 ^{0}C and 750 mm Hg. What pressure is required to compress this quantity of gas into a 400 ml vessel at a temperature of 50 ^{0}C ?

Solution: Given that: P_1 = 750 mm Hg T_1= 273 + 15 = 288 K V_1 = 500 ml

P_2 = ? T_2= 273 + 50 = 323 K V_2 = 400 ml

Therefore, according to the gas equation , we have

$$\frac{P1V1}{T1} = \frac{P2V2}{T2}$$

or ,
$$\frac{750 \; X \; 500}{288} = \frac{P2 \; X400}{323}$$

or, P_2 = 1051 mm

Hence, the given gas should be compressed to 1051 mm pressure.

6.8 DEFINATION OF ACID AND BASE

The different theories to define acids and bases are discussed below:

6.8.1 Arrhenius theory (Water system concept, 1884): In 1884, the Swedish chemist Arrhenius defined acid as the species which ionize in water to produce H^+ ion or ($H3O$ + ions) and bases as the substances that ionize in water to produce OH^- ions.

For example: Hydrochloric acid in the water ,undergoes a dissociation reaction to produce an H^+ ion and a Cl^- ion, as explained below. The concentration of the H+ ions is increased by forming hydronium ions.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$
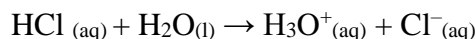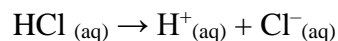
In an aqueous solution, NaOH completely dissolves to give hydroxide ions and sodium ions, to increase the concentration of hydroxide ions.

$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Limitations :

1. Arrhenius theory explains acids and bases in terms of their presence in aqueous solution and not as a substance.
2. Arrhenius theory is applicable only to acids having the formula HA. For example: HCl, HBr. It is not applicable for SO_2, CO_2, etc.
3. This theory is only applicable to bases having the formula BOH. For example: NaOH, KOH. It is not applicable for K2CO3, NH_3 and pyridine.
4. This theory fails to explain the properties of acids and bases in any solvents like benzene , acetone any gases, other than water.

6.8.2. Bronsted–Lowry acids and bases theory (Protonic concept, 1923):

Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.So, according to Bronsted–Lowry concept:

$$HCl(aq) + NH_3(aq) \rightarrow NH^{+4}(aq) + Cl-(aq)$$
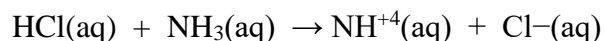
Here, hydrochloric acid (HCl) "donates" a proton (H^+) to ammonia (NH_3) which "accepts" it , forming a positively charged ammonium ion (NH_4^+) and a negatively charged chloride ion (Cl^-). Therefore, HCl is a Brønsted-Lowry acid (donates a proton) while the ammonia is a

BrønstedLowry base (accepts a proton). Also, Cl^- is called the conjugate base of the acid HCl and NH_4^+ is called the conjugate acid of the base NH_3.

Hence," A Brønsted-Lowry acid is a proton donor,and base is a proton acceptor".

Limitations :

1.This theory can't be explain acid base behaviour of aprotic solvents.

2.Some acidic oxide like sulphur di oxide (SO_2), calcium oxide (CaO),magnesium oxide (MgO) ,

 etc can't be explain the acid base behaviour because there is no proton transfer reaction occure.

6.8.3 Lewis concept: Electron pair acceptor-donor concept (1923):

Lewis' theory used electrons instead of proton transfer and specifically stated that an acid is a species that accepts an electron pair while a base donates an electron pair.

For example:

Lewis acid react lewis base to formed adduct

In Lewis acid have vacant orbitals ,and in lewis base have lone-pair electrons.When,the reaction of a Lewis acid and a Lewis base , lewis base donates its electrons to the Lewis acid, produce a coordinate covalent bond and this product is referred to as a Lewis adduct.

 lewis acid are:

- Simple cations, with low lying empty orbitals like :Ag^+ , Cu^{2+} , Cd^{2+} etc.
- Elements which have a sextant of electrons in their valence shell , like: O,S

- Molecules whose central atoms have vacant p and d-orbital's act as a Lewis acid. like :BF_3 ,AlF_3, $AlCl_3$, GeX_4, $TeCl_4$, SF_4, SbF_3 etc.

- Molecules whose central atom is linked with more electronegative atom by double bonds. like :

$$CO_2 \: [\overset{-\delta}{O} = \overset{+2\delta}{C} = \overset{-\delta}{O}], \quad SO_2 \: [\overset{-\delta}{O} = \overset{+2\delta}{S} = \overset{-\delta}{O}]$$

lewis base are:

- Anions can donate electrons, so they act as Lewis bases.like: H^-, F^-, OH^-, CN^-etc

- Any molecule, atom, or ion with a lone pair of electrons can act as Lewis bases.like: NH_3, H_2O etc.

- The pi-electron systems which are rich in electrons act as Lewis bases. Like:benzene, alkenes, alkynes, etc **Limitations:**

1.The concept fails to recognise the relative strength of acids and bases.

2.Formation of a coordination compound is a slow process but acid-base reactions are   fast. This concept could not explain this behaviour.

3.The reactions catalyzed by Lewis acids are generally not catalyzed by the protonic acids.

4.This concept was not applied to acid- base reactions. It could not explain the energy release during covalent bond formation.

6.9 SUMMARY

In this chapter you have studied different gas laws, namely: Boyle's law, Charle's law, Avogadros law, and derivation of ideal gas equation. There are different theories like Arrhenius , Bronsted–Lowry concept, Lewis theory, which classify and define the compounds into acids and bases.

6.10 TERMINAL QUESTIONS

Q.State and mathematically explain Boyle's Law?

Q.State and mathematically explain Charles' Law? How the law can be represented graphically?

Q.Derive ideal gas equation for n moles of a gas. Define the various unit of gas constant R ?

Q.Convert ^0C to Kelvin : a) 28 ^0C b) -71^0C

Q.Calculate the moles of hydrogen (H_2) present in a 500 ml of hydrogen gas at a pressure of 1 bar and 27^0C.

Q. Discuss Arrhenius theory of acids and bases.

Q. Discuss Lewis acid and base concept

Q. Discuss Bronsted–Lowry concept theory of acids and bases.

Q. At 300 K a certain mass of a gas occupies 1×10^{-4} dm^3 by volume. Calculate the volume of the gas at 450 K at the same pressure.

Q.Define the characteristics' of Lewis acid and Lewis base?

Q. Determine the volume of occupied by 2.2 grams of carbon dioxide gas at STP.

Q.What do you understand by S.T.P ?

6.11 REFERENCES FOR FURTHER STUDIES

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3. Br. R. Puri, L. R. Sharma and K. C Kalia. Principles of Inorganic Chemistry, Milestone Publishers & Distributors, Meerut, 2013.
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BLOCK-III:HYDROCARBON AND BIOMOLECULE

UNIT 7: HYDROCARBONS AND FUNCTIONAL GROUPS

CONTENTS

7.1 INTRODUCTION

Nineteenth-century chemists classified hydrocarbons as either aliphatic or aromatic on the basis of their sources and properties. Aliphatic (from Greek aleiphar, "fat") described hydrocarbons derived by chemical degradation of fats or oils. Aromatic hydrocarbons constituted a group of related substances obtained by chemical degradation of certain pleasant-smelling plant extracts. This unit define , in organic chemistry, a functional group is a substituent or moiety in a molecule that causes the molecule's characteristic chemical reactions.Explain the rule used to IUPA naming for different type of functional group, and its characterstices.

7.2. OBJECTIVES

By the end of the course the student should be able to:

- Recognize the hydrocarbon families, functionally substituted derivatives of alkanes.
- Give the IUPAC names of the simple hydrocarbons and different functional groups.
- Recognize by common name and structure of the hydrocarbons and different functional groups.
- Know the various method of preparation of alkane, alkenes alkynes, alcohols, ethers, aldehydes, ketone and carboxylic acids.
- Physical and chemical properties of alkane alkenes alkynes, alcohols, ethers, aldehydes, ketone and carboxylic acids.
- Use Marknovnikov's rule to predict the major product of an addition reaction of an alkene.

7.3. INTRODUCTION OF HYDROCARBONS

Hydrocarbon, any of a class of organic chemical compounds composed only of the elements carbon (C) and hydrogen (H). The carbon atoms join together to form the framework of the compound, and the hydrogen atoms attach to them in many different configurations.

Aliphatic hydrocarbons are divided into three main groups according to the types of bonds they contain: alkanes, alkenes, and alkynes. Alkanes have only single bonds, alkenes contain a carbon-carbon double bond, and alkynes contain a carbon-carbon triple bond.

Aromatic hydrocarbons are cyclic, planar compounds that resemble benzene in electronic configuration and chemical behavior. Benzene has the molecular formula C_6H_6 and is the simplest aromatic hydrocarbon.

7.3.1 Alkanes:

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula C_nH_{2n+2}. The root or parent name for an unbranched alkane is taken directly from the number of carbons in

the chain according to a scheme of nomenclature established by the **International Union of Pure and Applied Chemistry (IUPAC),** as shown below:

Name	Condensed Structure
Methane	CH_4
Ethane	CH_3CH_3
Propane	$CH_3CH_2CH_3$
Butane	$CH_3(CH_2)_2CH_3$
Pentane	$CH_3(CH_2)_3CH_3$
Hexane	$CH_3(CH_2)_4CH_3$
Heptanes	$CH_3(CH_2)_5CH_3$
Octane	$CH_3(CH_2)_6CH_3$
Nonane	$CH_3(CH_2)_7CH_3$
Decane	$CH_3(CH_2)_8CH_3$
Undecane	$CH_3(CH_2)_9CH_3$
Dodecane	$CH_3(CH_2)_{10}CH_3$

The IUPAC rules for naming linear and branched alkanes are given below: i)The IUPAC name for an alkane is constructed of two parts:

a) a prefix (meth... eth... prop..., etc.) which indicates the number of carbons in the main, or parent, chain of the molecule, and

b) the suffix ...**ane** to indicate that the molecule is an alkane.

ii)For branched-chain alkanes, the name of the parent hydrocarbon is taken from the**longest continuous chain** of carbon atoms.

iii)Groups attached to the parent chain are called **substituents** and are named based on the number of carbons in the longest chain of that substituent, and are numbered using the number of the carbon atom on the parent chain to which they are attached. In simple alkanes, substituents are called **alkyl groups** and are named using the prefix for the number of carbons in their main chain and the suffix ...**yl**. For example, methyl, ethyl, propyl, dodecyl, etc.
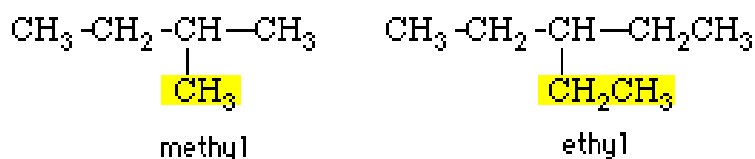
methyl   ethyl

iv)If the same substituent occurs more than once in a molecule, the number of each carbon of the parent chain where the substituent occurs is given and a multiplier is used to indicate the total number of identical substituents; i.e., **di**methyl... **tri**methyl... **tetra**ethyl..., etc.

2,3-dimethylbutane   2,3,4-trimethylpentane
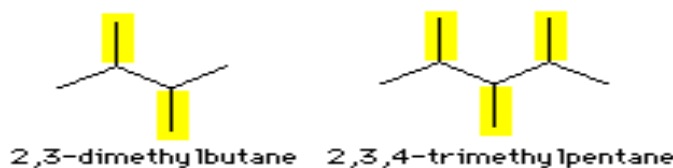
v)Numbering of the carbons in the parent chain is always done in the direction that gives the lowest number to the substituent which is encountered first, or, the lowest number at the first point of difference. If there are different substituents at equivalent positions on the chain, the substituent of lower alphabetical order is given the lowest number.

3-ethylheptane   *not* 5-ethylheptane

3-ethyl-5-methylheptane   *not* 5-ethyl-3-methylheptane
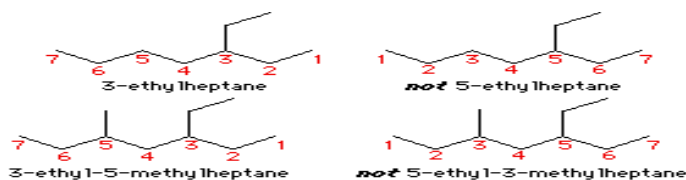
vi)In constructing the name, substituents are arranged in alphabetical order, without regard for multipliers.

2,2,5-trimethylhexane   2,3,5-trimethylhexane
not 2,5,5-trimethylhexane   *not* 2,4,5-trimethylhexane

4-ethyl-2-methylhexane   2,2-dimethylpentane
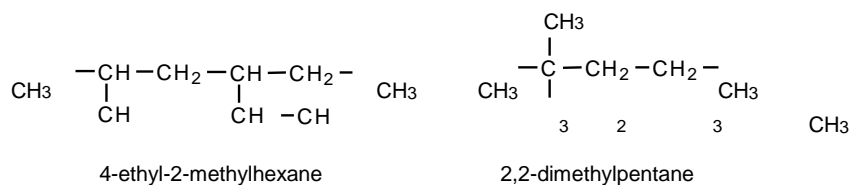
7.3.2 Alkenes :

The simplest alkenes, with only one double bond, form a homologous series, ***the alkenes*** with general formula C_nH_{2n}. A double bond is a □ bond and a □ bond. A □ bond is weaker than a □ bond and hence more reactive than □ bonds. Due to this, □ bonds are considered to be a functional group. Alkenes are also called olefins (from Greek: 'oil-formers') and vinyl compounds.

According to IUPAC nomenclature, alkenes are identified by the suffix –ene. Number the chain beginning at the end closest to the double bond so that the double bond will have the lowest carbon number.

□ Name branched or substituted alkenes in a manner similar to alkanes.

□ Number the carbon atoms, locate and name substituent groups, locate the double bond, and name the main chain.

□ *Cis* and *trans* isomers must be designated by the appropriate *cis-* or *trans-* prefix.
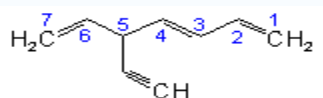
5-Ethynyl-1,3,6-heptatriene   3,4-Dipropyl-1,3-hexadien-5-yne
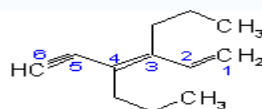
$CH_2=CH(CH_2)_5CH_3$ $CH_2(CH_2)_2C=C-CH_3$ 1-

octene   2- hexene

$CH_2=CH_2$ $CH_3CH=CH_2$ $CH_3C(CH_3)=CH_2$
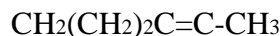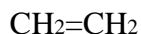
Ethene   Propene   2-Methylpropene

$CH_3CH_2CH_2CH_2CH==CH_2$

1-Hexene

| 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 | 5 | 6 |

CH₂=CH — CH2CH3   CH3CH = CH — CH2CH2CH3
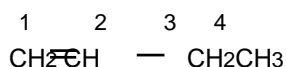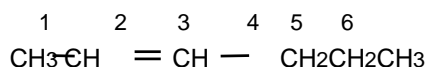
but-1-ene   hex-2-ene   **Isomers of alkenes:**

The geometry of the C=C bond is determined by the π-bond. The rotation about the carboncarbon double bond is very difficult and therefore severely restricted. As a consequence substituted alkenes exist as one of two isomers called a cis isomer and a trans isomer. When similar groups

are on the same side of the double bond the alkene is said to be cis. When similar groups are bound to opposite side of the double bond it is said to be trans.

For Example:

cis-2-butene   trans-2-butene

7.3.3 Alkynes :

The alkynes are unsaturated hydrocarbons that contain one triple bond, the general formula of alkynes C_nH_{2n-2} and the triple bond is known as the 'acetylenic bond'. Many alkynes have been found in nature. The naming of the alkynes follows the exact rules as those used for naming alkenes except, of course, that the suffix – *yne* is used to indicate that a triple bond is now present.

Naming Alkynes: 1.Name the main chain. Find the longest carbon chain of carbons containing the triple bond. The names of alkynes end with -yne. When there is more than one multiple bond, use numerical prefixes (diene, diyne, triene, triyne, etc.)

$$-CH_3\ CH_2\ CH_2\ C\ C-CH_3-$$

Name as *hexyne* - a six C chain containing a triple bond

2. Number the carbon atoms in the main chain. Begin at the end nearer the multiple bond. If the multiple bond is at the same distance from both ends, begin numbering at the end nearer the first branch point.

$$CH_3-\ \equiv\ -CH_2-CH_2-CH_2-CH-$$

CH_3 1 2C   3C   4   5   6   7

C8H3
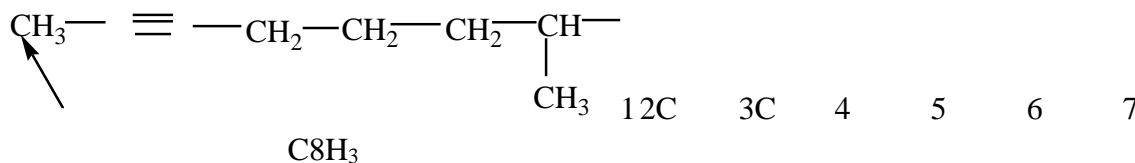
The lef t end is closer to the triple bond.

3.Write the full name. Assign numbers to the branching substituents, and list the substituents alphabetically. Indicate the position of the multiple bond(s) in the chain by giving the number of

the first multiple-bonded carbon. If more than one multiple bonds is present, identify the position

of each multiple bond and use the appropriate ending diene, triene, tetraene, and so forth.

$$CH_3 — CH_2 — CH_2 — C \equiv C — CH3$$
$$654321$$

2-hexyne or
hex-2-yne
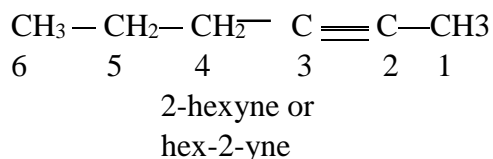
Some common alkynes and their naming:

Structure	Common Name	IUPAC
CH$\equiv$CH	Acetylene	ethyne
CH$\equiv$ —C CH$_3$	methyl acetylene	propyne
CH$_3$— C$\equiv$ — C CH$_3$	dimethyl acetylene	2-butyne
CH —C —CH$_2$-CH$_3$	ethyl acetylene	1-butyne

Structure and bonding in alkynes:

The triple bond in alkynes occurs due to the overlap of the carbon–carbon (C–C) bond's *sp* orbitals

forming a sigma (σ) bond, and the lateral overlapping of the $2p_y$ and

$2p_z$ orbitals forming the two pi (π) bonds, respectively. The overlap of the carbon *sp* orbital with

the 1*s* orbital of the hydrogen atom results in the carbon–hydrogen (C–H) *sp*–1*s* sigma bond of

the alkyne. Alkynes show an *sp* hybridization with a 50% *s* character. As electrons in the *s* orbital

show lower energies than the *p* orbitals, an increase in the atom's *s* character increases its

electronegativity.
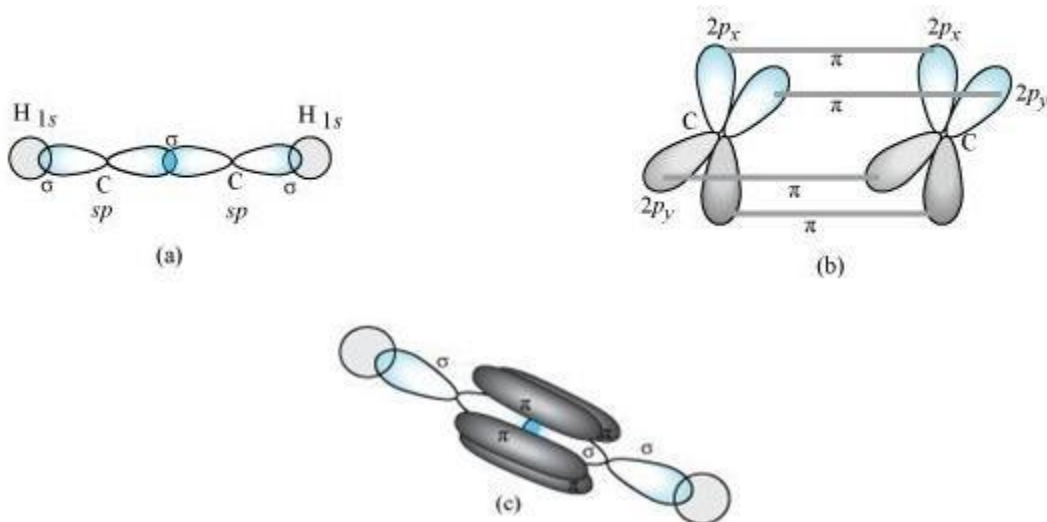
7.3.4 Aromatic hydrocarbons:

The aromatic hydrocarbons are **"Unsaturated hydrocarbons which have one or more planar sixcarbon rings called benzene rings, to which hydrogen atoms are attached".** Many aromatic hydrocarbons contain a benzene ring (also referred to as an aromatic ring). The benzene ring is stabilized by resonance and the pi electrons are delocalized in the ring structure.

The carbon atoms in benzene are linked by six equivalent σ bonds and six π bonds. The six p electrons are shared equally or delocalized among the donating carbon atoms, forming a continuous ring of orbitals above and below the plane of the carbon atoms. These delocalized π bonds are more stable than isolated double bonds. All the carbon-carbon bonds in benzene are the same length (1.397 Å), and all of the bond angles are 120°.

The aromatic hydrocarbons which do not contain a benzene ring are commonly referred to as heteroarenes. All of these heteroarenes obey Huckel's rule (total number of pi electrons in a monocyclic ring = 4n + 2 where n is any positive integer or zero).

In this series benzene is first and most important member. These are called benzenoid compounds.

Example:

1. Alkyl benzenes:

CH$_3$

CH₃

Toluene   Ethyl benzene   *tert*-Butyl benzene

2. Alkenyl benzenes:

Styrene

3-Phenyl propene-1
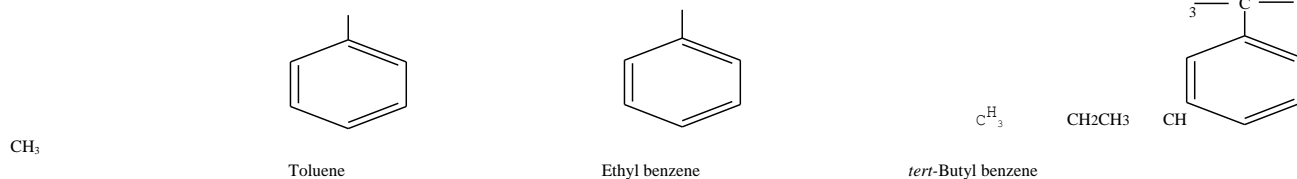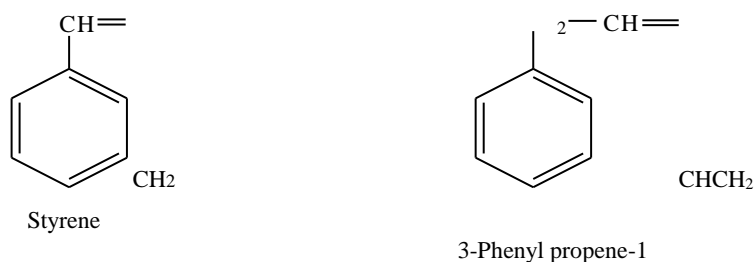
Aromatic hydrocarbons which have different those chemical properties then benzene are called non benzenoid aromatic compound.

Example:

Pyridene   Cyclopenta dienyl anion
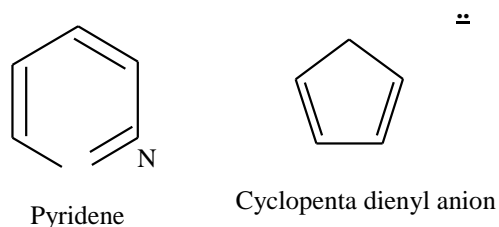
In these types of compounds, a minimum of one carbon is replaced by either nitrogen, oxygen, or sulphur. Common examples of heteroarenes include furan (contains oxygen) and pyridine (contains nitrogen)

Nomenclature of benzene derivatives

Nomenclature of benzene derivatives depends on IUPAC system and some derivatives have common names.

1.Monosubstituted benzene: These are named by prefixing the name of the substituent to ' benzene'. Like:

Toluene   **Phenol**   **Aniline**   **Benzoic acid**   **Benzaldehyde**

BASICS OF CHEMISTRY
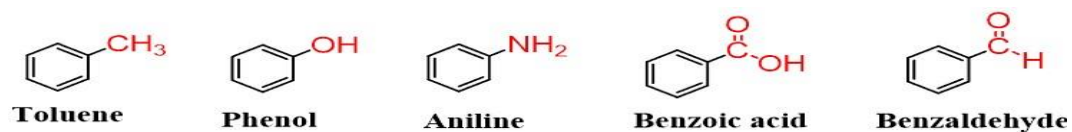
2.Disubstituted benzene: When there are two substitutents on the ring, three positional isomers are possible and their positions are indicated by ortho, meta and para or by numbers.

Example:

Mono   Ortho   Meta   Para
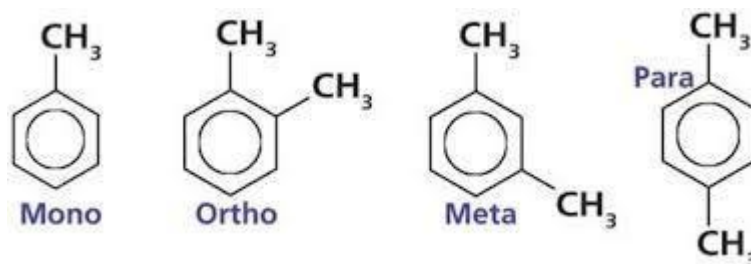
3. Polysubstituted benzene: When three or more substituent are placed on benzene then numbers are used to indicate the position.

Example:

2,4,6-trinitro toluene
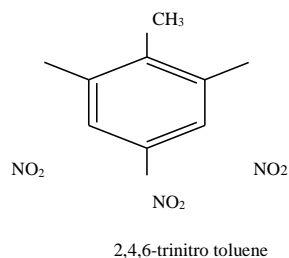
4. Fused polycyclic arenes : There are many polycyclic arenes having one or more benzene rings fused in ortho positions.

naphthalene $C_{10}H_8$ anthracene $C_{14}H_{10}$ phenanthrene $C_{14}H_{10}$
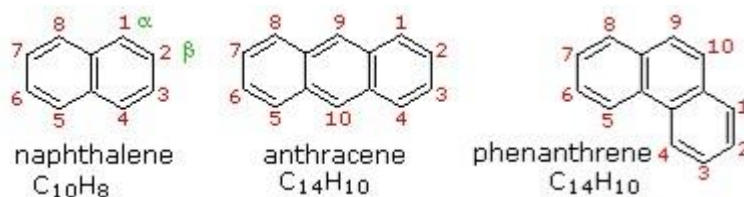
7.4 PREPARATION AND PROPERTIES OF ETHANE AND ETHYNE

7.4.1 Methods of formation Alkanes(Ethane):

 i)**Wurtz reaction :**When two alkyl halides are treated with sodium metal in presence of dry ether to form a higher alkane.

$$2 \text{ R−X} + 2 \text{ Na} \rightarrow \text{R−R} + 2 \text{ NaX}$$

$$2\,CH_3-Br \quad + 2Na \xrightarrow{\text{ether}} CH_3-CH_3 + 2NaBr$$
methyl bromide $\qquad\qquad\qquad\qquad$ ethane
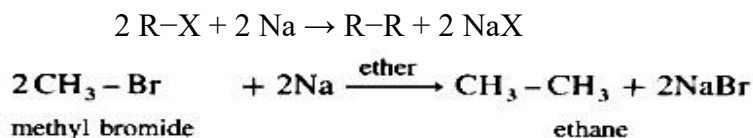
ii)**By Sabatier and senderen's method:** Alkenes and alkynes on catatlytic hydrogenation give

alkanes. Catalyst Ni is used in finely divided form.

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni,200^{\circ}C} CH_3\text{-}CH_3$$

$$CH{\equiv}CH + 2H_2 \xrightarrow{Ni,200^{\circ}C} CH_3\text{-}CH_3$$
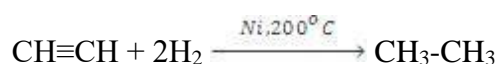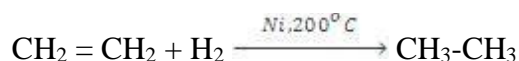
iii) **Kolbe's electrolysis method:** Alkanes are formed, on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated mono carboxylic acids of fatty acid.

$$2RCOONa + 2H_2O \xrightarrow{electrolysis} \underset{alkane}{R-R} + 2CO_2 + 2NaOH + 2NaOH + H_2$$
sodium salt
of fatty acid
$\qquad\qquad\qquad\qquad\qquad$ anode $\qquad\qquad$ cathode

Eg.

$$2CH_3COONa + 2H_2O \xrightarrow{electrolysis} \underset{ethane}{H_3C-CH_3} + 2NaOH + H_2$$
sodium acetate
$\qquad\qquad\qquad\qquad\qquad$ anode $\quad$ cathode
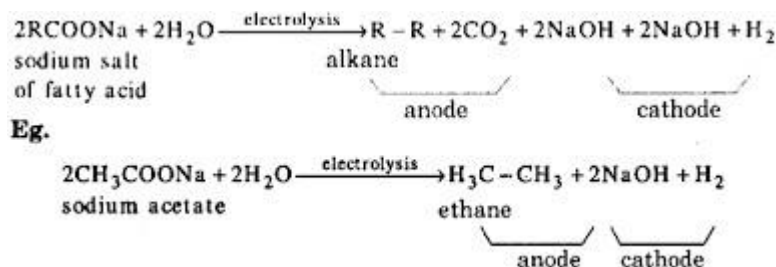
7.4.2 Properties of Alkanes(Ethane):

i)All the carbon atoms present in an alkane are sp^3 hybridised.

ii)The melting point of alkanes follows the same trend as their boiling point, that is, it increases with an increase in molecular weight.

iii)Alkanes readily undergo combustion reactions when ignited. When sufficient oxygen is present to support total combustion then carbon dioxide and water are formed.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + energy$$
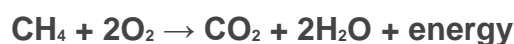
iv)Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms.

$$CH_3\text{-}CH_3 + Br_2 \rightarrow CH_3\text{-}CH_2\text{-}Br + HBr$$

7.4.3 Methods of formation Alkenes(Ethene) Alkenes:

i)When alkyl chlorides treated with a strong base it many convert to corresponding alkene. It is also called a **β-elimination reaction** .


$${}^{\beta}CH_3 - {}^{\alpha}CH_2Cl + KOH \longrightarrow CH_2 = CH_2 + KCl + H_2O$$
EthylChloride   Ethylene

$$CH_3 - CH_2 - CH_2Cl + KOH \longrightarrow CH_3 - CH = CH_2 + KCl + H_2O$$
1 – Chloropropane   Propene
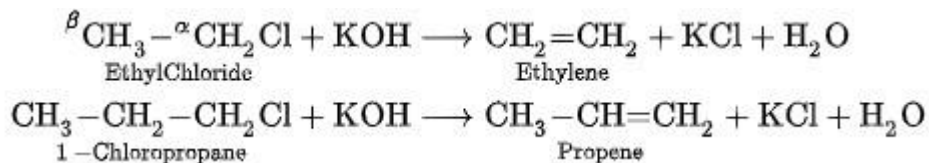
Note:Saytzeff's rule

Saytzeff's rule predicts the regioselectivity of the olefin (alkene) . During the elimination reaction, the proton is removed from the carbon atom having less number of substituents.

ii) Dehydration of Alcohols:

Alcohol upon reaction with protic acids tends to lose a molecule of water to form alkenes. These reactions are known as dehydrogenation or dehydration of alcohols.

tert-Butyl alcohol   **2-Methylpropene (84%)**
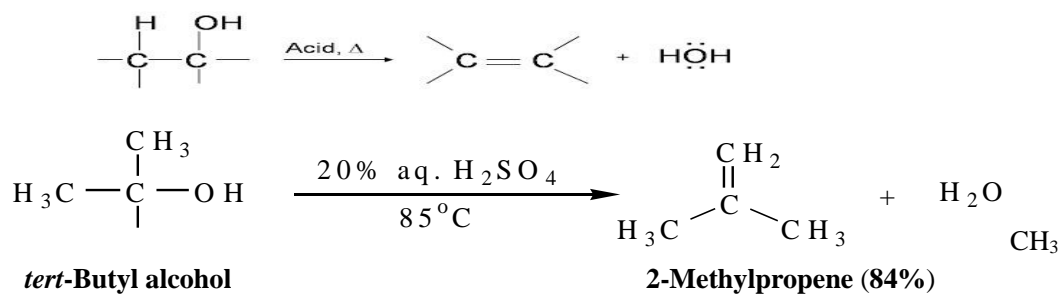
7.4.3 Properties of Alkenes(Ethene) :

i)Alkenes are slightly more reactive than alkanes due to the presence of double bonds.The dipole moments exhibited by alkenes are more than alkanes.

ii)In the presence of finely divided metals like Ni, Pt, Pd, Rh, and Ru, addition of a hydrogen molecule takes place on alkene at room temperature.

Ni, Pd or Pt

$$CH_2=CH_2 + H_2 \xrightarrow{\hspace{3cm}} CH_3-CH_3$$

$$CH_3CH=CH_2 + H_2 \xrightarrow[°C]{Ni, Pd \text{ or } Pt} CH_3CH_2-CH_3 \, 25$$
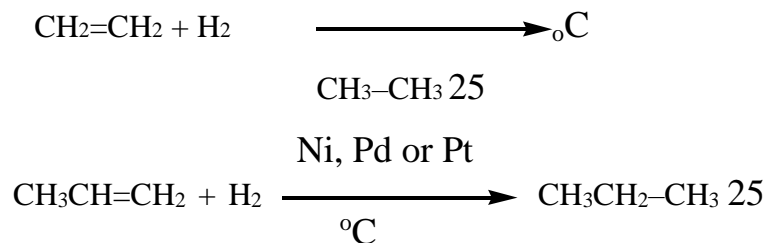
iii)The final product, haloalkane produce ,when H-Br has been added across the double bond according to the Markovnikov rule.
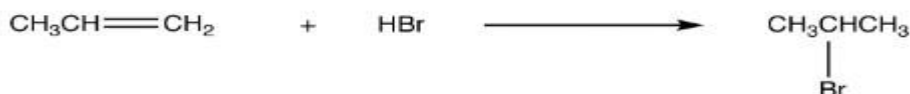
Note: Markovnikov rule:

According to this rule "The addition of a halogen acid to the double bond of an unsymmetrical alkene results in a product with the acid hydrogen bound to the carbon atom that already has the greater number of hydrogens attached."

iv)Ozone adds to carbon-carbon double bonds forming a number of intermediates the most important of which is ozonide. Reactive ozonide is reduced by zinc in the presence of water to give aldehydes or ketones depending on the degree of substitution of the double bond.
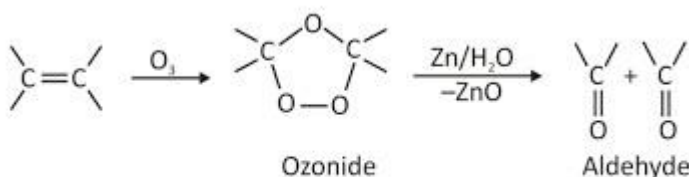
v) Addition polymerisation in alkenes occurs when the double bonds of the alkene molecules are broken and new single bonds are formed between the carbon atoms of adjacent monomers. This results in the formation of a long chain of carbon atoms, or polymer.

Ethylene   Polyethylene
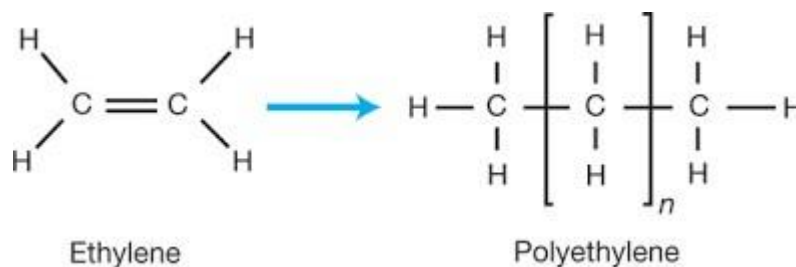
Similarly, when vinyl chloride is polymerized in the presence of peroxide catalyst, it forms polyvinyl chloride (PVC).
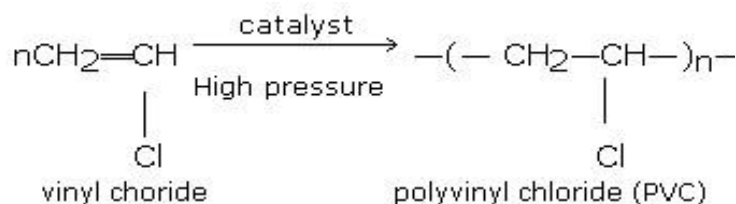
7.4.5 Methods of formation Alkynes(Ethyne):

i) From tetra halides: Tetra halides on react with Zn form alkynes.
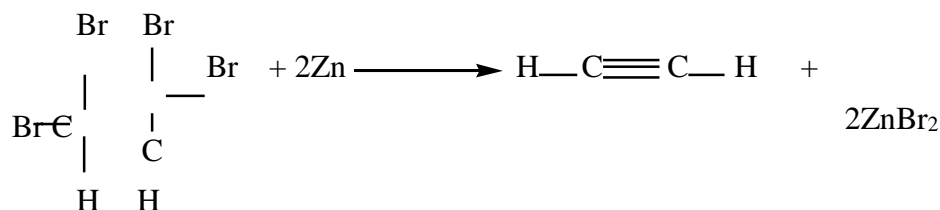
ii) Alkynes are obtained from vicinal dihalides by dehydrohalogenation which is carried out in two steps:The first step is to prepare the unsaturated halides. The halides formed have a halogen attached to a double-bonded carbon. These halides are called vinylic halides which are not reactive in nature. These halides are made to react with the strong base which results in the formation of alkynes
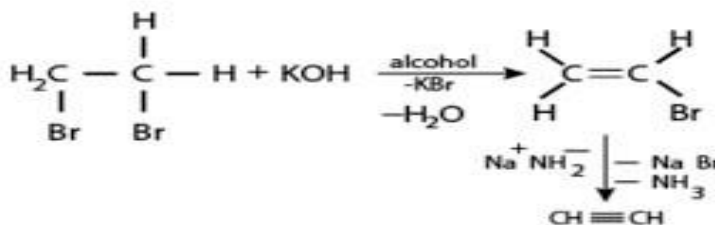
iii)From Kolbey's electrolysis method: The Na or K salt of malic acid on react with H_2O and after electrolysis gives acetylene and CO_2 at anode and H_2 and NaOH at cathode.

CH━COONa
‖   + $2H_2O$ ⟶ H C≡C━H+ $2CO_2$ + $2NaOH$ + H_2
CH━COONa
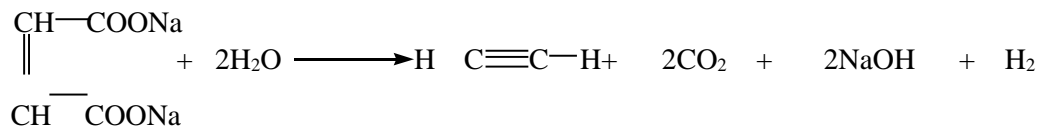
Sodium malate

7.4.6 Properties of Alkynes(Ethyne)

**i)** All alkynes are odourless and colourless with the exception of ethylene which has a slight distinctive odour.

ii) The boiling points of alkynes are slightly higher than those of their corresponding alkenes, due to the one extra bond at the carbon site.

iii)Addition Reactions: Alkynes give electrophilic addition reactions as they show reactivity due to the presence of Carbon-carbon triple bond.

For Example:Addition of H_2 and Br_2

ethyne   ethane   ethane

$H - C \equiv C - H_{(g)} + Br_{2(l)} \xrightarrow{FeCl_3} BrCH = CHBr + Br_{2(l)}$

$Br_2HC - CHBr_2$
1,1,2,2- tetrabromoethane
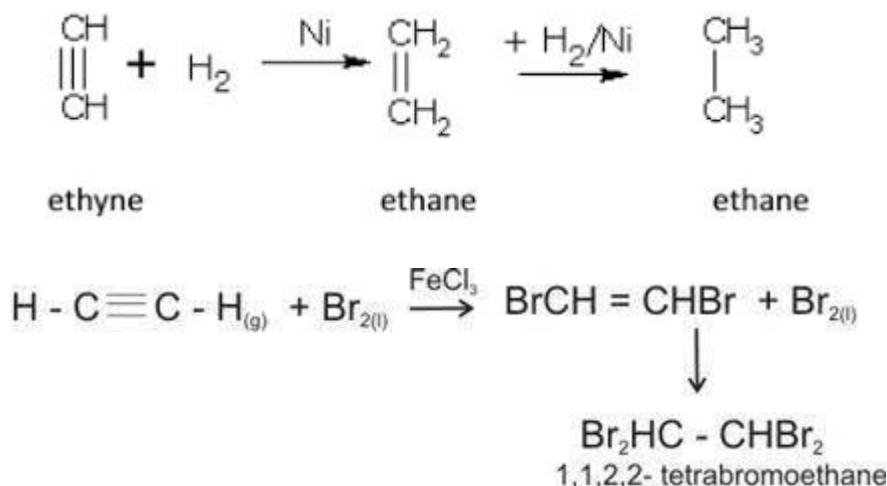
iv)Ozonolysis: In the presence of CCl_4 alkyne on react with O_3 gives alkyne ozonimide which on react with Zn/H_2O gives di-carbonyl compound.

o

Ozonide

di- carbonyl compound
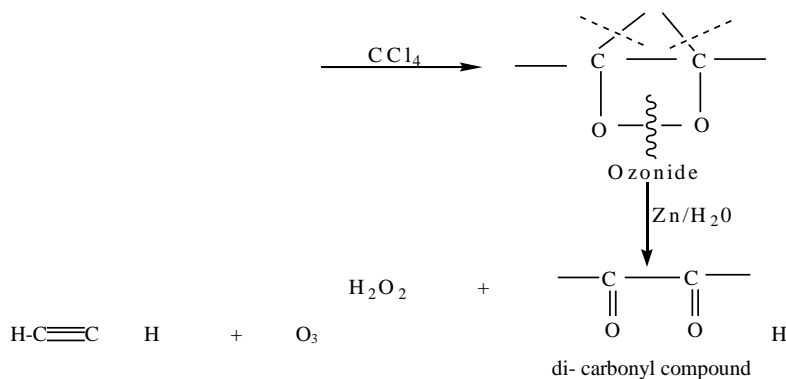
v)Ethyne on passing through a red hot iron tube at 873 K undergoes cyclic polymerisation to produce one molecule of benzene.

Ethyne   Benzene
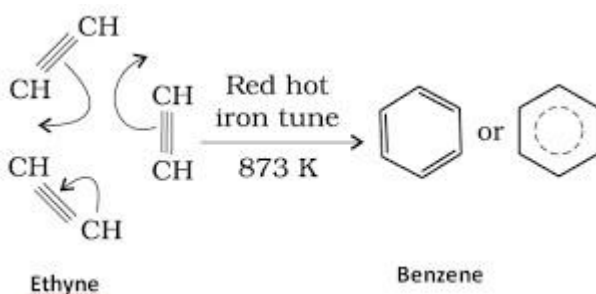
7.5 FUNCTIONAL GROUP IN ORGANIC COMPOUNDS- ALCOHOLS, ETHERS, ALDEHYDES, KETONE AND CARBOXYLIC ACIDS.

7.5.1.ALCOHOLS:

In chemistry, an **alcohol** is a type of organic compound that carries at least one hydroxyl (−OH) functional group bound to a saturated carbon atom. The general formula for a simple acyclic alcohol is $C_nH_{2n+1}OH$, where n=1, 2, 3, etc.

Classification of alcohols:

Alcohols are classified into following types on the basis of Carbon atom is bonded to number hydroxyl group (–OH) present in the molecule as follow:

i)**Monohydric Alcohols:**The compounds in which only one -OH group is attached to an aliphatic carbon chain are called monohydric alcohols.

ii) **Dihydric Alcohols:** The alcohol containing two -OH groups attached to an aliphatic carbon chain are called as dihydric alcohols.

iii)   **Trihydric Alcohols:** Alcohols containing three hydroxyl groups attached to an aliphatic carbon chain are called trihydric alcohol.
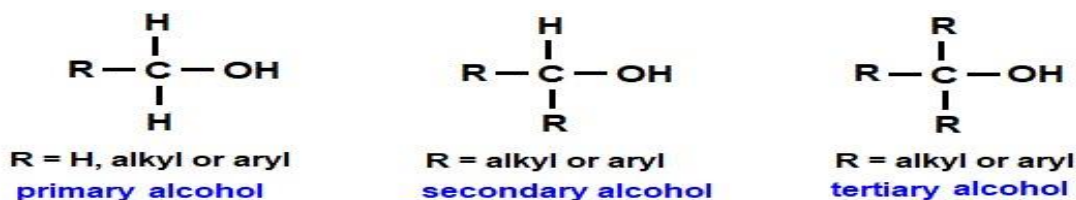
Example:

H_3C-CH_2-OH

Ethanol
(Monohydric alcohol)

H_2C-CH_2
| |
OH   OH

Ethane-1,2-diol
(Dihydric alcohol)

$H_2C-CH-CH_2$
| | |
OH   OH   OH

Propane-1,2,3-triol
(Trihydric alcohol)
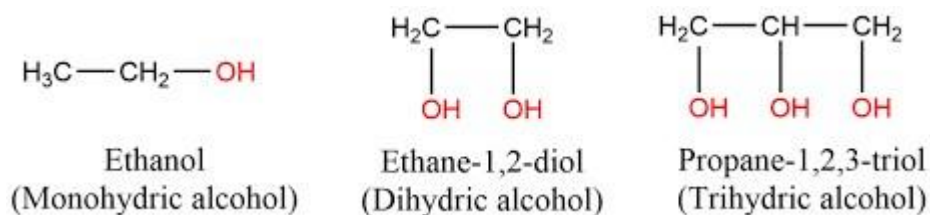
On the basis of nature of carbon atom attached with -OH group the mnohydric Alcohols can be further classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon atoms bound to the hydroxyl-bearing carbon.

i) **Primary alcohols (1°) :** Those alcohols where the carbon atom of the hydroxyl group(-OH) is attached to only one single alkyl group.

ii)**Secondary alcohols (2°) :** Those alcohols where the carbon atom of the hydroxyl group(-OH) is attached to two alkyl groups on the either sides.

iii) **Tertiary alcohols (3°):** Those alcohols where the carbon atom of the hydroxyl group(-OH) is attached to three alkyl groups on the either sides.

H
|
R — C — OH
|
H

R = H, alkyl or aryl
primary alcohol

H
|
R — C — OH
|
R

R = alkyl or aryl
secondary alcohol

R
|
R — C — OH
|
R

R = alkyl or aryl
tertiary alcohol

According to the IUPAC, alcohols are named by changing the ending of the parent alkane name to -ol. Here are some basic IUPAC rules for naming alcohols:

1.The longest continuous chain of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
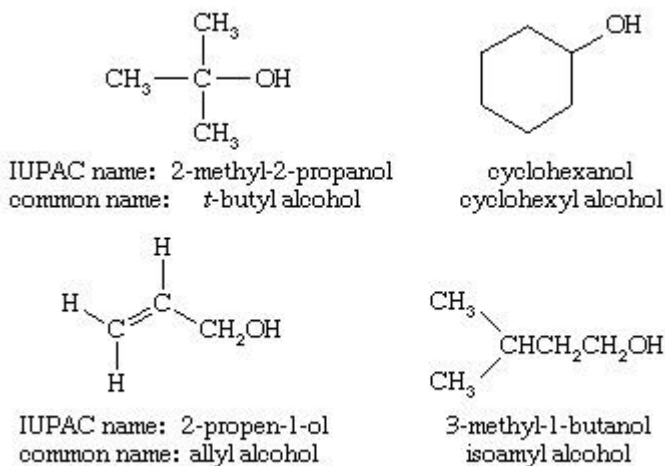
2.The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the -e ending of the parent alkane is replaced by the suffix -*ol*.

3.If more than one OH group appears in the same molecule(polyhydroxy alcohols), suffixes such as -*diol and -triol* are used. In these cases, the -*e* ending of the parent alkane is retained.

Example:

Alcohols	Common name	IUPAC name
CH3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	n-Propyl alcohol	1-Propanol
$CH_3CHOHCH_3$	Isopropyl alcohol	2-Propanol
$CH_3(CH_2)_2CH_2OH$	n-Butyl alcohol	1-Butanol
$CH_3(CH_2)_3CH_2OH$	n-Pentyl alcohol	1-Pentanol

Some other example of alcohols:

IUPAC name: 2-methyl-2-propanol
common name: *t*-butyl alcohol

cyclohexanol
cyclohexyl alcohol

IUPAC name: 2-propen-1-ol
common name: allyl alcohol

3-methyl-1-butanol
isoamyl alcohol

7.5.2 Ethers:

Ethers are a class of organic compounds that mostly contain an ether group wherein the oxygen atom is bonded to two alkyl or aryl groups. The general formula, of ethers is $C_nH_{2n+2}O$. Thus, ethers can be represented as R -O –R', where R and R' may be alkyl or aryl groups.

Classification of Ethers

Ethers can be classified into two broad categories based on the substituent group attached to its oxygen atom: symmetrical ethers and asymmetrical (or unsymmetrical) ethers.

Symmetrical ethers are those ethers where two identical groups are attached to the oxygen atom.Example:

$$CH_3 - CH_2 - O - CH_2 - CH_3 \text{ (Diethyl ether)}$$
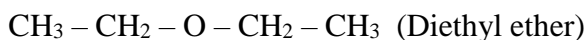
Asymmetrical ethers are those where two different groups are attached to the oxygen atom.Example:
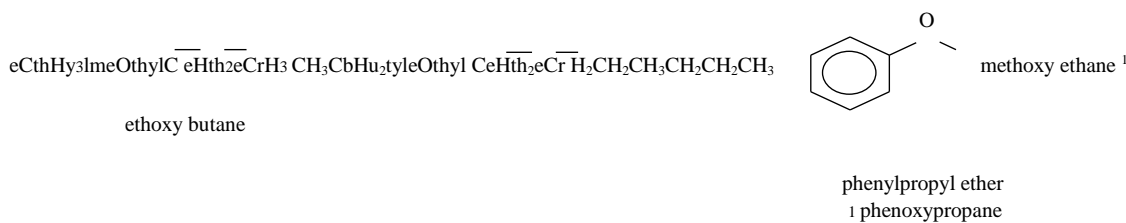
$$CH_3 - O - CH_2 - CH_3 \text{ (Ethyl methyl ether)}$$
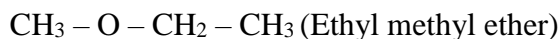
Ether Nomenclature

The nomenclature of ethers rotates around two standard ways of naming, which are given below.
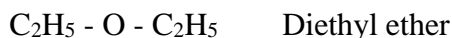
- Common nomenclature of ethers
- IUPAC nomenclature of ethers

Nomenclature of Ethers Rules

- The common ether nomenclature follows the rule of naming different alkyl/aryl groups that are attached in alphabetical order to the oxygen atom on either side and adding the word ether to it finally.

  For example :

  eCthHy3lmeOthylC eHth2eCrH3 CH3CbHu2tyleOthyl CeHth2eCr H2CH2CH3CH2CH2CH3   methoxy ethane [1]

  ethoxy butane

  phenylpropyl ether
  [1] phenoxypropane

- The oxygen atoms of ethers attached to the same group on either side are named using Greek numerical prefixes like "di." Ethers of these kinds are named by adding the suffix "di" before the aryl/alkyl groups, attached to the oxygen atom.

  $$C_2H_5 - O - C_2H_5 \qquad \text{Diethyl ether}$$

- In a substituent group having more carbon atoms is chosen as parent hydrocarbon. Whereas, the other substituent group attached to the same oxygen atom is named by using a prefix "oxy."
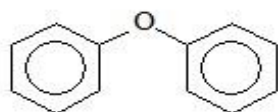
$$CH_3CH_2-O-CH-CH_2CH_3$$
$$\underset{CH_3}{|}$$

$$CH_3-O-CH_2CH_2CH_3$$

1 methoxypropane

2 ethoxybutane
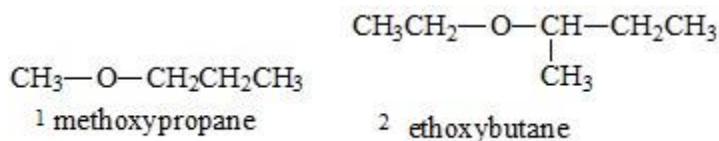
Common Nomenclature of Ethers:
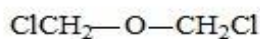
According to the formula R_1–O–R_2, ethers are the compounds having two alkyl or aryl groups bonded to an oxygen atom. The functional group of ether does not have a characteristic IUPAC nomenclature suffix, so it is required to indicate it as a substituent. So as to make it, the common alkoxy substituents are given names derived from their alkyl component, as tabulated below.

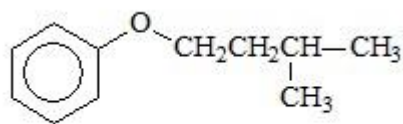| Alkyl Group - Name	Alkoxy Group - Name
CH_3 - Methyl	CH_3O - Methoxy
CH_3CH_2 - Ethyl	CH_3CH_2O - Ethoxy
$(CH3)_2CH$ - Isopropyl	$(CH3)_2CHO$ - Isopropoxy
$(CH3)_3C$ - Tert-Butyl	$(CH3)_3CO$ - Tert-Butoxy
C_6H_5 - Phenyl	C_6H_5O - Phenoxy

Ethers can be named by naming two each carbon group as a separate word followed by a space with the word ether. The -OR group can be named as a substituent by using the alkox group name.Some examples of IUPAC names of ethers are given below:
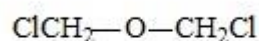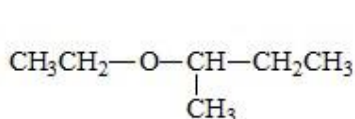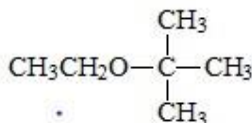
diphenyl ether

$$ClCH_2-O-CH_2Cl$$

bis(chloromethyl)ether

3 methylbutoxybenzene

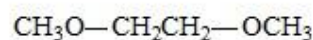$ClCH_2$—O—CH_2Cl

bis(chloromethyl)ether

CH_3CH_2—O—CH—CH_2CH_3
|
CH_3

2 ethoxybutane

CH_3CH_2O—C—CH_3
(with CH_3 above and CH_3 below the C)

2 ethoxy 2 methylpropane

CH_3O—CH_2CH_2—OCH_3
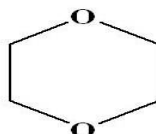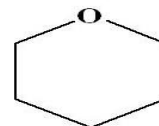
1, 2 dimethoxyethane

Cyclic ethers generally termed as epoxides in IUPAC system. Epoxide contains a 3-membered ring between oxygen and two carbons ethers.

Oxacyclopropane
(oxirane, ethylene oxide)

Oxacyclobutane
(oxetane)

Oxacyclohexane
(tetrahydropyran)

Oxacyclopentane
(tetrahydrofuran)

1,4-Dioxacyclohexane
(1,4-dioxane)

7.5.3 Aldehydes:

Aldehyde, any of a class of organic compounds in which a carbon atom shares a double bond with an oxygen atom, a single bond with a hydrogen atom, and a single bond with another atom or group of atoms (designated R in general chemical formulas and structure diagrams). The double bond between carbon and oxygen is characteristic of all aldehydes and is known as the carbonyl group and the group without alkyl/aryl moeity, also known as the formyl group.

Structure of carbonyl group:

Carbonyl carbons are sp^2 hybridized, with the three sp^2 orbitals forming soverlaps with orbitals on the oxygen and on the two carbon or hydrogen atoms. These three bonds adopt trigonal planar

geometry. The remaining unhybridized 2p orbital on the central carbonyl carbon is perpendicular to this plane, and forms a 'side-by-side' pbond with a 2p orbital on the oxygen.
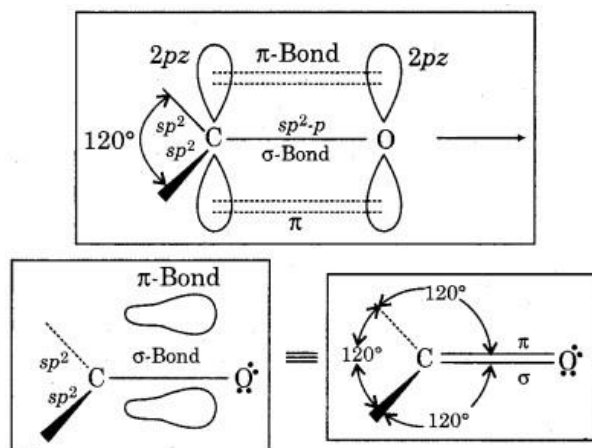
Orbital diagram of formation of carbonyl group

The carbon-oxygen double bond is polar: oxygen is more electronegative than carbon, so electron density is higher on the oxygen side of the bond and lower on the carbon side. Recall that bond polarity can be depicted with a dipole arrow, or by showing the oxygen as holding a partial negative charge and the carbonyl carbon a partial positive charge.


Nomenclature of Aldehyde:

- According to the IUPAC system of nomenclature **-al** is attached as a suffix to parent alkane for the naming of aldehydes.

- For example, $H_2C=O$ is named as per the IUPAC system as methanal, commonly known as formaldehyde.

- The aldehyde group is always attached at the end of the main carbon chain, and hence the 1st position in the numbering is always assigned to it.

- For aldehydes ,the names are reflected in Greek and Latin terms. Greek letters such as α, β etc. are used for the location of the substituents in the carbon chain.

- The α-carbon is directly attached to the aldehyde group, β-carbon is attached to the carbon adjacent to the aldehyde group and so on.For Example:
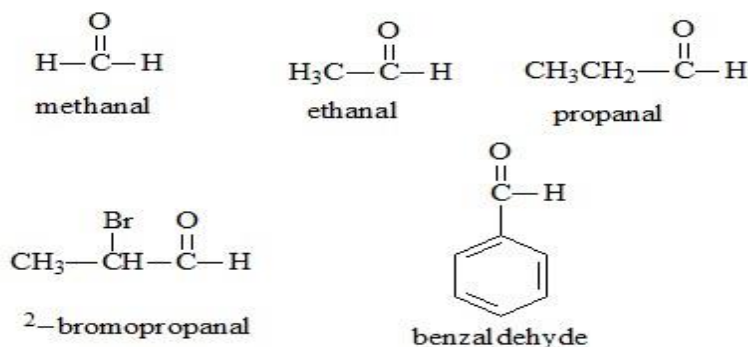
□-hydrogen :- A carbon next to the carbonyl group is called □- carbon and the hydrogen attached with it is referred to as an □-hydrogen. □-hydrogens of carbonyl carbon are acidic in nature with some pK_a values. Abstraction of □ hydrogen by a nase (B⁻) results in the formation of anion (enolate ion) which is reasonance stabilized by delocalisation of charge onto electronegative oxygen.
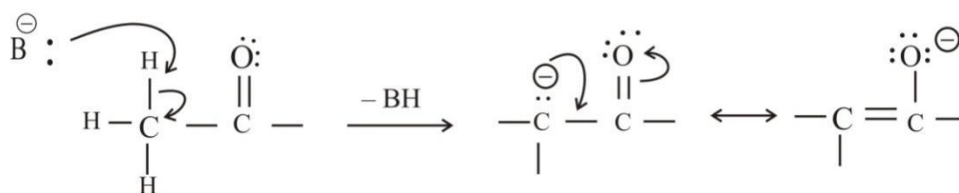
□- carbon of the enolate ion is an ambident ion. It can act as nucleophile and attack at electrophillic carbonyl carbon of other carbonyl group containing molecules and leads to condensation. Enolate ion can attach an alkyl group to the reactive carbon and it is called **Calkylation.** Alkylation at oxygen is uncommon but protonation leads to **alkenol**.

Nucleophilic addition to the carbonyl (C=O) group:

- A key reaction mechanism of carbonyls is nucleophilic addition (1,2 addition)
- Attack of a nucleophilic (Nu) on the trigonal planar carbon results in a tetrahedral product.

carbon is
trigonal planar (sp²)

carbon becomes
tetrahedral (sp³)
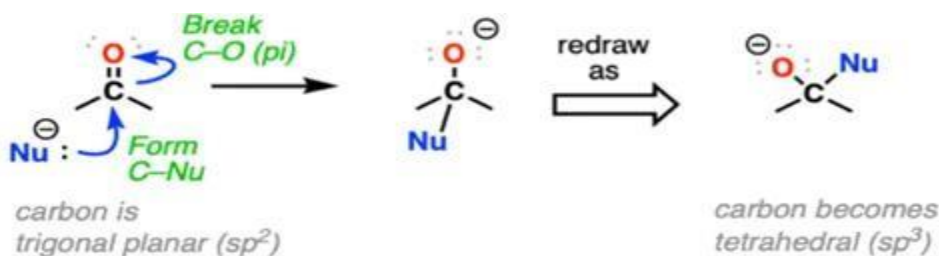
7.5.4 Ketones:

In chemistry, a ketones (alkanone) are an organic compound with the structure RC (=O) R', where R and R' can be a variety of carbon-containing substituents. Structurally the ketone carbon is often described as "sp^2 hybridized", a description that includes both their electronic and molecular structure. Ketones are trigonal planar around the ketonic carbon, with C−C−O and C−C−C bond angles of approximately 120°
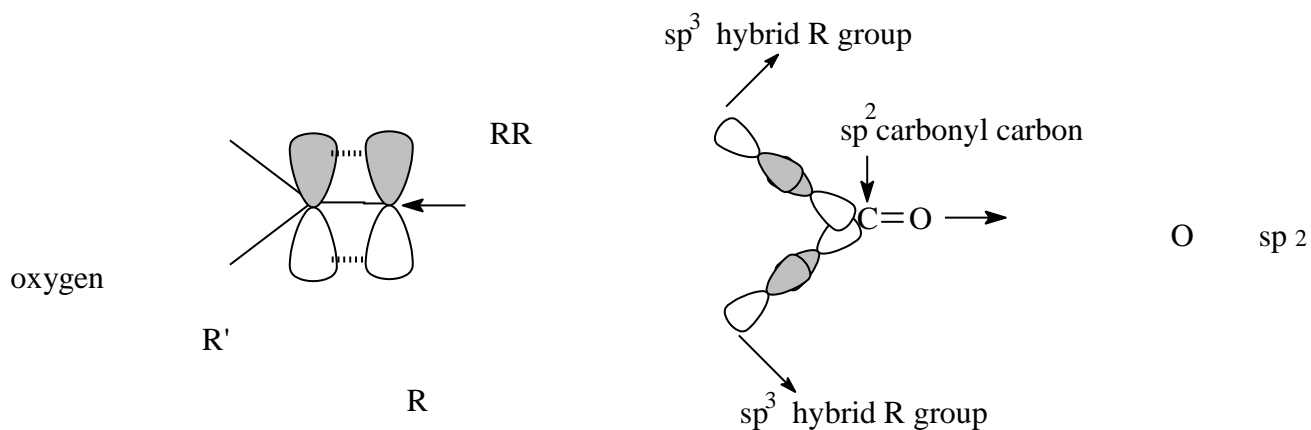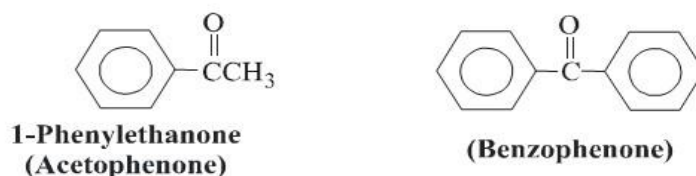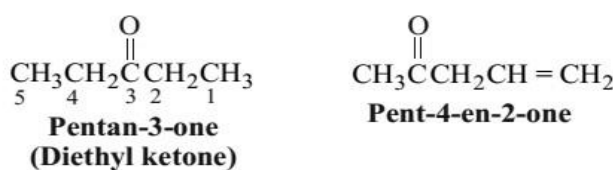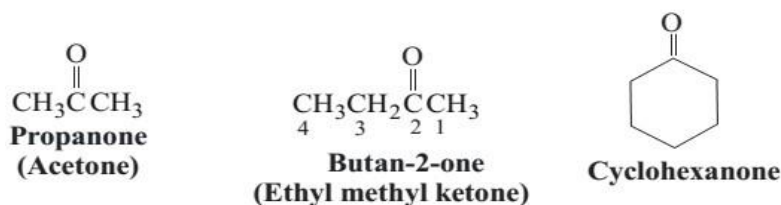

Basic skeletal structure of carbonyl group in ketone is same (Planer) as in aldehydes.

Nomenclature of Ketone:

- Now let's discuss the naming of ketones, according to IUPAC guidelines, the suffix *–one* is assigned for the ketones.

- Prefix is the name of hydrocarbon (Alkanones).

- Numbering the chain lowest number is given to carbonyl carbon.

- If there are two carbonyl groups in a molecule, it is named as Alkanedione.

Example:

CH$_3$CCH$_3$
Propanone
(Acetone)

CH$_3$CH$_2$CCH$_3$
4 3 2 1
Butan-2-one
(Ethyl methyl ketone)

Cyclohexanone

CH$_3$CH$_2$CCH$_2$CH$_3$
5 4 3 2 1
Pentan-3-one
(Diethyl ketone)

CH$_3$CCH$_2$CH = CH$_2$
Pent-4-en-2-one

CCH$_3$
1-Phenylethanone
(Acetophenone)

(Benzophenone)

Nucleophilic addition of ketone:

When a nucleophile reacts with the carbonyl carbon of an aldehyde or ketone, there is no leaving group – the incoming nucleophile simply 'pushes' the electrons in the pi bond up to the oxygen. After the carbonyl has reacted with the nucleophile, the negatively charged oxygen has the capacity to act as a nucleophile. However, most commonly the oxygen acts as a base, abstracting a proton from a nearby acid group in the solvent or enzyme active site. The generic mechanism for a strong nucleophile generally occurs under basic conditions as shown below.

Nu:⁻ R H or R'

R——H or R'
Nu
tetrahedral
intermediate

H—A

OH
R——H or R'
Nu
nucleophilic
addition
product
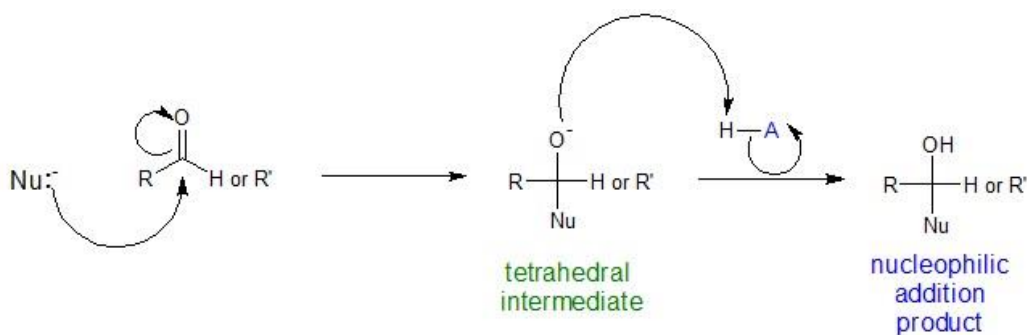
7.5.5 Carboxylic acids:

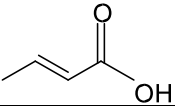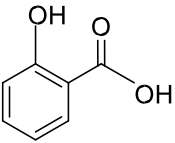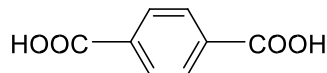In organic chemistry, a **carboxylic acid** is an organic acid that contains a **carboxyl group** $(C(=O)OH)^[$attached to an R-group. The general formula of a carboxylic acid is **R−COOH** or **R−CO₂H**, with R referring to the alkyl, alkenyl, aryl, or other group. Carboxylic acids are classified as mono, di, tri, or polycarboxylic acids according to the number of carboxyl groups present in the molecule. For example, the one –COOH group containing hydrocarbons such as formic acid, acetic acid, propionic acid, lactic acid, malic acid, benzoic acid etc. are called monocarboxylic acids whereas the two –COOH groups containing compounds such as oxalic acid, succinic acid, adipic acid, fumeric acid, malic acid, tartaric acid phthalic acid etc. are called dicarboxylic acids similarly like citric acid contains three -COOH group and termed as tri-carboxylic acid

Nomenclature of carboxylic acids :

- The common names of carboxylic acids end with the suffix −ic acid and have been derived from Latin or Greek names of their natural sources.

- In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending −e in the name of the corresponding alkane with −oic acid giving first priority to carboxyl group.

- If there are two -COOH groups are present in an acid; the acid is called dicarboxylic acid. To construct the IUPAC name of these compounds, add the suffix *–dioic* acid.

- Aromatic carboxylic acids are named by adding the suffix **"-carboxylic aci**d" to the name of a parent hydride.

- If a carboxylic compound contains double bond (alkene), then replace the infix from "–an to –en" and the placement of the infix is determined by the numbering, 1, 2, 3, 4 etc**.**

Example:

Formula	IUPAC name
HCOOH	Methanoic acid
CH_3COOH	Ethanoic acid
$CH_3(CH_2)_3COOH$	Pentanoic acid
HOOC – COOH	Ethane 1,2 dioic acid
$HOOC.CH_2CH_2COOH$	Butane1,2 dioic acid
$CH_3CHOHCOOH$	2-hydroxypropanoic acid

HOC(COH)((CH$_2$)COOH)$_2$	2-hydroxypropane-1,2,3 tri carboxylic acid
	trans-2-Butenoic acid
	2-hydroxybenzene carboxylic acid
	1,4-benzenedicarboxylic acid

Structure of carboxylic acid:

Carboxylic acids are organic compounds which incorporate a carboxyl functional group, COOH.The carbon and oxygen in the carbonyl are both sp2 hybridized which give a carbonyl group a basic trigonal shape. The hydroxyl oxygen is also sp2 hybridized which allows one of its lone pair electrons to conjugate with the pi system of the carbonyl group. This make the carboxyl group planar an can represented with the following resonance structure.

Resonance structures of Carboxylate Ion

7.6 SUMMARY

This unit containing different types of functional group, in this explain the major characteristics of each functional groups.In unit define , hoe to write the IUPAC of different functional group? Which rule is applied for different types of formulas, different types of functional groups.The major characteristics of variety of addition reactions, of alkenes alkynes or double bonded compounds,and substitution reactions of hydrocarbons , benzene.

Alcohols are compounds in which a hydrogen of alkane has been replaced by an –OH group and are classified as monohydric, dihydric, trihydric or polyhydric on the basis of –OH group present. The monohydric alcohols can be classified into 1º, 2º and 3º alcohols. In IUPAC name alcohols are designated as alkannol by replacing 'e' with –ol from the corresponding alkane.We also learned that ethers are characterized by the C-O-C bond and can be classified into symmetrical and non symmetrical ether. Unit will be able to explain the basic characteristic's ,and structures' of functional groups like ,alkane, alkene, alkynes, benzene -OH, CHO, R-O-R, -COOH.

7.7 TERMINAL QUESTIONS

Q.1. Draw structures corresponding to the following IUPAC names.

  a. 2-chloro-3,3- diethylhexane   b. 4- sec-butyl-2-chlorononan

  c. o-nitroaniline   d. m-chlorobenzonitrile

  e. 2,5 dinitrobenzaldehyde   f. o-xylene

Q.2. Discuss Kolbe's electrolytic method to prepare acetylene?
Q.3. How will you distinguish between Ethane and Ethyne? Give reaction.

Q.4. Write down the Classification of monohydric alcohols?

Q.5. Write short note on:-

  a. Satuzaff's rule   b. Markovnikov Rule

Q.6. Carbonyl compounds undergo nucleophillic addition reactions, why?

Q.7. Write the IUPAC name of the following:

```
        F    H
        |    |
   ——— C ——— C ———
1       |    |     Cl
        F    Br
        F
```

 2.

3.
CH₃-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃
                    |
                  CH-CH₃
                    |
                  CH-CH₃
                    |
                   CH₃

4.
$CH_3C=CHCH_2CHCH_3$ with CH_3 substituents

$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$
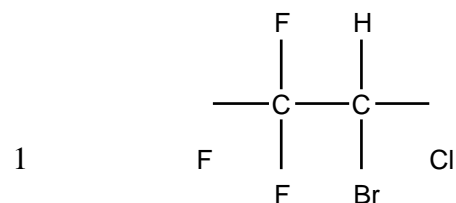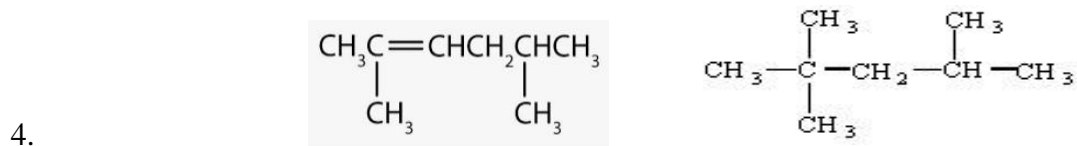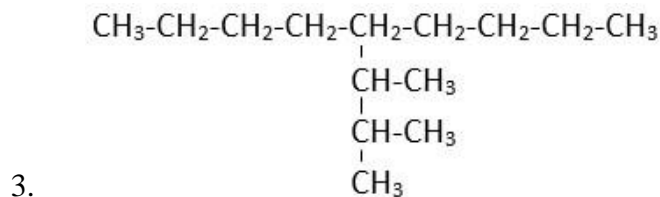
Q.8 Explain the following reactions:

a) β-elimination reaction   b) Wurtz reaction

c) Ozonolysis   d) Dehydration of Alcohols Q.9.

Write down the properties of ethane and ethyne?

Q.10. Define the IUPAC name rule of the ether and alcohol?

7.8 REFERENCES FOR FURTHER STUDIES

1. I.L Finar, Organic Chemistry Vol. II., 5th edition, ELBS & Longman group Ltd., 1974.

2. B.S. Bahal, A. Bahal. Advanced Organic Chemistry. S. Chand & Company Ltd. Ram Nagar, New Delhi 1993.

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UNIT 8: CARBOHYDRATES

CONTENTS

8.1. Introduction

8.2. Objectives

8.3. Classification and Nomenclature

8.4. Monosaccharides

8.5. Mechanism of osazone formation

8.6 Interconversion of glucose and frutose

8.7 Summary

8.8 Terminal questions

8.9 References for further studies

8.1 INTRODUCTION

Carbohydrates are a class of naturally occurring organic compounds of carbon, hydrogen and oxygen which are primarily produced by plants. They are extremely widespread in plants comprising upto 80% of dry weight. These are ultimate source of our food. In higher animals the simple sugar glucose is an essential constituent of blood and occurs in a polymeric form as glycogen in the liver and muscle.

In the green plants, carbohydrates are produced by a process called photosynthesis. This process involves the conversion of simple compounds CO_2 and H_2O into glucose ($C_6H_{12}O_6$) and is catalysed by green colouring pigment chlorophyll present in the leaves of plants. The energy required for this conversion is supplied by sun in the form of sunlight.

Carbohydrates are very useful for human beings. They provide us all the three basic necessities of life i.e., foog (starch containing grain), clothes (cellulose in the form of cotton , linen and rayon) and shelter (cellulose in the form of wood used for making our houses and furniture etc.).
Carbohydrates are also important to the economy of many nations. For example, sugar is one of the most important commercial commotidies.

The term carbohydrates arose because the general formula for most of them could be written as C_x $(H_2O)_y$ and thus they may be regarded as hydrates of carbon. However, this definition was not found to be correct e.g., rhamnose, a carbohydrate, is having the formula $C_6H_{12}O_5$ while acetic acid having formula $C_2H_4O_2$ is not a carbohydrate. Simple carbohydrates are also known as sugars or saccharides (Latin: Saccharum; Greek : Sakcharon, Sugar) and the ending of the names of most sungars is –ose. Examples: glucose, fructose, sucrose, maltose, arabinose, etc.

Chemically, carbohydrates contain mainly two functional groups, carbonyl group (aldehyde or or ketone) and a number of hydroxyl groups. Accordingly carbohydrates are now defined optically active polyhydroxy aldehydes or polyhydroxy ketones or the compound that can be hydrolysed to either of them.

8.2 OBJECTIVES

After going through this unit you will be able to:

- Define carbohydrates,
- Differentiate and classify the three major groups of carbohydrates,
- Define anomers, mutarotatation, configuration and mechanism of osazone formation,

8.3 CLASSIFICATION AND NOMENCLATURE

8.3.1 Classification

Carbohydrates, in general, may be classified into two classes:

i)Sugars. These are crystalline substances which are sweet and water soluble. For examples, glucose, fructose and cane sugar.

ii)Non-sugars. These are tasteless, insoluble in water and amorphous. For example. Starch, cellulose, etc.

However, these days Carbohydrates are systematically classified into three major group:
a)Monosaccharides. The simplest carbohydrates that cannot be hydrolysed into simpler carbohydrates, are called monosaccharides.depending upon whether they contain an aldehyde or keto groups, they may be called aldoses or ketoses. For example, a five carbon monosaccharide having aldehyde group is called aldopentose and six carbon monosaccharide containing a keto group is called keto-hexose. A few examples of monosaccharides are given below:

Aldotetroses. Erythrose and Threose; $CH_2OH(CHOH)_2 CHO$.

Ketotetroses. Erythrulose, $CH_2OHCOCHOHCH_2OH$.

Aldopentoses. Ribose, arabinose, Xylose and Lyxose. $CH_2OH(CHOH)_3 CHO$.

All have a common molecular formula but different structures.

Ketopentoses. Ribulose and Xylulose; $CH_2OHCO(CHOH)_2 CH_2OH$.

Aldohexoses. Glucose, mannose, galactose; $CH_2OH(CHOH)_4 CHO$.

Ketohexoses. Fructose, Sorbose etc. $CH_2OHCO(CHOH)_3 CH_2OH$.

b)Oligosaccharides. These are the carbohydrates which can be hydrolysed into a definite number of monosaccharide molecules. Depending upon the number of monosaccharides that are obtained from them on hydrolysis, they may be called di-, tri- or tetra-saccharides: For example:

Disaccharides: sucrose, lactose, maltose. All these have the same molecular formula $C_{12}H_{22}O_{11}$.

Trisaccharides: raffinmose ($C_{18}H_{32}O_{16}$).

Tetrasaccharides: stachyose ($C_{24}H_{42}O_{21}$).

c)Polysaccharides. Carbohydrates that yield a large number of molecules (more than ten molecules) of monosaccharides on hydrolysis are called polysaccharides. The common examples are starch, cellulose, glycogen, etc.

8.3.2 Nomenclature

Carbohydrates contain hydroxy and aldehydic or ketonic groups. They are named according to IUPAC system of nomenclature

Compound	Common name	IUPAC name
$CH_2OHCHOHCHO$	Glyceraldehyde	2, 3-dihydroxy propanol
$CH_2OHCOCH_2OH$	Dihydroxyacetone	1,3-dihydroxy propanone
$CH_2OH(CHOH)_4 CHO$	Glucose	2,3,4,5,6-pentahydroxyhexanal
$CH_2OH(CHOH)_3COCH_2OH$	Fructose	1,3,4,5,6-pentahydroxyhexan-2-one

8.4 MONOSACCHARIDES

The monosaccharides are again classified on the basis of two factors:

1.By the carbonyl function. Those containing the aldehydic function,-CHO, are called aldoses. Others containing the keto group, -CO-, are called ketoses.

2.By the number of Carbonyl atoms in the molecule. These monosaccharides containing 3,4,5,6 etc., carbon atoms are designated as trioses, tetroses, pentoses, hexoses, and so on.

Monosaccharides are polyhydric aldehydes and ketones which cannot be hydrolysed into simpler carbohydrates.

8.4.1 Structures of monosaccharides

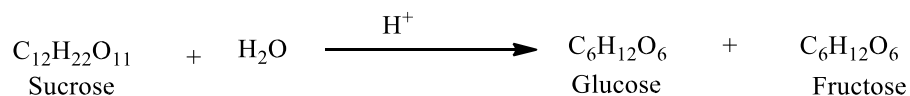The common monosaccharides are given in table.Table. Monosaccharides

No of carbon atoms	Class	Molecular formula aldoses	Structural formula	Examples
1	aldotrioses	$C_3H_6O_3$	$CH_2OHCHOHCHO$	Glyceraldehyde
2	aldotetroses	$C_4H_8O_4$	$CH_2OH(CHOH)_2CHO$	Erythrose, Threose
3	Aldopentose	$C_5H_{10}O_5$	$CH_2OH(CHOH)_3CHO$	Arabinose, Ribose, Xylose, Lyxose
4	aldohexoses	$C_6H_{12}O_6$	$CH_2OH(CHOH)_4CHO$	Glucose, galactose, mannose, allose, talose, gulose, iodose, etc.
5	ketotrioses	$C_3H_6O_3$	$CH_2OHCOCH_2OH$	dihydroxyacetone
6	ketotetroses	$C_4H_8O_4$	$CH_2OHCOCHOHCH_2OH$	erythrulose
7	ketopentoses	$C_5H_{10}O_5$	$CH_2OHCO(CHOH)_2CH_2OH$	Ribulose, Xylulose
8	ketohexoses	$C_6H_{12}O_6$	$CH_2OHCO(CHOH)_3CH_2OH$	Fructose, Sorbose, Tagatose, Psicose

8.4.2 Glucose

Glucose is most common monosaccharide. It is known as Dextrose because it occurs in nature principally as optically dextrorotatory isomer. Glucose is found in most sweet fruits, especially grapes (20-30%), and honey. It is an essential constituent of human blood. The blood normally conatains 65 to 110 mg (0.06 to 0.1%) of glucose per 100 ml. In diabetic persons the level may be much higher. In combined form glucose occurs in abundance in cane sugar and polysaccharides such as starch and cellulose. **Preparation of Glucose**

1.From sucrose (Cane sugar)

When sucrose in boiled with dilute HCl or H2SO4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

2.From Starch

Glucose is produced commercially by the hydrolysis of starch by boiling it with dilute H2SO4 at high temperature under pressure.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{HCl} nC_6H_{12}O_6$$
$$\text{Starch} \qquad\qquad\qquad\qquad \text{Glucose}$$
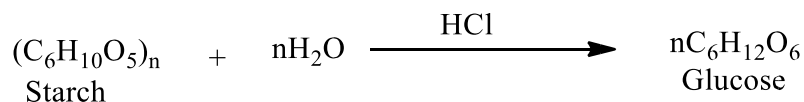
in this process, an aqueous solution of starch obtained from corn is acidified with dilute H2SO4. It is then heated with high pressure steam in an autoclave. When the hydrolysis is complete, the liquid is neutralized with sodium carbonate to pH of 4-5. The resulting solution is concentrated under reduced pressure to get the crystals of glucose.

Physical properties of glucose

Some important physical properties of glucose are mentioned as under:

1. It is colourless sweet crystalline compound having m.p.419 K.

2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.
3. It forms a monohydrate having m.p. 391 K.
4. It is optically active and its solution is dextrorotatory. The specific rotation of fresh solution is $+ 112^0$ C.

5. It is about three fourth as sweet as sugarcane i.e., sucrose.

Chemical properties of glucose

Chemical properties of glucose can be studied under the following headings:

A)Reactions of aldehydic group

1. **Oxidation**. (a) Glucose gets oxidized to gluconic acid with mild oxiding agents like bromine water

$$CH_2OH\,(CHOH)_4CHO \xrightarrow[Br_2, H_2O]{[O]} CH_2OH\,(CHOH)_4COOH$$
$$\text{Glucose} \qquad\qquad\qquad\qquad \text{Gluconic acid}$$
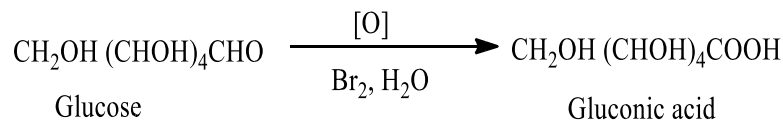
Only-CHO group is affected.

(b) A strong oxidizing agent like nitric acid oxidizes both the terminal groups viz. –

CH2OH and –CHO groups and saccharic acid or glucaric acid is obtained.

$$CH_2OH(CHOH)_4CHO \xrightarrow[\text{[O]}]{HNO_3} COOH(CHOH)_4COOH$$

Glucose   Glucaric acid
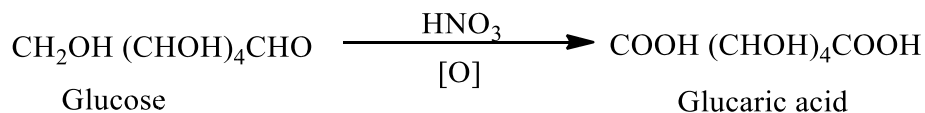
c)Glucose gets oxidized to gluconic acid with ammonical silver nitrate (Tollen's reagent) and alkaline copper sulphate (Fehling solution). Tollen's reagent is reduced   to metallic silver (silver mirror) and Fehling solution to cuprous oxide which is a red precipitate.

    (i)   With Tollen's reagent

$$AgNO_3 \;+\; NH_4OH \longrightarrow AgOH \;+\; NH_4NO_3$$

$$2AgOH \longrightarrow Ag_2O \;+\; H_2O$$

$$CH_2OH(CHOH)_4CHO \;+\; Ag_2O \longrightarrow CH_2OH(CHOH)_4COOH \;+\; 2Ag\downarrow$$

Glucose   Gluconic acid   Silver mirror

    (ii)   With Fehling solution

$$CuSO_4 \;+\; 2NaOH \longrightarrow Cu(OH)_2 \;+\; Na_2SO_4$$

$$Cu(OH)_2 \longrightarrow CuO \;+\; H_2O$$

$$CH_2OH(CHOH)_4CHO \;+\; 2CuO \longrightarrow CH_2OH(CHOH)_4COOH \;+\; Cu_2O$$

Glucose   Gluconic acid   Red ppt.
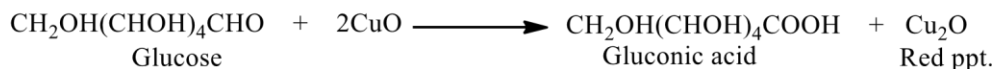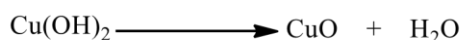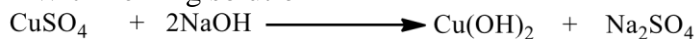
2.Reduction a) glucose is reduced to sorbitol or Glucitol on treatment with sodium amalgam and water.

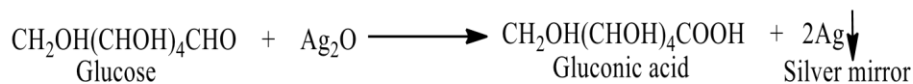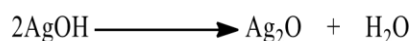$$CH_2OH(CHOH)_4CHO \;+\; 2[H] \xrightarrow[H_2O]{Na/Hg} CH_2OH(CHOH)_4CH_2OH$$

Glucose   Sorbitol
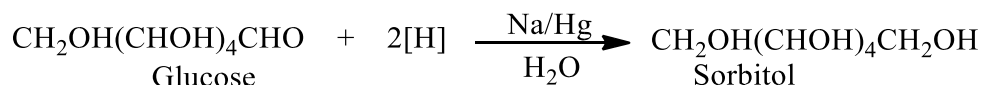
b) On reduction with conc. HI and red P at 373 K glucose gives a mixture of n-hexane and 2idohexane

$$CH_2OH(CHOH)_4CHO \xrightarrow{HI/red\ P} CH_3(CH_2)_4CH_3 \;+\; CH_3(CH_2)_3CHICH_3$$

Glucose   n-hexane   2-Iodohexane
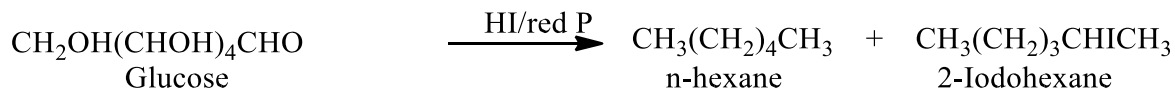
2.Reaction with HCN. Like aldehydes, glucose reacts with HCN forming cyanohydrins.

$$CH_2OH(CHOH)_4CHO \;+\; HCN \longrightarrow CH_2OH(CHOH)_4CH{\overset{\displaystyle OH}{\underset{\displaystyle CN}{<}}}$$

Glucose   Glucose cyanohydrin
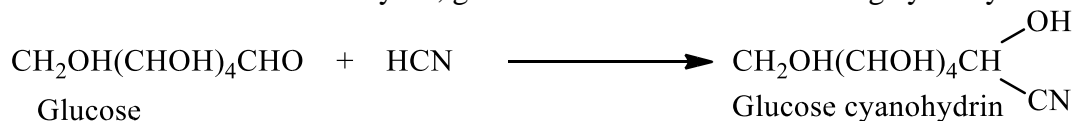
3.Reaction with hydroxylamine. Glucose forms glucose oxime.

$$CH_2OH(CHOH)_4CHO \quad + \quad NH_2OH \longrightarrow CH_2OH(CHOH)_4CH{=}NOH \; + \; H_2O$$

Glucose   Glucose oxime
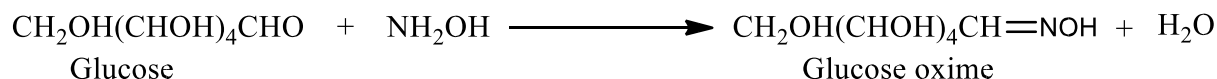
B)Reactions of hydroxyl groups

1. **Reaction with acetic anhydride or acetyl chloride**. Glucose forms penta acetate with acetic anhydride of acetyl chloride.
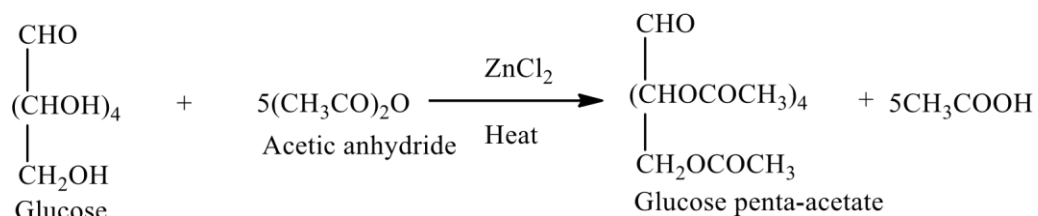
2. **Reaction with methyl alcohol**. Glucose reacts with methy alcohol in the presence of dry HCl gas to form methyl glucoside.

$$C_6H_{11}O_5\,OH \quad + \quad H\,OCH_3 \xrightarrow{\text{Dry HCl}} C_6H_{11}O_5OCH_3 \quad + \quad H_2O$$

Glucose   Methyl glycoside
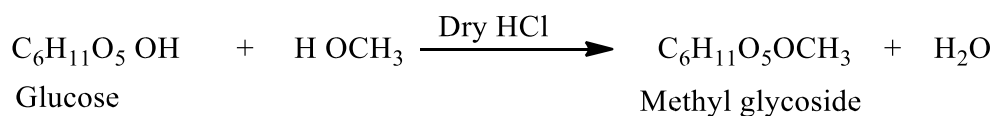
3. **Reaction with metallic hydroxides**. Glucose reacts with calcium hydroxide to form calcium glucosate which is water soluble.

$$C_6H_{11}O_5\,OH \quad + \quad H\,OCaOH \longrightarrow C_6H_{11}O_5OCaOH \quad + \quad H_2O$$

Glucose   calcium hydroxide   calcium-glucosate
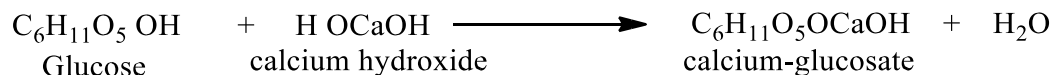
C)Miscellaneous reactions

1. Action of acids. On warming with conc.HCl, glucose forms 5-hydroxy methyl furfural, which on further reaction gives laevulinic acid.
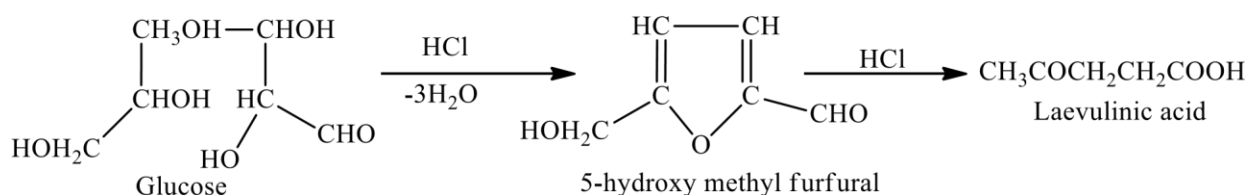
2. Fermentation. Glucose undergoes fermentation into ethyl alcohol in the presence of the enzyme zymase.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH \;+\; 2CO_2$$

Glucose   Ethyl alcohol
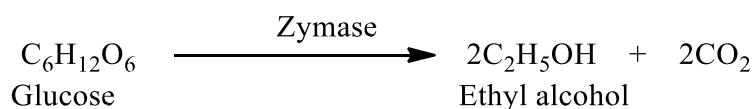
This reaction called alcoholic fermentation is the basis of manufacture of wines and alcohol.

3. Reaction with Alkalies. When warmed with strong sodium hydroxide solution, glucose forms a brown resinous product. In dilute alkali solution, D-glucose rearranges to give a mixture of D- glucose, D-mannose and d-fructose.

D-Glucose   D-Mannose   D-Fructose
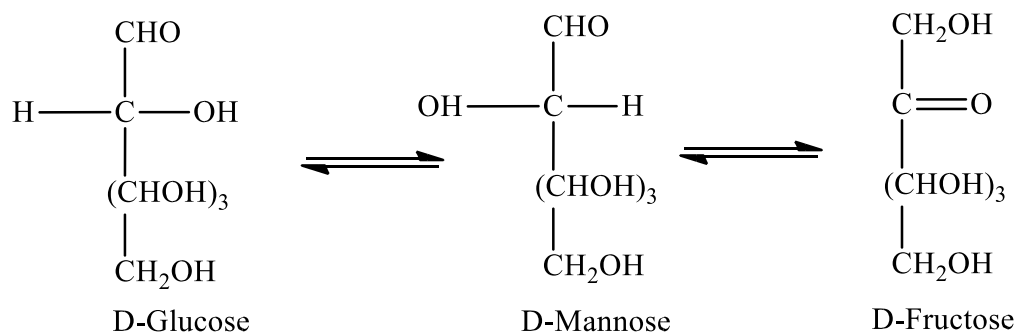
The above equilibrium is established via the enediol starting from any of these three hexoses.

D-Glucose   Enediol   D-Mannose
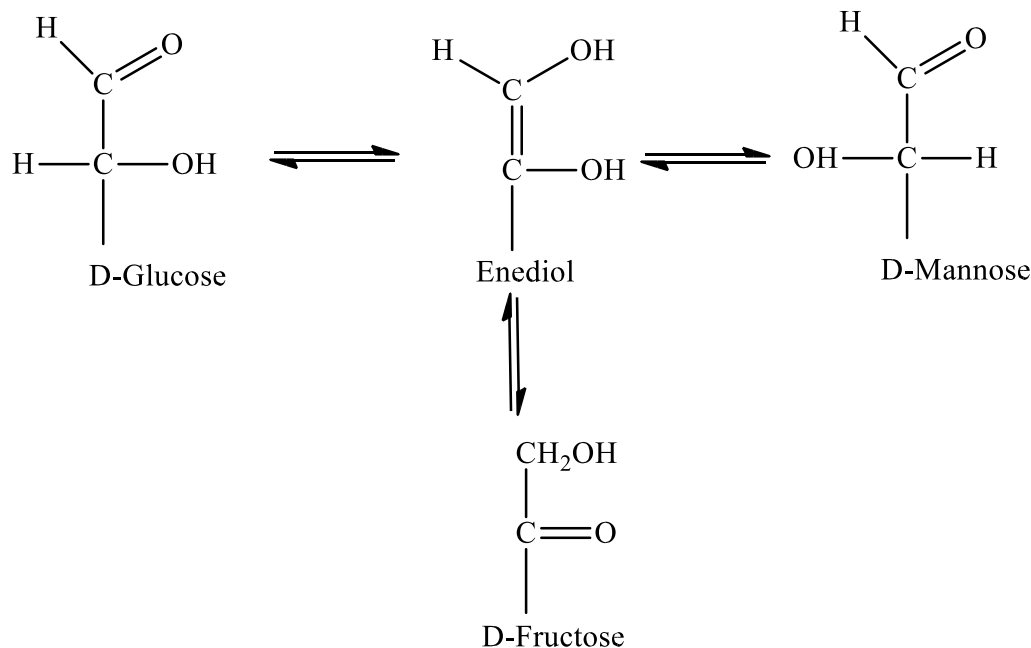
D-Fructose

That is why D-Fructose, although it has a ketonic C=O group, reduces Fehling's solution or Tollen's reagent. The rearrangement reaction of a monosaccharides in weakly alkaline solutions to give a mixture of isomeric sugars, is named as Lobry de Bruyn Van Ekestein rearrangement.

Structure of glucose

1. On the basis of elemental analysis and molecular weight determination the molecular formula of glucose is $C_6H_{12}O_6$.

2. The reduction of glucose with red phosphorus and HI gives n-hexane.

$$C_6H_{12}O_6 \xrightarrow{\text{HI/redP}} CH_3CH_2CH_2CH_2CH_2CH_3$$

Glucose   n-hexane
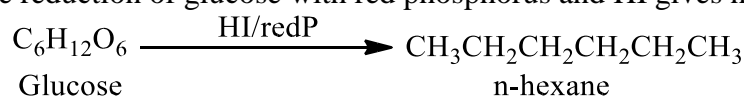
Therefore, the six carbon atoms of glucose form a straight chain.

3. It forms penta acetate on treatment with acetic anhydride which indicates the presence of five hydroxyl groups in the molecule.

4. Glucose reacts with hydroxyl amine to form an oxime and with hydrogen cyanide to form cyanohydrins. It indicates the presence of a carbonyl group. It also forms phenylhydrazone on treatment with phenylhydrazine.

5. The mild oxidation of glucose with bromine water or sodium hypobromide yields a monocarboxylic acid (gluconic acid) containing same number of carbon atoms as in glucose, i.e., six. This indicates that the carbonyl group must be aldehyde group.

6. The catalytic reduction of glucose gives a hexahydric alcohol (sorbitol) which gives hexaacetate on treatment with acetic anhydride. The sixth hydroxyl group must be obtained by the reduction of aldehyde group, thus further confirming the presence of an aldehyde group and five hydroxyl groups in glucose.

7. Oxidation of gluconic acid with nitric acid yields a dicarboxylic acid (glucaric acid) with the same number of carbon atoms as in glucose. Thus besides aldehyde group, glucose must contain a primary alcoholic group also, which generates the second carboxylic group on oxidation.

8. Glucose is a stable compound and does not undergo dehydration easily, indiacating that not more than one hydroxyl group is bonded to a single carbon atom. Thus all the hydroxyl groups are attached to different carbon atoms.

Open –chain structure of glucose On the basis of above reactions, Fisher assigned an open chain structure of glucose shown below as structure I

```
              CHO
       H ─────┼───── OH
       H ─────┼───── OH
      HO ─────┼───── H
       H ─────┼───── OH
            CH₂OH
              I
        D-(+)-Glucose
```
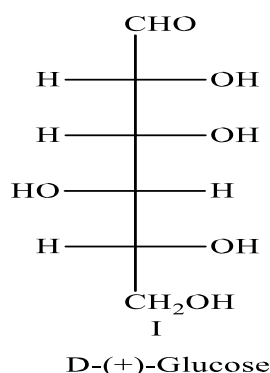
The above structure of glucose is also confirmed by the cleavage reaction of glucose with periodic acid. Five moles of periodic acid are consumed by one mole of glucose giving five moles of formic acid and one mole of formaldehyde.

$$C_6H_{12}O_6 \ + \ 5HIO_4 \longrightarrow HCHO \ + \ 5HCOOH \ + \ 5HIO_3$$
Glucose   Periodic acid
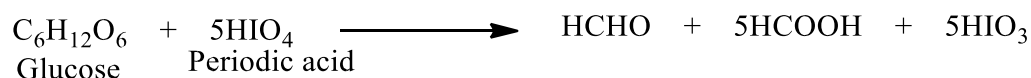
Configuration of D-Glucose

The configuration of D-glucose was proved by Emil Fisher by arguments similar to the ones stated below.

1. Construction of four possible D-pentoses. Taking the configuration of D-glyceraldehyde as the standard, two possible D-aldotetroses (A and B) may be constructed by adding a CHOH just below CHO, placing OH to the right and then to the left.

```
      CHO                          CHO                       CHO
                    +CHOH
 H ────┼──── OH   ────────►   H ────┼──── OH          H ────┼──── OH
     CH₂OH                    H ────┼──── OH          H ────┼──── OH
                                  CH₂OH                    CH₂OH
 D-glyceraldehyde                   A                        B
```
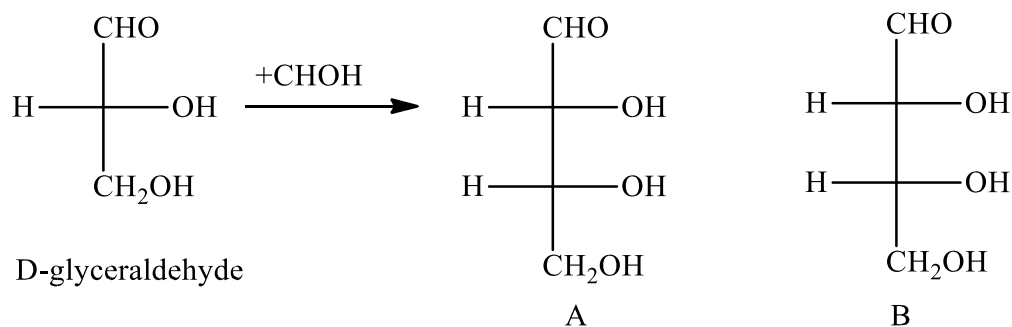
Similarily, each of the two D-tetroses (A and B) gives two D-aldopentoses. Thus four possible D-aldopentoses are:

CHO — H—OH — H—OH — H—OH — CH₂OH (I)

CHO — OH—H — H—OH — H—OH — CH₂OH (II)

CHO — H—OH — OH—H — H—OH — CH₂OH (III)

CHO — OH—H — OH—H — H—OH — CH₂OH (IV)

From A   From B
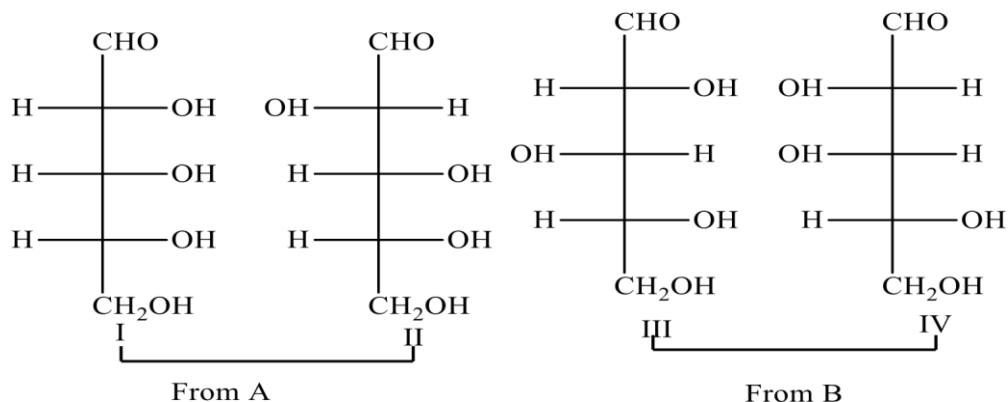
2. D-Arabinose has configuration II or IV. Oxidation of D-arabinose with nitric acid oxidizes the terminal CHO and CH₂OH groups yielding two optically active dicarboxylic acids. The forms II and IV can form two optically active diacids, while I and III can give meso acids only that have a plane of symmetry, therefore, D-arabinose is either II or IV.

3. Configyration II confirmed for D-arabinose. D-arabinose by Killiani-Fisher synthesis yields two epimeric aldohexoses, D-glucose and D-mannose. Thses of oxidation with nitric acid form two optically active dicarboxylic acids. This is theoretically possible only if D-arabinose has the configuration II and not IV.
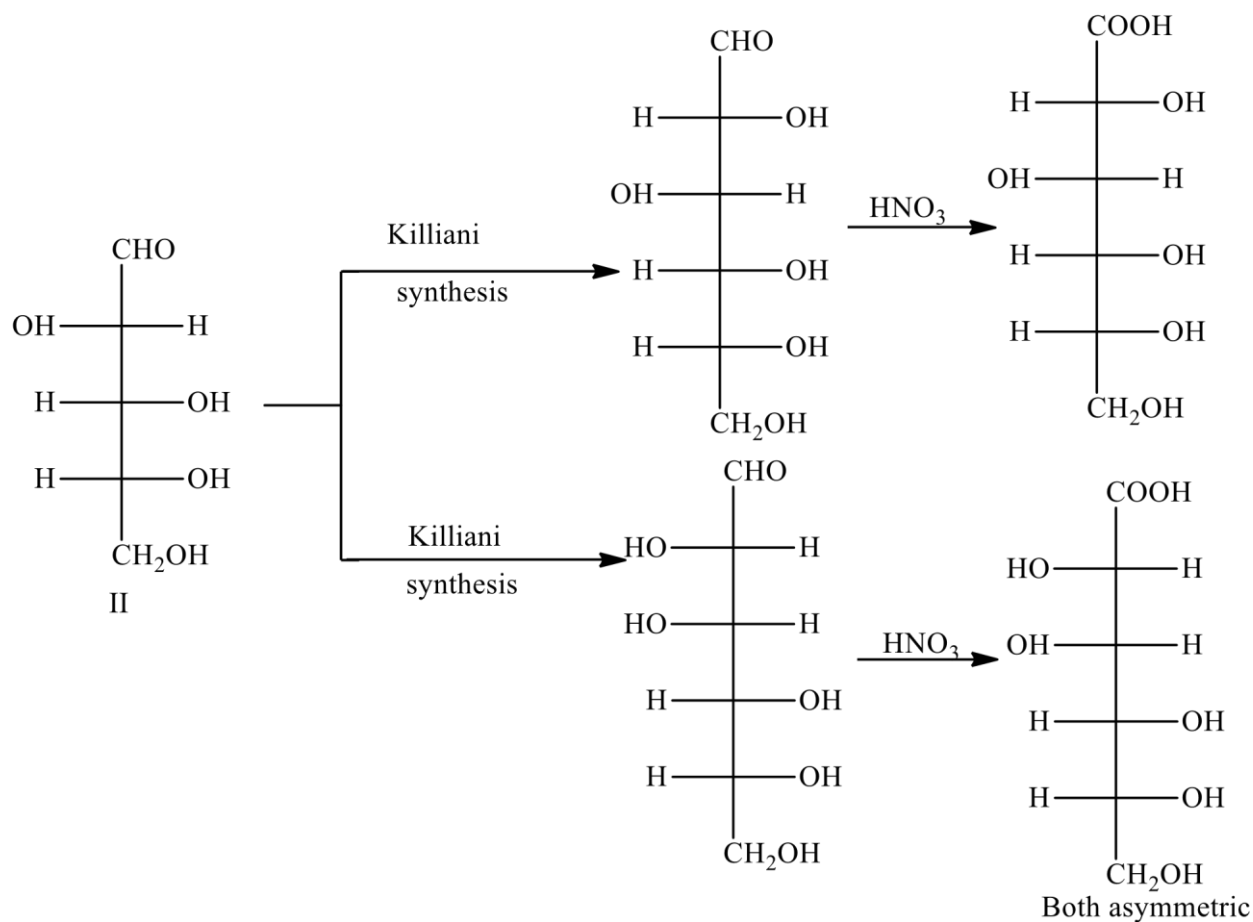
Proceeding similarily, you will find that if D-arabinose had configuration IV, of the two dicarboxylic acids derived from it, one would be meso and one asymmetric. Hence D-arabinose has the configuration II.

4.Ruff degradation of D-glucose and D-mannose produces D-arabinose in each case. In ruff degradation the CHOH below CHO is destroyed. Therefore , the configuration of the two aldohexoses, D-glucose and D-mannose, can be derived by adding a new CHOH below CHO in form II of D-arabinose.
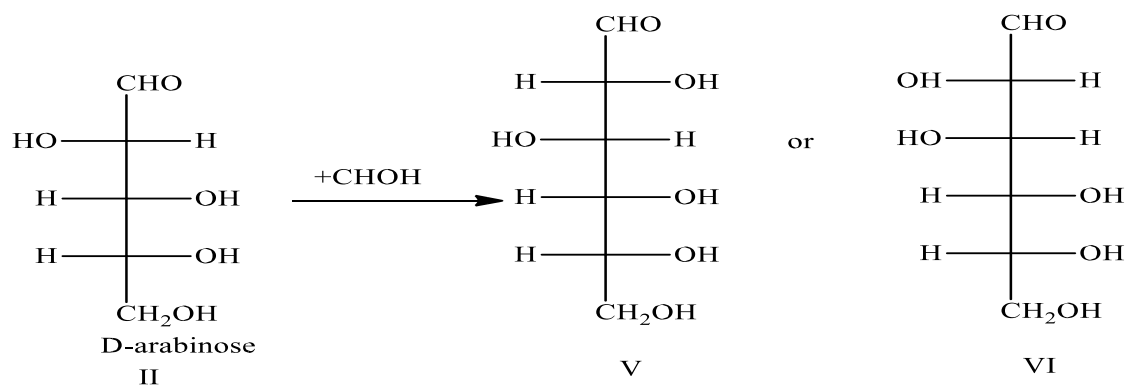
Hence D-glucose has configuration V or VI.

5.D-Glucose and L-Glucose yield the same dicarboxylic acid. This means thattwo sugars differ only in respect of the position of the terminal groups (CHO and CH_2OH). Therefore , the exchange of the terminal groups in D-glucose should be able to give a different aldohexose (Lglucose). Let us now examine configuration formula V and VI (one of which is D-glucose) from the angle.
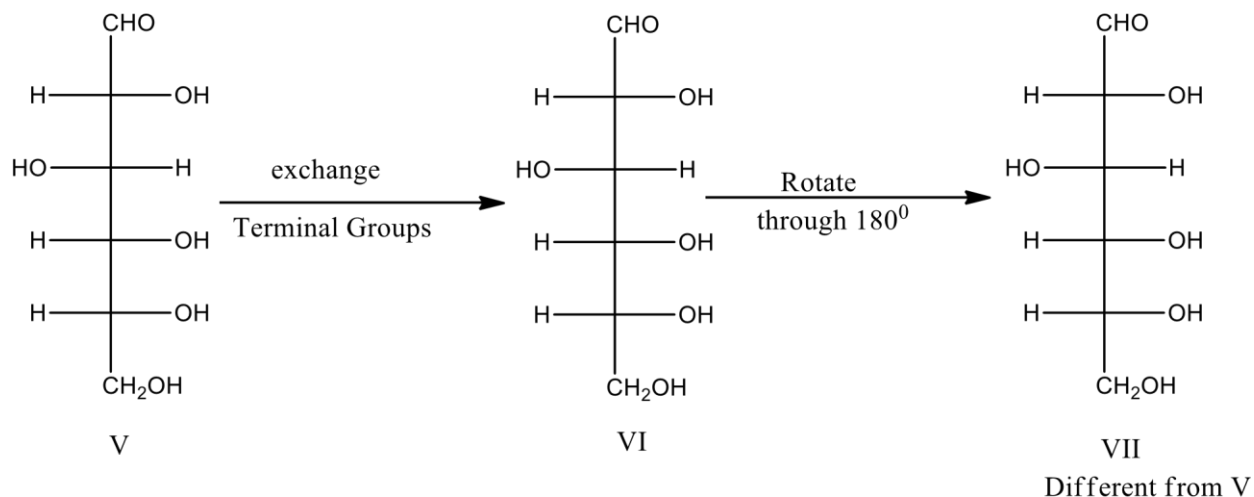
If VII is rotated through 180^0 in the plane of paper, it gives an aldohexose VII, different from V. a similar procedure with formula VI does not give rise to a different sugar.

From the above arguments it is evident that D-glucose has the configuration as shown by the form V.

Cyclic structure of D-Glucose

The open chain structure of glucose explained most of its properties. However, it could not explain the following facts.

1.Despite having an aldehyde group, glucose does not undergo certain characteristic reactions of aldehyde,

a)Glucose does not react with sodium bisulphate to form addition product.

b)Glucose does not react with ammonia.

c)Glucose does not give Schiff's test and 2, 4-DNP test like other aldehydes.

2.Glucose reacts with hydroxylamine to form an oxime but glucose pentaacetate does not react with hydroxylamine. This shows that –CHO group is not present in glucose pentaacetate.

3.D (+)-Glucose exist in two stereoisomeric forms i.e., α- D (+)-Glucose and β- D (+)Glucose.

These two forms are crystalline and have different m.p and optical rotations. When glucose was crystallized from a concentrated solution at 303 K, it gave α-form of glucose having m.p 419 K and $[\alpha]_D = +111^0$. On the other hand, the β-form of glucose is obtained on crystallization of glucose from a hot saturated solution of at a temperature above 371 K. The βform of glucose has m.p 423 K and $[\alpha]_D = +19.2^0$.

4.Mutarotation. When either of two forms of glucose (α- D-glucose and β- D-glucose) are dissolved in water and allowed to stand, these get slowly converted into other form and a equilibrium mixture of both α- D-glucose (36 %) and β- D-glucose (about 64%) is formed. The formation of equilibrium mixture can be explained as:

The α- D-glucose has a specific rotation of $+111^0$, while β- D-glucose has a specific rotation of $+19.2^0$. When α-form is dissolved in water, its specific rotation falls until a constant value of $+52.5^0$ is reached. On the other hand, when β-form is dissolved in water, its specific rotation increases and becomes constant at 52.5^0.

This spontaneous change in specific rotation of an optically active compound with time to an equilibrium value is called mutarotation.(Latin, muto means to change).

Thus, there is an equilibrium mixture of α- and β-forms in the solution

α-D-glucose	⇌	Open chain form	⇌	β-D-glucose
Sp.rotation		Sp.rotation		Sp.rotation
$= +111^0$		$= +52.5^0$		$= +19.2^0$
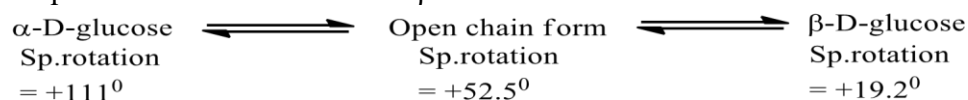
5.Glucose forms isomeric methyl glucosides. When glucose is heated with methanol in the presence of dry HCl, it gives two isomeric monomethyl derivatives known as α-D-glucoside (m.p. = 438 K) and β-D-glucoside (m.p. 380 K).

$$C_6H_{11}O_5 \, OH \quad + \quad H \, OCH_3 \quad \xrightarrow{\text{Dry HCl}} \quad C_6H_{11}O_5OCH_3 \quad + \quad H_2O$$

$$\text{Glucose} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{Methyl glycoside}$$

These two glucosides do not reduce Fehling's solution and also do not react with HCN or NH_2OH indicating that the free –CHO group is not present but it is converted to –COOH group. **Cyclic structure of Glucose**

Anomers:

Glucose forms a hemiacetal between the –CHO group and the -OH group on the C_5 atom. As a result, of cyclisation, C_1 becomes asymmetric (chiral) and the newly formed –OH group may be either on the left or on the right in Fisher projection formulae. These results in the formation of two isomerswhich differ in the orientation of H and –OH groups around C1 atom. These isomers are known as α- D-glucose and β- D-glucose. The isomer having the –OH group on the right is called α- D-glucose and one having the –OH group on the left is called β- D-glucose. Such pairs of optical isomers which differ in the configuration only around C_1 atom are called anomers.

These two forms are not mirror image of each other, hence are not enantiomers. The C1 carbon is known as anomeric carbon or glycosidic carbon.
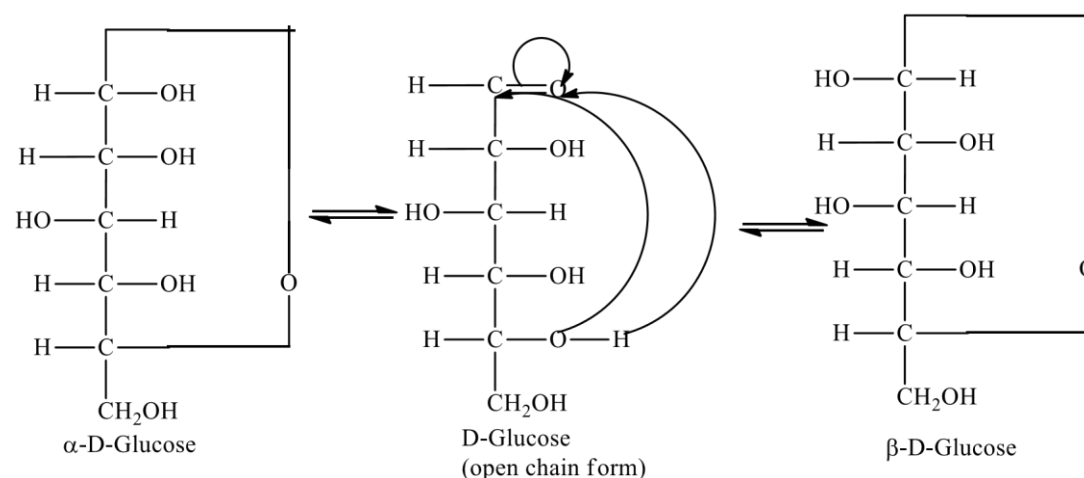
The above representations are called Fisher projection formulae.

Haworth projection formulae or pyranose structures of D-Glucose.

 In Haworth structures drawn with the heterocyclic oxygen in the upper right corner, the α-form has the –OH group on C_1 pointing "down". The β-form has the same group pointing "up". For Dsugars, the free –CH2OH group of an aldohexose is drawn above the plane of ring when ring oxygen is in the upper right. The rest is the simple, the groups on the left of the Fisher projection are up and those on the right are down in the Haworth structure.

α-D-Glucose
or
α-D-Glucopyranose

β—D-Glucose
or
β-D-Glucopyranose
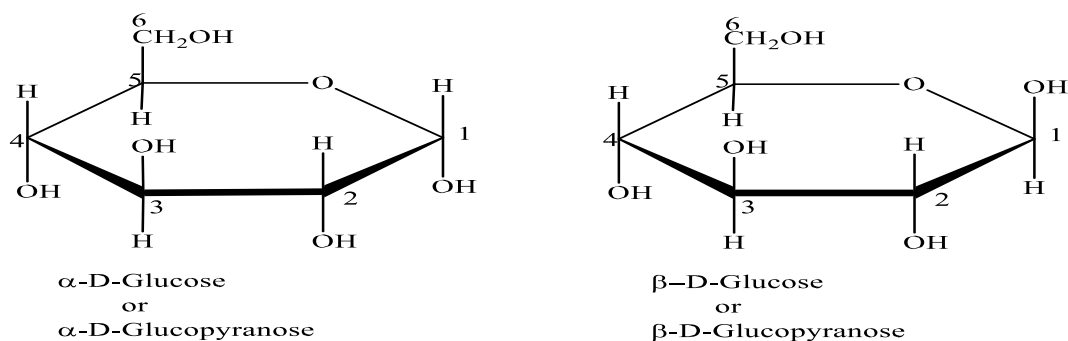
Fructose

Fructose is another commonly known monosaccharide having the same molecular formula as glucose. It is laevorotatory because it roatates plane polarized light towards the left. It is present abundantly in fruits. That is why it is called fruit-sugar also.

Physical properties

     1. It is sweetest of all known sugars.

     2. It is readily soluble in water, sparingly soluble in alcohol and insoluble in ether.

     3. It is white crystalline solid with m.p. 375 K.

     4. Fresh solution of fructose has a specific rotation -133^0. **Chemical properties of fructose**

Chemical properties of fructose can be studied under the following heads:

    (A) Reactions due to ketonic group

    1. **Reaction with HCN**. Fructose reacts with HCN to form cyanohydrins.
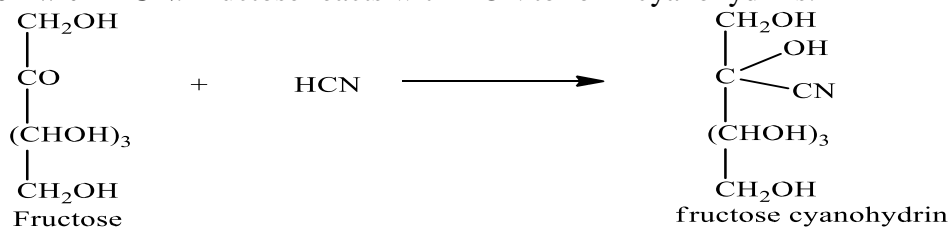
2. **Reaction with hydroxylamine**. Fructose reacts with hydroxylamine to form an oxime.

$$
\begin{array}{c}
CH_2OH \\
| \\
CO \\
| \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{Fructose}
\end{array}
\quad + \quad H_2\ NOH \quad \longrightarrow \quad
\begin{array}{c}
CH_2OH \\
| \\
C=\!=\!NOH \\
| \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{fructose oxime}
\end{array}
$$
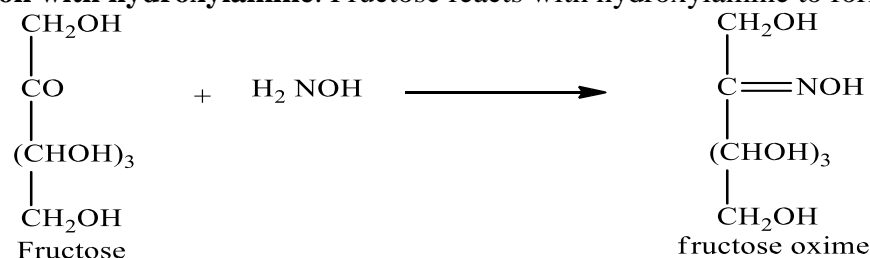
3. **Reduction**. Fructose gives a mixture of sorbitol and mannitol on reduction with Na-Hg and water or catalytic hydrogenation.

$$
\begin{array}{c}
CH_2OH \\
| \\
CO \\
| \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{Fructose}
\end{array}
\ + \ 2[H] \ \longrightarrow \
\begin{array}{c}
CH_2OH \\
| \\
HO-\!\!\underset{|}{C}-\!\!H \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{Mannitol}
\end{array}
\ + \
\begin{array}{c}
CH_2OH \\
| \\
H-\!\!\underset{|}{C}-\!\!OH \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{Sorbitol}
\end{array}
$$
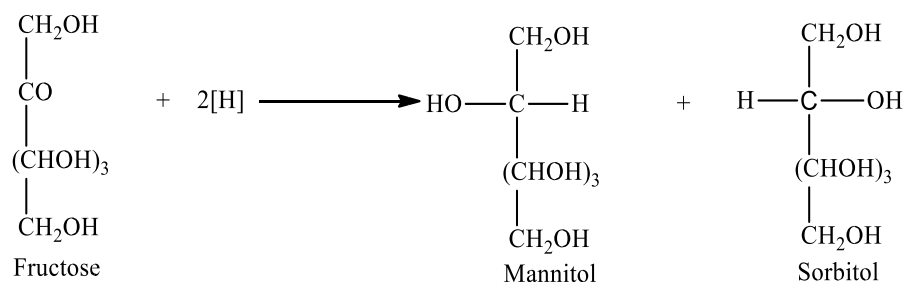
4. **Oxidation.** (i) there is no action of mild oxidizing agent like bromine water on fructose. (ii) Strong oxidizing agents like nitric acid oxidize fructose into a mixture of trihydroxy glutaric, glycolic and tartaric acids.

$$
\begin{array}{c}
CH_2OH \\
| \\
CO \\
| \\
(CHOH)_3 \\
| \\
CH_2OH \\
\text{Fructose}
\end{array}
\ \xrightarrow{[O]} \
\begin{array}{c}
COOH \\
| \\
(CHOH)_3 \\
| \\
COOH \\
\text{Trihydroxy} \\
\text{glutaric acid}
\end{array}
\ + \
\begin{array}{c}
CH_2OH \\
| \\
COOH \\
\text{Glycollic acid}
\end{array}
\ + \
\begin{array}{c}
COOH \\
| \\
(CHOH)_2 \\
| \\
COOH \\
\text{tartaric acid}
\end{array}
$$
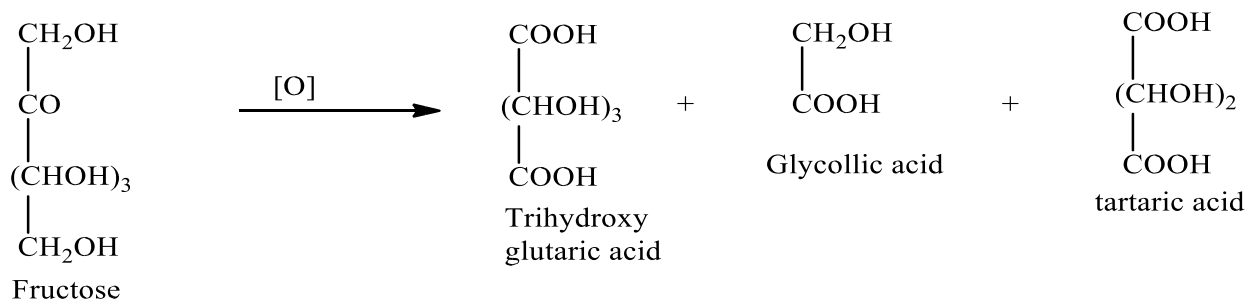
iii) Unlike other ketones, it reduces Tollen's reagent and Fehling solution. This is due to the presence of traces of glucose in alkaline medium.

[B] reactions of the alcoholic group

1. Acetylation . with acetic anhydride or acetyl chloride, fructose forms penta-acetate.

CH$_2$OH

CO　　　+　　　5 (CH$_3$CO)$_2$O ⟶
　　　　　　　　　　　Acetic anhydride

(CHOH)$_3$

CH$_2$OH
Fructose

CH$_2$OCOCH$_3$

CO　　　　　　+　　　5 CH$_3$COOH

CHOCOCH$_3$

CH$_2$OCOCH$_3$
Fructose penta-acetate
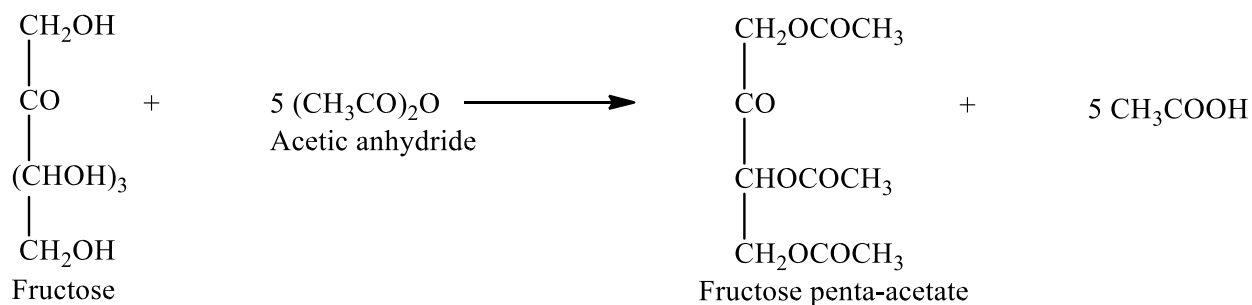
2. Reaction with methyl alcohol (glucoside formation). Fructose reacts with methyl alcohol in the presence of dry HCl gas forming methyl fructoside.

$$C_6H_{11}O_5\,OH \quad + \quad H\,OCH_3 \xrightarrow{\text{Dry HCl}} C_6H_{11}O_5OCH_3 \quad + \quad H_2O$$
　　　Fructose　　　　　　　　　　　　　　　Methyl fructoside

3. Reaction with metallic hydroxides (fructosate formation)

$$C_6H_{11}O_5\,OH \quad + \quad H\,OCaOH \longrightarrow C_6H_{11}O_5OCaOH \quad + \quad H_2O$$
　　　Fructose　　　　calcium hydroxide　　　　calcium-fructosate

Structure of Fructose

1. elemental analysis and molecular weight determination of fructose show that it ahs the molecular formula C$_6$H$_{12}$O$_6$.

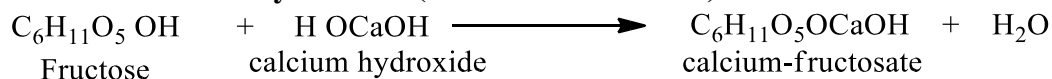2. fructose on reduction gives sorbitol which on reduction with HI and red P gives a mixture of n-hexane and 2-Iodohexane. This reaction indicates that six carbon atoms in fructose are in a straight chain.

3. Fructose reacts with hydroxylamine, HCN and phenylhydrazine. It shows the presence of _CHO or C=O group in the molecule of fructose.

4. On treatment with bromine water , no reaction takes palce. This rules out the possibility of presence of –CHO group.

5. on oxidation with nitric acid, it gives glycollic acid and tartaric acids which contain smaller number of carbon atoms than fructose. This shows that a ketonic group is present at position 2. It is at this point that the molecule is broken.

Cyclic structure of D-Fructose

Fructose shows the property of mutarotation. This means that it exists in two forms α-fructose and β-fructose which are cyclic in structure and change into each other via the open chain structure. The cyclic and pyranose structures of α-D-fructose and β-D-fructose are represented below:
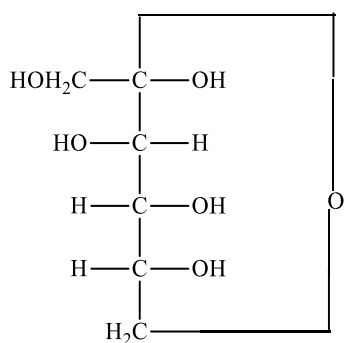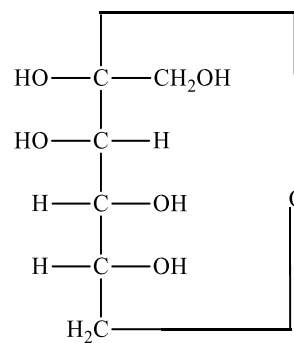
α-D-fructose

β-D-fructose

Haworth Pyranose structure
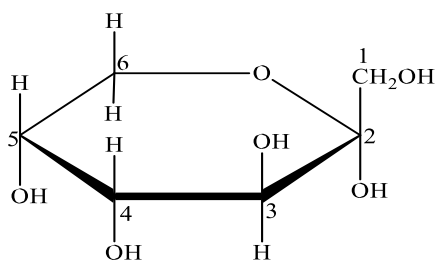
α-D-fructopyranose
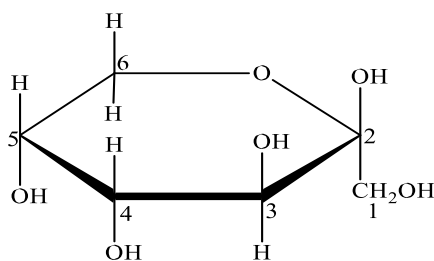
β-D-fructopyranose

However, when fructose is linked to glucose in a sucrose molecule, it has the furanose structure as shown below:
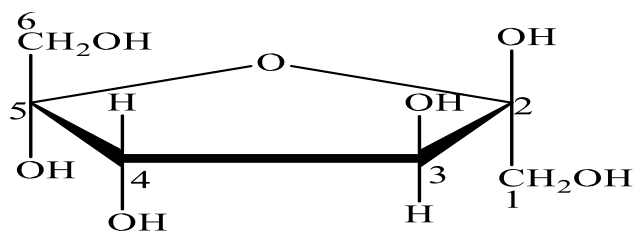
β-D-fructofuranose

8.5 MECHANISM OF OSAZONE FORMATION

Glucose and fructose react with one equivalent of phenylhydrazine, forming phenylhydrazone. In contrast, α-hydroxy carbonyl compounds react with three equivalents of phenylhydrazine to form bis-phenylhydrazones, commonly called osazones.
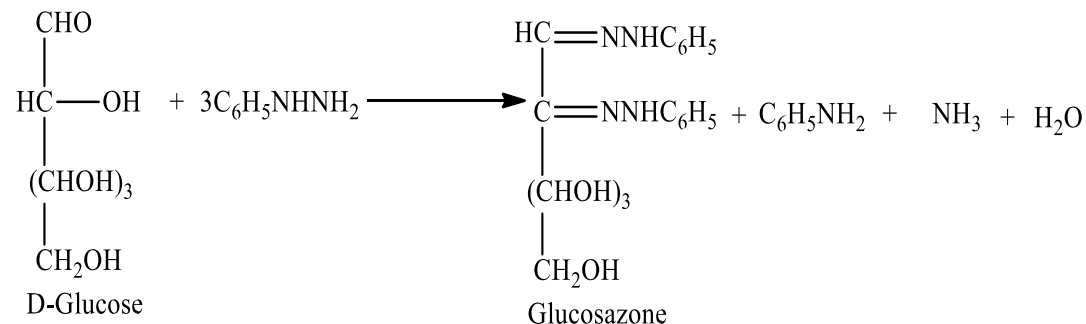
Phenylosazones crystallize readily and are useful derivatives for identifying sugars.

Mechanism: the first equivalent of phenylhydrazine forms phenylhydrazone with the aldehyde or ketone group as expected. Phenylhydrazone the ungergoes the rearrangement , known as Amadori rearrangement, to give α-iminoketone (IV) with the loss of aniline.
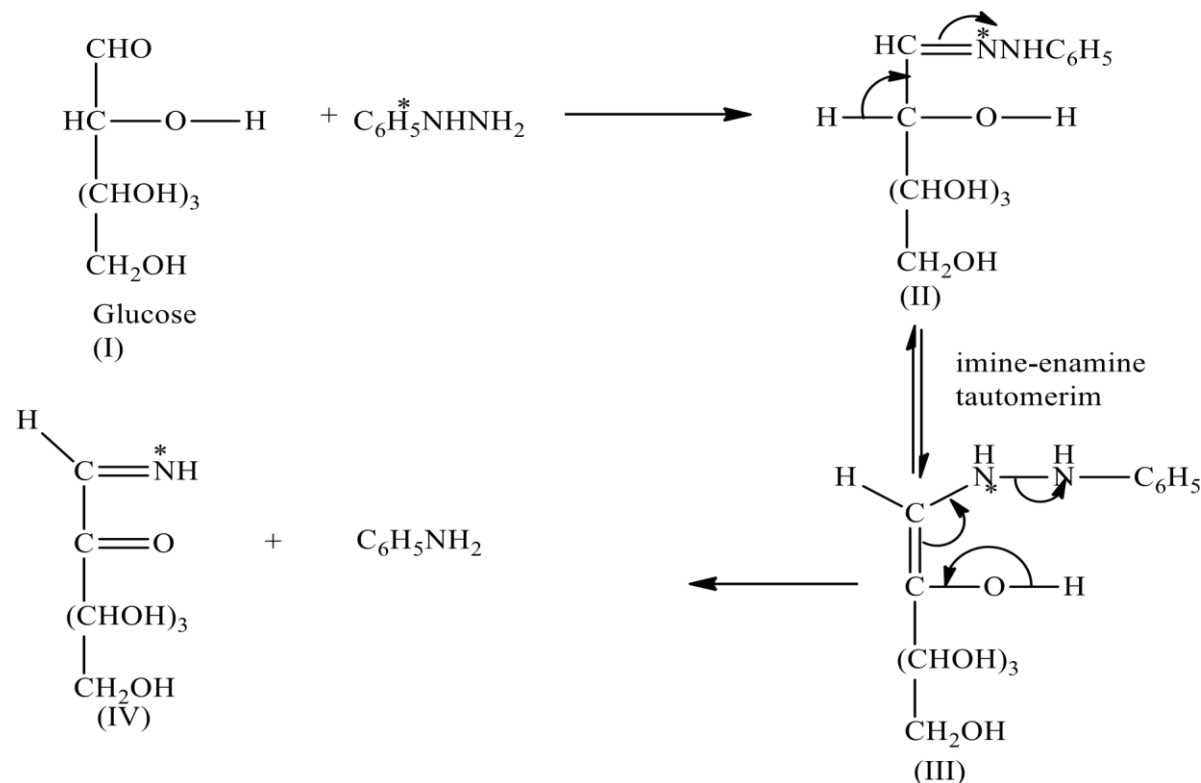
Subsequent attack of two moles of phenylhydrazine on the iminoketone (scheme-a) or on the ketoaldehyde (scheme-b) results in the formation of osazone accompanied by the elimination of ammonia.

The given mechanism is supported by the observation that when phenyl hydrazone prepared by the reaction of glucose with N^{15} (N^*) labeled phenylhydrazine is treated with ordinary phenylhydrazine, unlabelled osazone is obtained accompanied by the expulsion of labelled ammonia.

8.6 INTERCONVERSION OF GLUCOSE AND FRUCTOSE

(a)   Conversion of an aldose into an isomeric ketose. The procedure used for this purpose may be illustrated by taking into account the conversion of glucose into fructose.


```
CHO                          HC=NNHC6H5                    CHO                     CH2OH
|                            |                             |                       |
CHOH    3C6H5NHNH2           C=NNHC6H5     H2O, H+          C=O    Reduction        C=O
|       ------------->       |             ------------>   |      ----------->     |
(CHOH)3                      (CHOH)3                        (CHOH)3   Zn/CH3COOH    (CHOH)3
|                            |                             |                       |
CH2OH                        CH2OH                         CH2OH                   CH2OH
Glucose                      Glucosazone                   Glucosone               Fructose
```
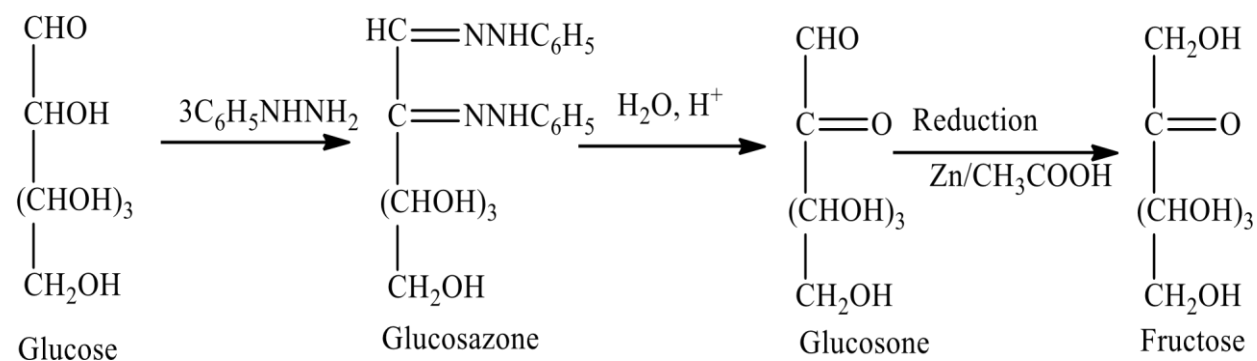
(b)   Conversion of ketose into an isomeric aldose. The procedure used here may be illustrated by taking into account the conversion of fructose into a mixture of epimeric aldoses, viz., glucose and mannose.

CH$_2$OH — C=O — CHOH — CHOH — CHOH — CH$_2$OH
Fructose

Na-Hg,H$_2$O
Reduction

CH$_2$OH — CHOH — CHOH — CHOH — CHOH — CH$_2$OH
Mixture of diasteromeric sorbitol and mannitol

HNO$_3$

COOH — CHOH — CHOH — CHOH — CHOH — CH$_2$OH
Mixture of diasteromeric gluconic and mannonic acid

Heat
-H$_2$O

C=O — CHOH — CHOH — HC — CHOH — CH$_2$OH — O
Mixture of diasteromeric g-lactones

Na-Hg,CO$_2$

CHO — CHOH — CHOH — CHOH — CHOH — CH$_2$OH
Mixure of epimeric glucose and mannose

8.7 CHAIN LENGTHENING AND CHAIN SHORTENING OF ALDOSE

(a) Lengthening of aldoses: Killiani-Fisher synthesis

The aldose chains may be lengthened by one carbon atom by a procedure known as **KillianiFisher synthesis.** Thus an aldose may be converted to the next higher member by the following steps: (1) Formation of cyanohydrins; (2) hydrolysis of –CN to –COOH, giving aldonic acid; (3) conversion of aldonic acid to lactone by heating; (4) reduction of lactone with sodium borohydride, NaBH$_4$, to get higher aldose. For illustration, the overall change is the creation of an asymmetric centre at C-2 where a new CHOH has been added. Therefore their result two aldoses with one carbon more and differing only in configuration at C-2.
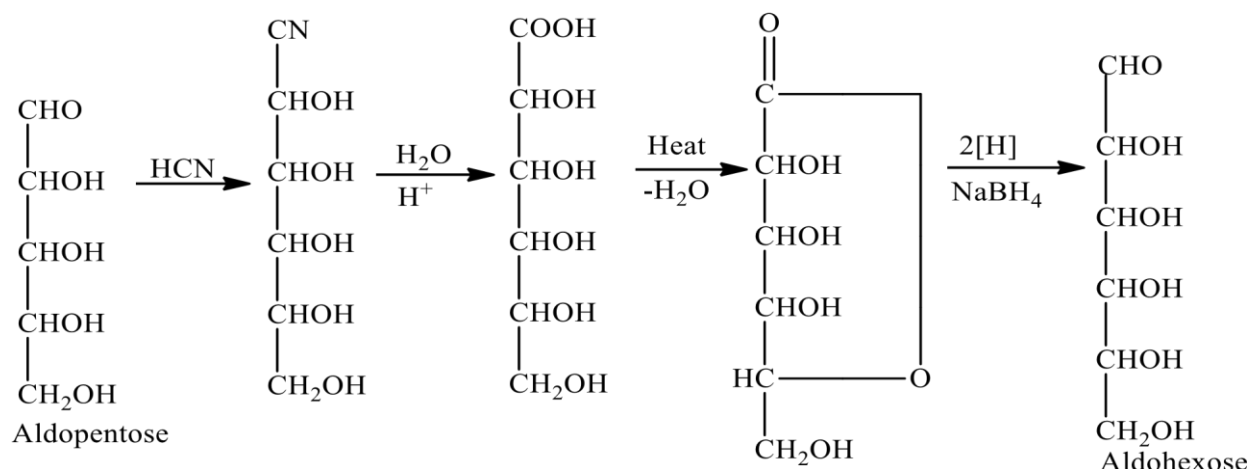
Taking a specific example, D-arabinose by killiani-Fisher synthesis gives two isomeric aldohexoses, D-glucose and D-mannose which differ only in the configuration at C-2
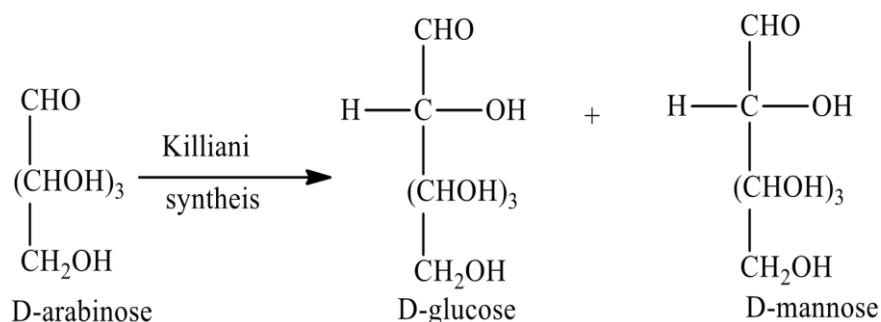
Such sugars which differ in configuration only at one asymmetric centre (C-2) are called Epimers.

(b) Shortening of aldoses

(1) Ruff degradation. An aldose may be converted into a lower aldose having one carbon atom less, i.e., the carbon chain may be shortened by Ruff degradation.

The method involves the oxidation of starting aldose into the corresponding aldonic acid. The acid is converted into its calcium salt which is treated with Fenton's reagent (H2O2 in presence of Fe^{+3} ion) to get the lower aldose. This method is illustrated as follows:

Glucose
An alohexose

Aldonic acid

Calcium salt

Arabinose
Aldopentose
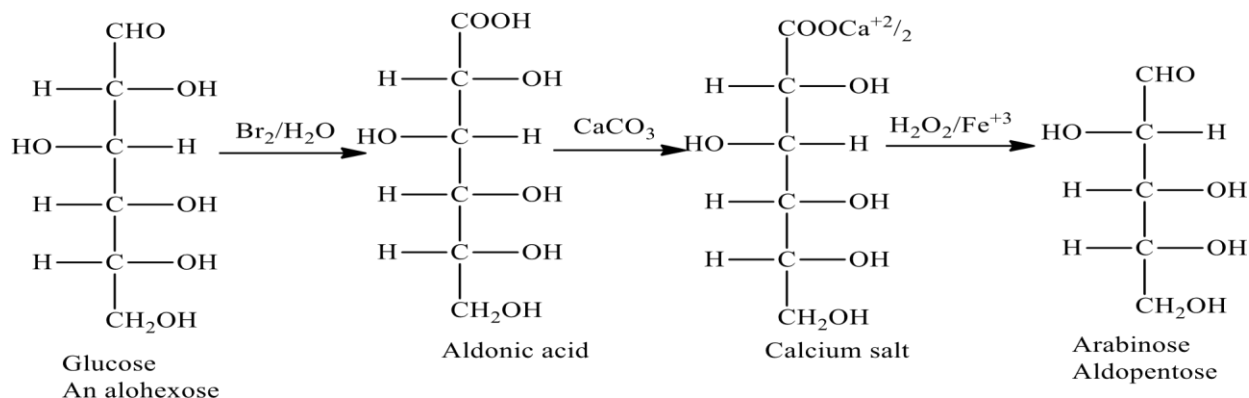
(2) Wohl's degradation for chain shortening in aldoses

In this degradation, the aldose is converted into its oxime by treatment with hydrgradazoxylamine. The oxime is treated with acetic anhydride when the oxime is dehydrated to nitrile. The nitrile is then treated with sodium methoxide. The cyanohydrin obtained undergoes degradation to a lower aldose. The reaction are written as under.

Aldohexose

Oxime

Aldopentose
+ HCN

$$H-C=\overset{*}{N}H$$
$$C=O$$
$$(CHOH)_3$$
$$CH_2OH$$

$\xrightarrow[-H_2O]{C_6H_5NHNH_2}$

$$H_2N-\overset{H}{N}-C_6H_5$$

$$H-C=\overset{*}{N}H$$
$$C=NNHC_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$

HOH/H^+

$$H-C=O$$
$$C=O$$
$$(CHOH)_3$$
$$CH_2OH$$

$+ \ \overset{*}{N}H_3$

$$H-\overset{*NH \ H}{\underset{C=NNHC_6H_5}{C}}-\overset{H}{\underset{H}{N^\oplus}}-\overset{H}{N}-C_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$

$2C_6H_5NHNH_2$

$$HC=NNHC_6H_5$$
$$C=NNHC_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$
Scheme-b

$$H-\overset{*NH_2}{\underset{C=NNHC_6H_5}{C}}-\overset{H}{N}-\overset{H}{N}-C_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$

$\xrightarrow{H^+}$

$$H-\overset{\overset{\oplus}{*NH_3} \ H}{\underset{C=NNHC_6H_5}{C}}-N-\overset{H}{N}-C_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$

$\overset{*}{N}H_3 \quad +$

$$HC=NNHC_6H_5$$
$$C=NNHC_6H_5$$
$$(CHOH)_3$$
$$CH_2OH$$
Scheme-a
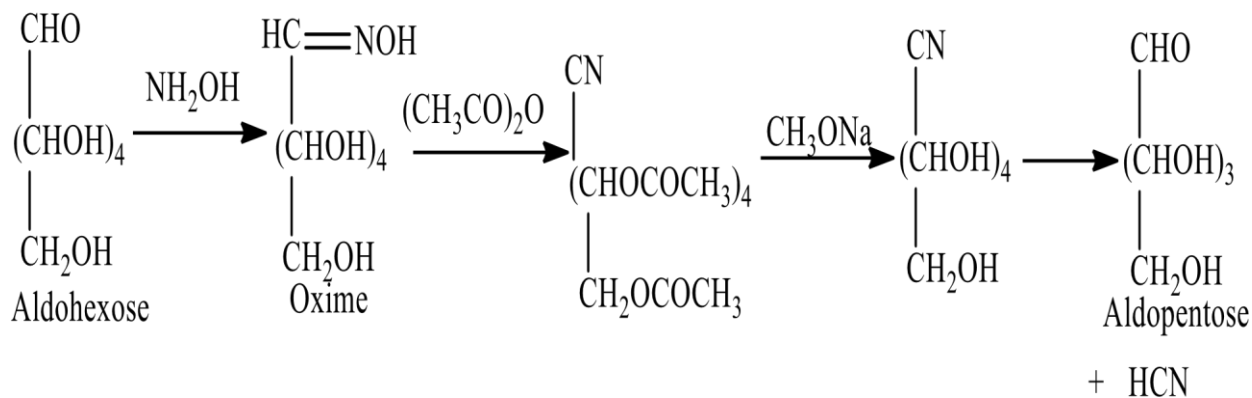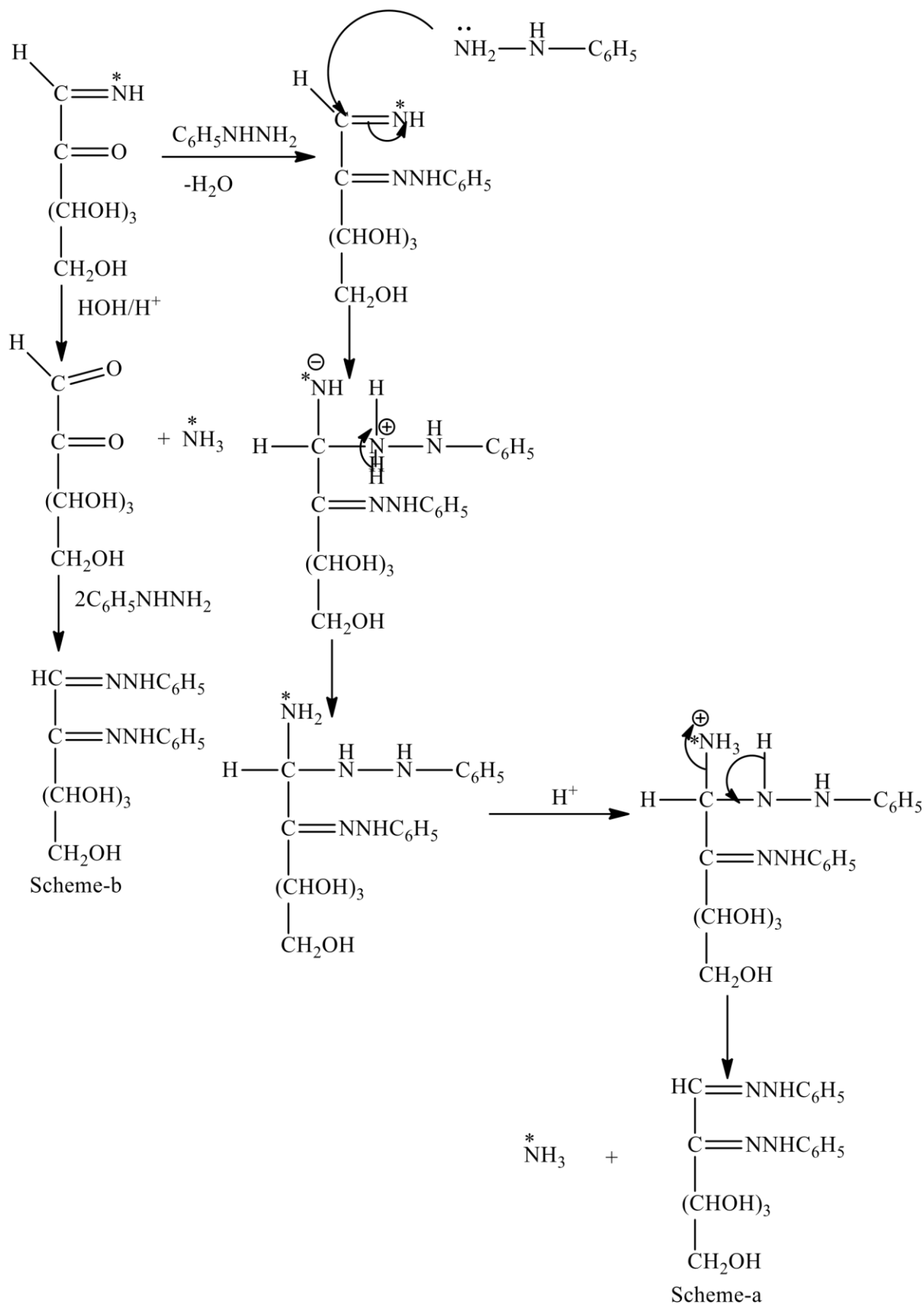
The osazone so formed does not undergo further amadori rearrangement. This is the reaction with phenylhydrazine stops at this stage; thus further reaction at C-3 –OH group dost not occur. This is because the osazone so formed, does not react further via intramolecular Amadori rearrangement involving C-3 –OH group because of the intramolecular hydrogen bomding as shown below:
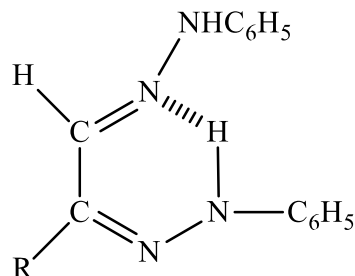
8.8. SUMMARY

- Carbohydrates are poly hydroxy aldehydes and ketones.
- Monosaccharides containing an aldehyde group are called aldoses and those with a keto group are called ketoses.
- Carbohydrates can also be classified as disaccharides, oligosaccharides, and polysaccharides consist of monosaccharides linked by glycosidic bonds.
- The most abundant monosaccharide in nature is 6- carbon sugar, D-glucose. It exists as α and β anomers with different optical rotations.
- If two monosaccharides isomers differ in configuration around one specific carbon atom [With exception of carbonyl carbon] they are called epimers of each other.

8.9 TERMINAL QUESTIONS

1. Define and classify carbohydrates with suitable examples.

2. Explain kiliani-Fisher synthesis and Ruff's degradation.

3. Explain the limitations of open chain D-glucose structure.

4. Establish the structure of glucose and fructose.

5. Write the product obtained when D-glucose reacts with a) H_2N—OH   b) HCN.

6.How you convert fructose to: a) Sorbitol   b) Tartaric acid

7. Describe the Haworth projection of D- glucose?

8.Describe the mechanism of osazone formation of glucose?

9.Write a short notes on anomeric carbon of glucose?

10.Explain mutarotation of glucose ?

8.10 REFERENCES AND FURTHER STUDIES

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2.Chemistry for degree students, R.L.madan, S.Chand & Compant Ltd.

3.Organic chemistry, Vol.III, Jagdamba singh and L.D.S Yadav, Prgati Prakashan.

4.Modern chemistry, S.P.Jauhar, Modern Publishers.

5.Organic chemistry, Francis A.Carey, Tata McGraw-Hill Company Ltd.

UNIT-9 NUCLEIC ACIDS

CONTENTS

9.1 INTRODUCTION

Nucleic acid, naturally occurring chemical compound that is capable of being broken down to yield phosphoric acid, sugars, and a mixture of organic bases (purines and pyrimidines). Nucleic acids are the main information-carrying molecules of the cell, and, by directing the process of protein synthesis, they determine the inherited characteristics of every living thing. They are composed of nucleotides, which are the monomers made of three components: a 5-carbon sugar, a phosphate group and a nitrogenous base. The two main classes of nucleic acids are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA is the master blueprint for life and constitutes the genetic material in all free-living organisms and most viruses. RNA is the
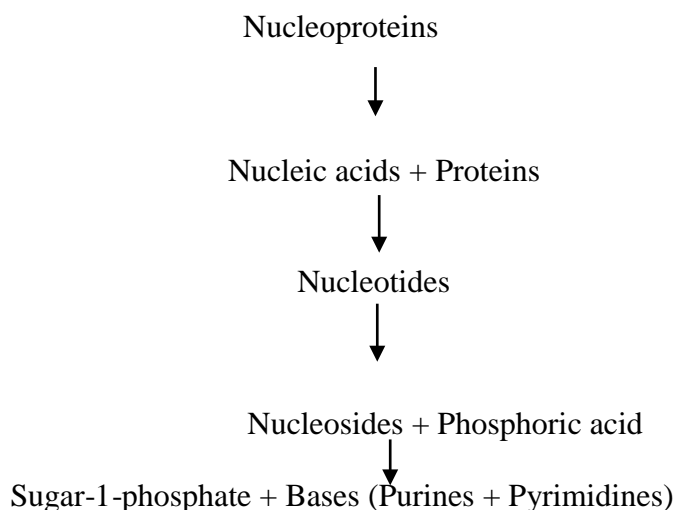
genetic material of certain viruses, but it is also found in all living cells, where it plays an important role in certain processes such as the making of proteins.

RNA is found in all subdivisions of the cell, nucleus and cytoplasm, in particles and supernatant fluid. However, ribosomes are the richest in RNA followed by mitochondria. Because of their abundance in yeast, RNA is also called yeast nucleic acids or plasmonucleic acids; similarly DNA is called thymus nucleic acids or chromonucleic acids, because of their abundance in chromosomes (thymus).

Ribonucleic acid (RNA) is a molecule that is present in the majority of living organisms and viruses. It is made up of nucleotides, which are ribose sugars attached to nitrogenous bases and phosphate groups. The nitrogenous bases include adenine, guanine, uracil, and cytosine. RNA mostly exists in the single-stranded form, but there are special RNA viruses that are doublestranded. The RNA molecule can have a variety of lengths and structures. An RNA virus uses RNA instead of DNA as its genetic material and can cause many human diseases.

The DNAs are macromolecules with molecular weight ranging from 6 to 16 million, although in some cases very high molecular weight (120 million) has been reported. On the other hand, RNAs are generally much smaller with the molecular weight range of 20,000 to 40,000.

The following chart shows the nature of the products obtained by the stepwise hydrolysis of nucleic acids.

Nucleoproteins

↓

Nucleic acids + Proteins

↓

Nucleotides

↓

Nucleosides + Phosphoric acid

↓

Sugar-1-phosphate + Bases (Purines + Pyrimidines)

9.2 OBJECTIVES

Nucleic acids are biopolymers, macromolecules, essential to all known forms of life.They are composed of nucleotides, which are the monomer components: a 5-carbon sugar, a phosphate group and a nitrogenous base.In all living cells it is major component of the nucleus and also a component of cytoplasmic structures such as the ribosomes. They are generally associated with protein to from nucleoproteins.The two main classes of nucleic acids are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). If the sugar is ribose, the polymer is RNA; if the sugar is deoxyribose, a version of ribose, the polymer is DNA.

The objective of this unit is the study of structure of Nucleic acid with their chemical constitution. In this unit we also studied structure of DNA and RNA in detail and explain the difference between DNA and RNA.

9.3 NITROGENOUS BASES

`Nucleotides are comprised of single-ringed or two-ringed nitrogenous bases. One-ringed nitrogenous base is called the pyrimidine and the two-ringed nitrogenous base is called the purine. Basic structure of purine or pyrimidine is shown in (Fig. 9.1). Pyrimidines are sixmembered aromatic rings containing two N-atoms. Purines' structure is a combination of pyrimidine ring and a five membered imidazole ring.

(a) Pyrimidine   (b) Purine
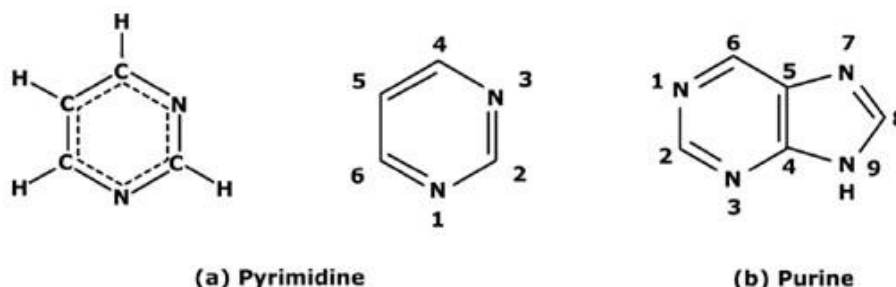
Fig. 9.1 Basic structure of purine or pyrimidine

- The Pyrimidines

    The pyrimidine bases are of three kinds: Cytosine (C), Uracil (U) and Thymine (T). Cytosine and Thymine are found in DNA while Cytosine and Uracil are found in RNA.

    Their structures are shown in Fig. 9.2

- The Purines

  Two kinds of purine bases exist in nucleotides: Adenine (A) and Guanine (G). Both are found in DNA as well as RNA.

Adenine   Guanine   Cytosine   Thymine   Uracil

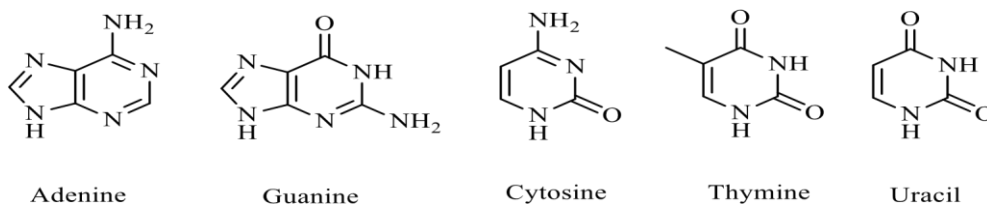**Fig. 9.2 Chemical structure of purine and pyrimidine bases**

B. Pentoses

Pentoses are the five-carbon sugars present in polynucleotides. RNA contains D-Ribose while DNA contains 2'-deoxy-D-ribose (Fig. 9.3). The hydroxyl group at the 2'-position is not present in DNA, rather a H atom is present there. We shall see in later sections how this minor difference has far-reaching consequences on their properties.

(a)   (b)
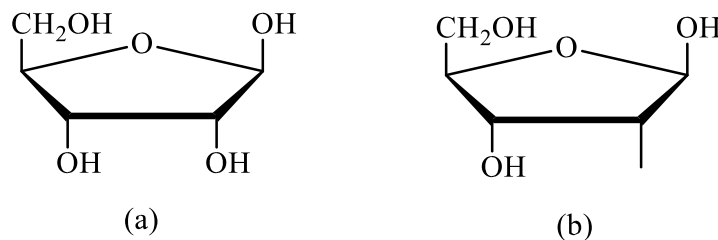
Fig.9.3The structure of pentoses: (a) D-Ribose and (b) 2'-deoxy D-Ribose

Out of the five important bases (adenine, guanine, uracil, thymine and cytosine(, adenine, guanine and cytosine occur in both thy types of the acids, i.e. R.N.A. as well as in D.N.A. whereas uracil is present only in R.N.A. and thymine only in D.N.A. for convenience, the purine and pyrimidne bases are usually abbreviated as the first letter of the name. Thus adenine is designated as A, guanine as G, uracil as U, thymine as T, and cytosine as C.

As already mentioned, nucleosides are the condensation products of the bases with sugar; so we can now name all the nuclecosides as below.

Base   +Sugar   Nucleoside

1. Adenine   +   Ribose or 2- $\longrightarrow$ deoxyribose Adenosine

2. Guanine   +   Ribose or 2- $\longrightarrow$ deoxyribose Guanosine

3. Cytosine   +   Ribose or 2- $\longrightarrow$ deoxyribose Cytidine

4. Uracil   +   Ribose Uridine $\longrightarrow$

5. Thymine   +   2-deoxyribose $\longrightarrow$ Thymidine

In purine nucleosides, the sugar moiety is $\longrightarrow$ attached via its C1 to the N9 of the base while in pyrimidine nucleosides the C1 of sugar is attached to the N3 of the base. Further the sugar occurs as B-furanoside; i.e. the size of the sugar ring is furanose and its configuration is B.
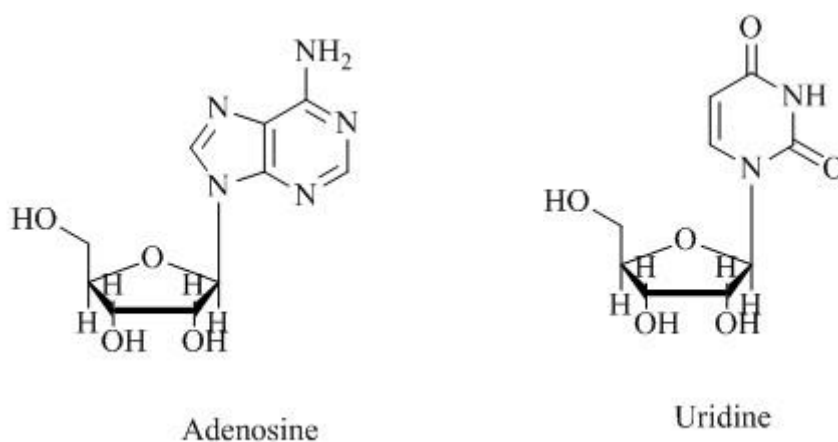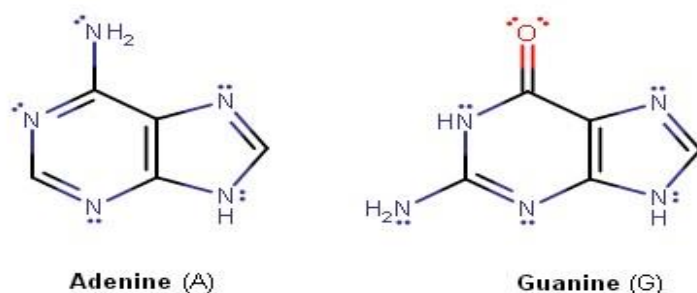

Adenosine

Uridine

Fig.9.4Structure of nucleosides

9.4 PURINES

Purines are heterocyclic systems consisting of a pyrimidine and an imidazole condensed at the 45 bond. The term "purine" (from "purum" and "uricum") was introduced in 1898 by Emil Fischer.Both DNA and RNA contain two major purine substituents - adenine and guanine:

Adenine (A)

Guanine (G)

Figure 9.5

Minor purines differing from adenine or guanine by the presence of alkyl (more commonly, methyl), acyl and other groups have also been isolated from some nucleic acids. The structural formulas of the minor purines present in nucleosides are presented in Figure 9.5

9.5 PYRIMIDINES:

Pyrimidines, also known as meta-diazines, are structurally akin to benzene and pyridine. Pinner (1885), who had noticed this analogy, coined a new term from the words "pyridine" and "amidine", emphasizing thereby that apart from aromaticity pyrimidines also exhibit properties inherent in amidines. Given below are the formulas of the pyrimidines whose compounds are nucleic acid constituents, such as uracil, thymine, and cytosine . Figure 9.6

pyrimidine (m-diazine)   uracil   thymine   cytosine
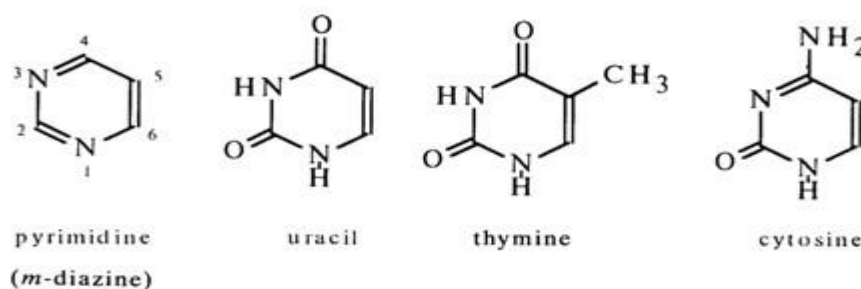
Figure 9.6

Thymines and cytosines are usually present in DNA, while those of uracil and cytosine are found in RNA. The DNAs of some phages are exceptional in that they contain 5-hydroxymethylcytosine or its glycosides associated with the 5-hydroxymethyl group instead of cytosine (even-numbered T phages) and 5-hydroxymethyluracil (phage SP8) or uracil (phage PBS1) instead of thymine. Figure 9.7
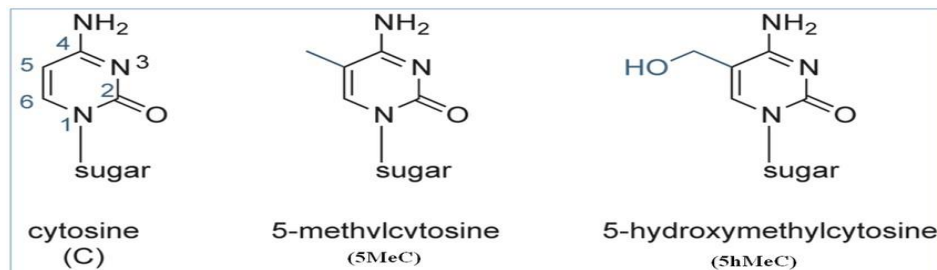
Figure 9.7

Uracil, thymine, and cytosine are ubiquitously present in nucleic acids in the form of the corresponding nucleosides in significant amounts .These compounds are usually referred to as the major pyrimidine bases of nucleic acids. In certain DNA and RNA species, some uracil and cytosine derivatives (usually N-alkyl ones) have been found. Such pyrimidine bases are referred to as rare or minor. Minor pyrimidine bases do not occur in all nucleic acids and the content of each base is usually below one or two per cent.

9.6 NUCLEOSIDES:

A nucleoside is a purine or a pyrimidine nucleobase with a pentose sugar component, which is either ribose or deoxyribose. Therefore:

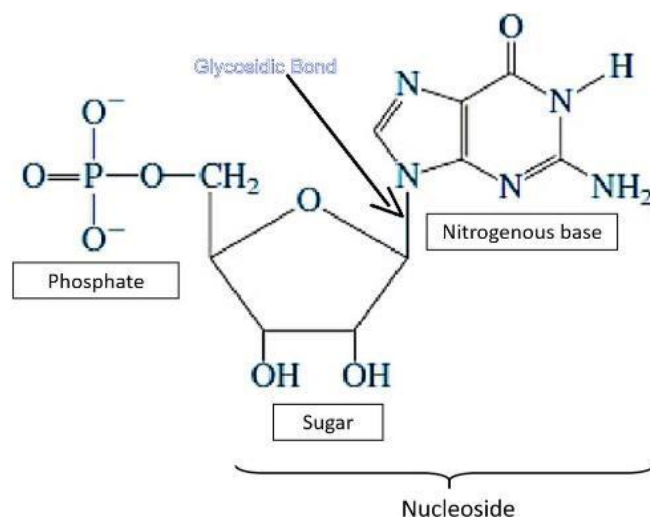**nucleoside = nucleobase + ribose or deoxyribose**

In a nucleoside, the anomeric carbon is linked through a glycosidic bond to the N9 of a purine or the N1 of a pyrimidine by a glycosidic bond..

Types of Nucleoside:

Depending on the pentose sugar component, a nucleoside may be a ribonucleoside or a deoxyribonucleoside.A ribonucleoside is a nucleoside with a ribose sugar component. Depending on the nucleobase component, the ribonucleoside may be:

Adenosine (nucleobase: adenine)

Guanosine (nucleobase: guanine)

Cytidine (nucleobase: cytidine)

Uridine (or 5-methyluridine) (nucleobase: uracil)

☐ A *deoxyribonucleoside* is a nucleoside with *deoxyribose* sugar. Depending on the nucleobase component, a deoxyribonucleoside may be:

Deoxyadenosine (nucleobase: adenine)

Deoxyguanosine (nucleobase: guanine)

Deoxycytidine (nucleobase: cytidine)

Thymidine (or deoxyuridine) (nucleobase: uracil)

Also, depending on the nucleobase component, the nucleosides may be grouped into either the"double-ringed" purine *or the "*single-ringed*"* pyrimidine.

9.7 NUCLEOTIDES

Nucleotides are phosphoric esters of nucleosides. These are obtained by the controlled hydrolysis of nucleic acids. On hydrolysis in neutral solution they give nucleosides and phosphoric acid. Thus the composition of the various important nucleotides can be represented as below.

Nucleotides   Nucleosides + H_3PO_4

1. Adenylic Acid $\longrightarrow$ Adenosine + H_3PO_4

   (Adenosine monophosphate, AMP)

2. Guanylic acid Guanosine+ H_3PO_4 $\longrightarrow$

   (Guanosine monophosphate, GMP)

3. Cytidylic acid Cytidine+ H_3PO_4 $\longrightarrow$

   (Cytidine monophosphate CMP)

4. Uridylic acid $\longrightarrow$ Uridine+ H_3PO_4

   (Uridine monophosphate UMP)

5. Thymidylic acid $\longrightarrow$ Thymidine+ H_3PO_4
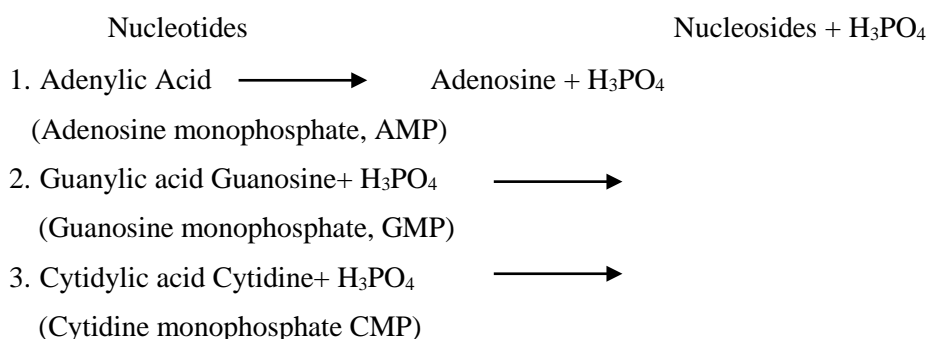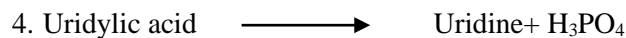
   (Thymidine monophosphate UMP)

When nucleotides are carefully hydrolysed, ribose monophosphate may be isolated from the products which proves that the phosphate group is attached to the ribose and not to the purine or pyrimidine base which are found to be free in the product. Thus the nucleotides may be represented as below.

Base-Pentose (Ribose or Deoxyribose) - Phosphoric acid.

It is clear from the structures of nucleosides that the point of attachment may be 2',3' or 5' in case of ribose[1] molecule and only 3' or 5' in case of deoxyribose molecule depending upon the nature of the source of nucleotides.
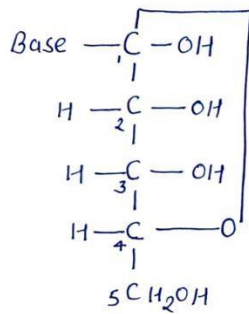
Ribose nucleoside
2', 3' or 5' Points of
linkage for phosphoric
acid
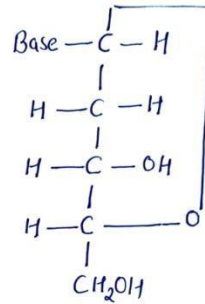
Deoxyribose nucleoside
3' or 5' point of linkage
for H_3PO_4

It is also
experimentally
above
positions may
linkage. The
linkage) of the
indicated by a
adenosine-3'
adenosine-5'

Adenosine 5'-monophosphate

Adenosine 2'-monophosphate

Adenosine 3'-monophosphate

Adenosine 2',3'-cyclic
monophosphate
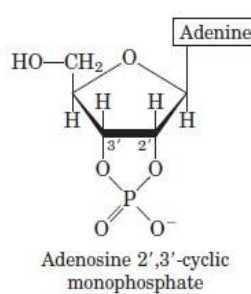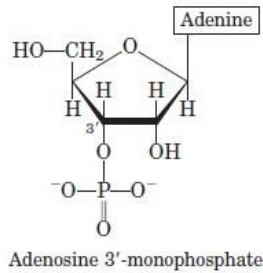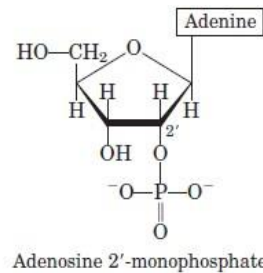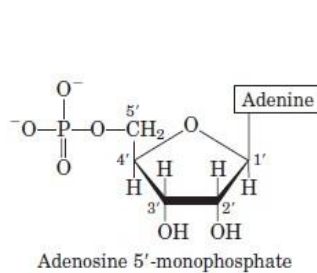
shown
that either of the
mentioned
be point of
position (point of
phosphate is
numeral, e.g.
phosphate,
phosphate, etc.

In addition to the above mentioned nucleotides, cyclic nucleoside phosphates (cyclic nucleotides) have been identified from the enzymatic hydrolysates of RNA. The cyclic nucleoside phosphates may be 2',3'-or 3',5'
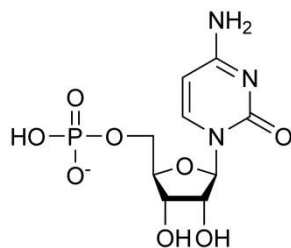
Cytidine-3′phosphate (in RNA)
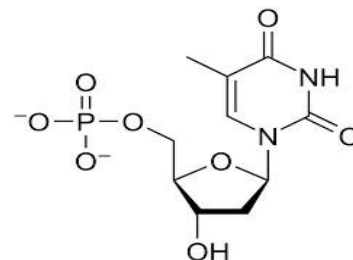
Deoxythymidine -5′phosphate (in DNA)

Cytidylic acid   Thymidylic acid

9.8 STRUCTURE OF RNA AND DNA MOLECULES

RNA is a single-stranded nucleic acid polymer of the four nucleotides A, C, G, and U joined through a backbone of alternating phosphate and ribose sugar residues (Fig. 9.8). It is the first intermediate in converting the information from DNA into proteins essential for the working of a cell. Some RNAs also serve direct roles in cellular metabolism. RNA is made by copying the base sequence of a section of double-stranded DNA, called a gene, into a piece of singlestranded nucleic acid.
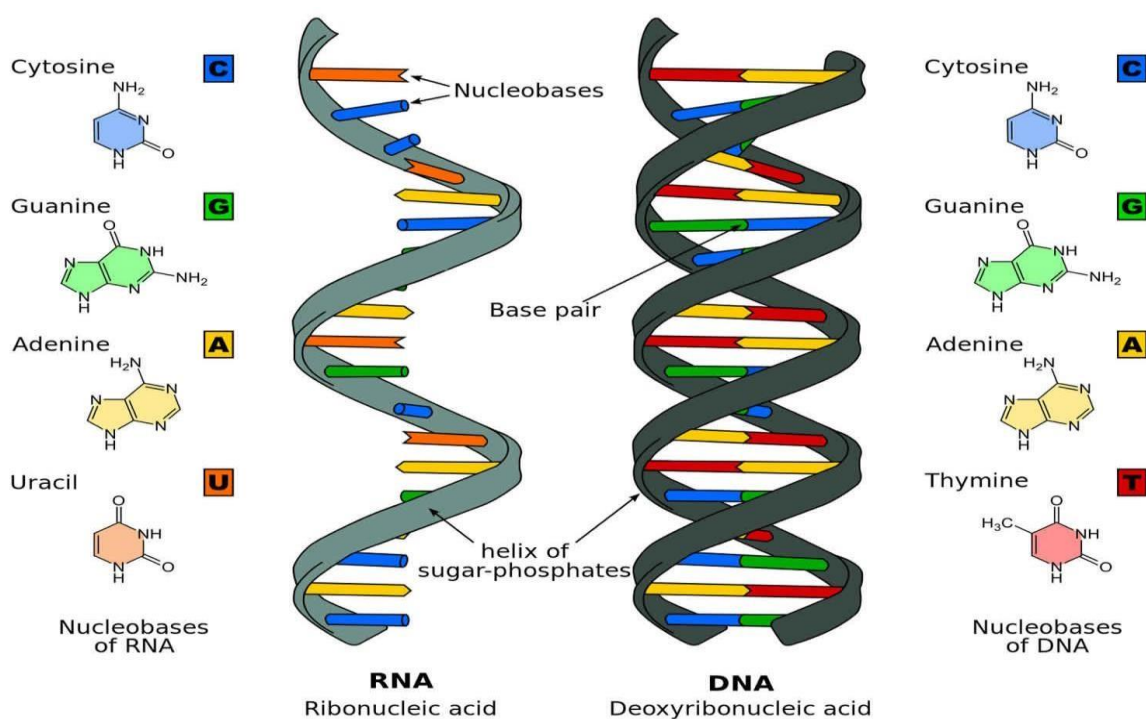
Fig. 9.8 Comparative structure of DNA and RNA

Whereas DNA provides the genetic information for the cell and is inherently quite stable, RNA has many roles and is much more reactive chemically. RNA is sensitive to oxidizing agents such as periodate that lead to opening of the 3′-terminal ribose ring. The 2′-hydroxyl group on the ribose ring is a major cause of instability in RNA, because the presence of alkali leads to rapid cleavage

of the phosphodiester bond linking ribose and phosphate groups. In general, this instability is not a significant problem for the cell, because RNA is constantly being synthesized and degraded.

In a cell, RNA exists in three predominant forms:

(a) messenger RNA (mRNA)

As the name suggests, this RNA is the messenger that carries the information of the DNA to protein synthesis machinery. Protein synthesis machinery translates this information into sequence of polypeptides. Messenger RNA have high molecular weight (Perhaps upto several million) and accounts for only about 1 percent of the total RNA of the cell. These RNAs are unstable and short lived and their synthesis is directed by DNA, and thus in base composition they resemble a strand of DNA. These are synthesized in the nucleus and then get transferred to cytoplasm

(b) transfer RNA (tRNA)

It is smallest RNA in the cell (~76 amino acids), and is found dissolved in the cytoplasm. tRNA serves as a carrier of amino acids (monomers for protein synthesis). Though it is also single stranded but it forms characteristic secondary structure by virtue of intrastrand hydrogen bonding. As the name indicates, transfer RNA transfers or carries activated amino acids during protein synthesis to the proper site on the RNA template of mRNA.

There is specific tRNA molecule for the transfer or carriage of each amino acid to be incorporated into proteins (c) Ribosomal RNA (rRNA) rRNA forms the part of ribosomes. Ribosomes, the protein synthesis machinery, comprises onethird proteins and two-third rRNA. rRNA is the most abundant RNA in the cell. They participate in the formation of peptide bonds (bonds that link any two amino acids in a protein chain), hence these are called Ribozymes or RNA enzyme.

Structure of Deoxyribonucleic acid (DNA) molecules:

DNA is a polymer of the four nucleotides A, C, G, and T, which are joined through a backbone of alternating phosphate and deoxyribose sugar residues. These nitrogen-containing bases occur in complementary pairs as determined by their ability to form hydrogen bonds between them. A always pairs with T through two hydrogen bonds, and G always pairs with C through three hydrogen bonds. The spans of A:T and G:C hydrogen-bonded pairs are nearly identical, allowing them to bridge the sugar-phosphate chains uniformly. This structure, along with the molecule's

chemical stability, makes DNA the ideal genetic material. The bonding between complementary bases also provides a mechanism for the replication of DNA and the transmission of genetic information.
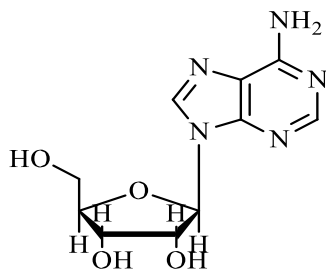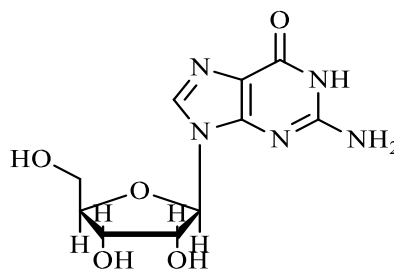
Adenosine   Guanosine
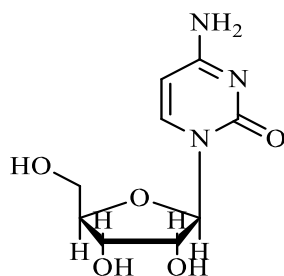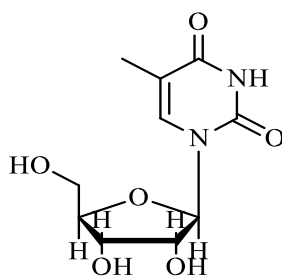
Cytidine   5-Methyluridine   Uridine

Ribonuleosides

Deoxyadenosine

Deoxyguanosine

Deoxycytidine

Deoxythymidine
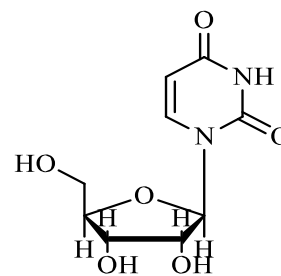
Deoxyuridine

Deoxyribonuleosides
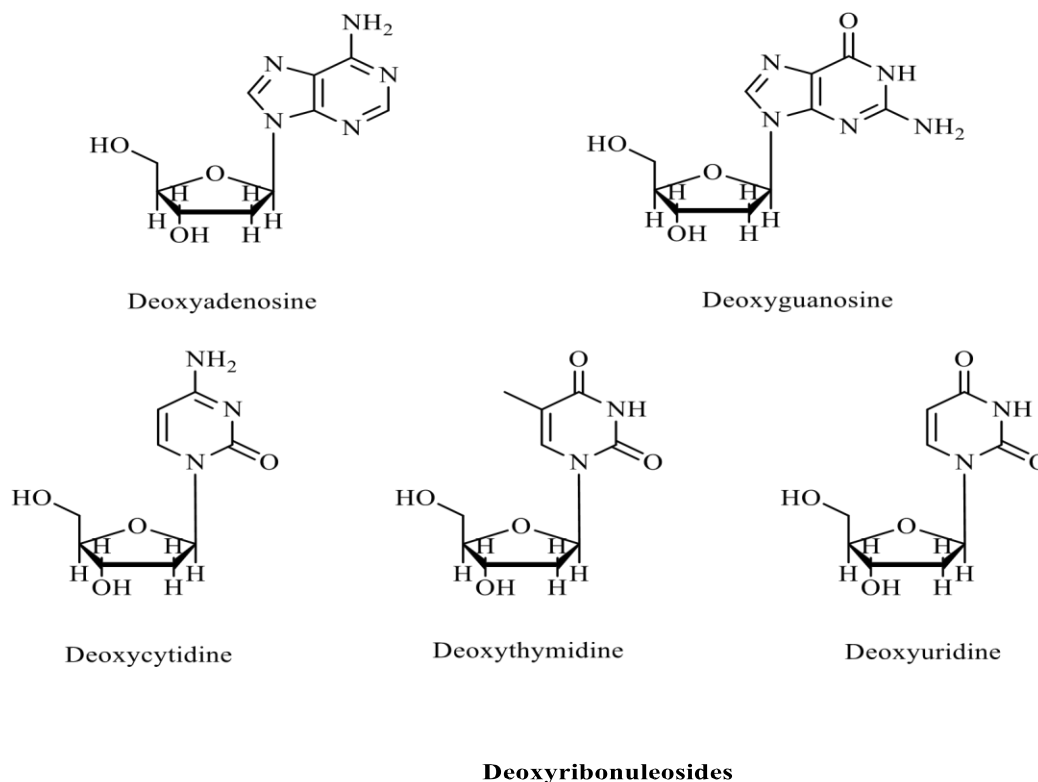
Fig. 9.9The structure and nomenclature of ribonucleosides and deoxyribonucleosides

In 1953 James D. Watson and Francis H.C. Crick proposed a three-dimensional structure for DNA based on low-resolution X-ray crystallographic data and on Erwin Chargaff's observation that, in naturally occurring DNA, the amount of T equals the amount of A and the amount of G equals the amount of C. Watson and Crick, who shared a Nobel Prize in 1962 for their efforts, postulated that two strands of polynucleotides coil around each other, forming a double helix. The two strands, though identical, run in opposite directions as determined by the orientation of the 5′ to 3′ phosphodiester bond. The sugar-phosphate chains run along the outside of the helix, and the bases lie on the inside, where they are linked to complementary bases on the other strand through hydrogen bonds (Fig. 9.10).
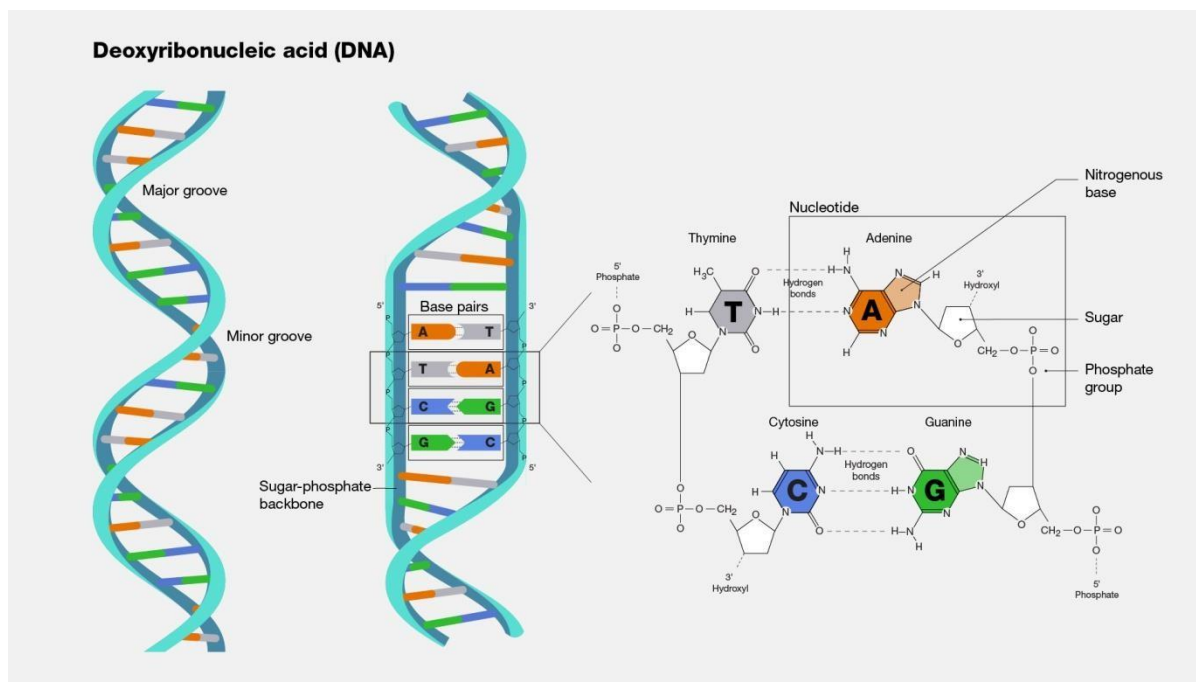
Fig. 9.10 DNA structure

9.8.1 Properties of DNA:

One of the most important properties of DNA is that it can make exact copies of itself. This process is called replications.

Replication is not quite the same as duplication. A duplicate is simply an exact copy of an original; a replica is a newly created structure made by using the original as a model or guide. The replication process is the very basis of life.The replication of DNA can be explained most simply by assuming that the two strands separate by breaking the hydrogen bonds. Each single strand (also called primer) has now an exposed row of bases that serves as a template. The bases of free deoxyriboncleotides (monomers) form hydrogen bonds with these exposed bases. The template strand dictates the sequence in which the free nucleotides are assembled, i.e. the bonds can only be made between complementary base pairs (A-T, T-A, C-G, G-C) and thus a complementary chain to the template is formed. For example, if a segment of the template has the arrangement ATTGACAA from the free 5' to the free 3' end, the newly synthesized chain will be TAACTGGT from the free 3' to the free 5 end. As each strand produces its complementary strand, the two newly formed strands combine into a DNA molecule identical to the original.

The complex chemistry of replication is catalyzed by several DNA polymereses and DNA ligase.Replication ensures that the genes, which are segments of the DNA molecule, are present in identical sets in all cells of the body or an individual. DNA fulfills the requirement of a genetical material, i.e., the ability to replicate.

Replication of DNA is shown diagrammatically as :

These chemical properties render stability of DNA making it more stable storage form of genetic information. 2'-OH of ribose in RNA makes it less stable than DNA. The vicinal hydroxyl group next to 3'-OH (i.e. 2'-OH) is absent in DNA rendering it more resistant to hydrolysis by alkali. This vicinal hydroxyl group in RNA makes the phosphodiester bond susceptible to nucleophilic cleavage.
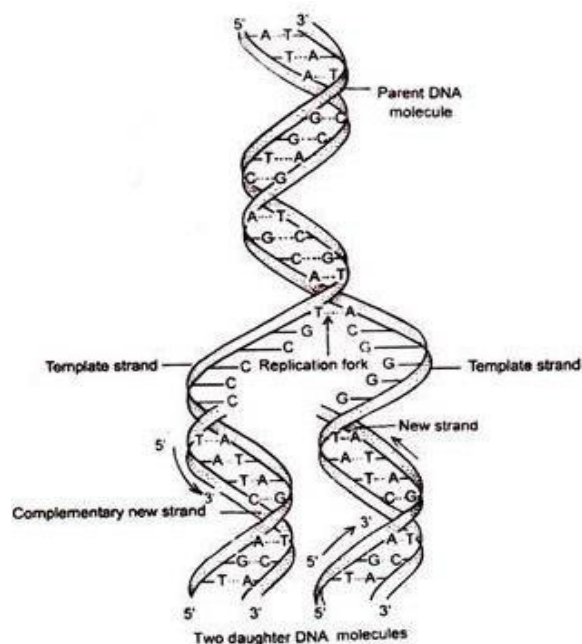
Figure 9.11

It was found that the triplet code is degenerate, i.e. there may be more than one triplet code for a particular amino acid. For example, UUU and UUC both are the codons for phenylalanine, while there are six codons : UUA, UUG, CUU, CUC, CUA and CUG, for leucine. **9.8.2 Differences between DNA and RNA**

1.	DNA is usually double-stranded	Most cellular RNA is single stranded.
2.	The base in DNA are Adenine (A),Thymine (T),Guanine(G) and Cytosine(C)	RNA share Adenine (A), Guanine(G) and Cytosine(C) with DNA but contains Uracil (U) rather than Thymine(T).
3.	DNA is the usual genetic material.	It is the genetic material of some viruses.
4.	The base pair in DNA is A-T, C-G	The base pair in RNA is A-U, C-G
5.	In DNA, the pentose sugar is deoxyribose	In RNA, the pentose sugar is robose
6.	There is only one general structure for the DNA molecule.	In RNA, the pentose sugar is robose.
7.	Pairing of bases is found throughout the length of the molecule.	Pairing of bases is found only in the helical region
8.	Most DNA is found in the cytoplasm of the cell.	Most RNA, although synthesized in the nucleus by DNA, is found in the cytoplasm of the cell.
9.	DNA is vulnerable to damage by UV light.	.RNA is more resistant to damage from UV light than DNA.
10.	DN replicates on its own it is self replicating.	Generally, RNA does not replicate own. It is synthesized from DNA when required.
11.	The function of DNA is the transmission of genetic information. It act as a medium for long term storage.	RNA is the critical for transmission of genetic code that is necessary for protein creation from the nucleus to the ribosome.
12.	Most of the DNA has been found in the chromosomes. Some DNA has also been found in the cytoplasm, e.g., in mitochondria and chloroplasts.	Most of the RNA has been found on the chromosomes and found in the nucleolus and cytoplasm. rRNA and rRNA are also found on the chromosomes and found in cytoplasm.

9.9 SUMMARY

Nucleic acids are high molecular weight polymers; there are constituents of practically all cells. In this unit we study the structure of nucleic acid. As nucleic acids are complex compound thus their structure studied with the structure of their component. In this unit we studied the structure of each component of nucleic Acid. We also discuss the different types of RNA present in the cells. In this unit we studied the DNA as a genetic material with structure also , difference between DNA and RNA.

9.10 TERMINAL QUESTIONS

1. How many type of nitrogenous bases are present in nucleic acid explain in detail?
2. What do you know about the structure of DNA? What is meant by replication of DNA?
3. Briefly outline the functional role of:
4. (a) Messenger RNA   (b) Transfer RNA   (c) Ribosomal RNA
5. Define two following terms. (a) Nucleotide (b) Nucleoside.
6. Write a short notes on: a) Purine base   b) Pyrimidine base.
7. Draw the structure of Nucleotide base?
8. Why is DNA a better genetic material than RNA?
9. What are the difference between DNA and RNA?
10. Define briefly on the structure of RNA and DNA.
11. What are Nucleoside ? Explain the Types of Nucleoside?

9.11 REFERENCES AND FURTHER STUDIES

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UNIT 10: METAL ION IN BIOLOGICAL SYATEM

CONTENTS:

10.1 INTRODUCTION

Bioinorganic chemistry is a branch of chemistry that deals with the study of the role of metals in biology or biological system. Bioinorganic chemistry includes the study of both natural phenomena (behaviour of metalloproteins) as well as artificially introduced metals (essential or non-essential metals in medicine and toxicology). Many biological processes like respiration depend upon the molecules which fall within the boundries of inorganic chemistry. This particular discipline also includes the study of inorganic models that mimics the behaviour of

metalloproteins. As a mixture of biochemistry and inorganic chemistry, bioinorganic chemistry is very important in elucidating the involvement of electron-transfer proteins, substrate bindings and activation, atom and group transfer chemistry and metal properties in biological chemistry. It also involves the study of role of metal species in biological systems.

10.2 OBJECTIVES

By going through this unit, you will be able to understand the following terms and definitions: Introduction to bio-inorganic chemistry, alkali and alkali earth metal ions study in biological system. In Bioinorganic chemistry deals with the role of metals and non- metals in biological systems. Now we shall however , confine our discussion to the role of metallic elements such as Na, K, Ca, Mg, whose ions are present in biological systems in bulk quantities , are called bulk metals.We also learn about metals such as Fe, Cu, Zn, Cr, Mn, Mo, W, Ni, etc, whose ions are present in trace amounts, are called trace metals. Both categories of metals are essential for sustaining life. There is a large number of biochemical's containing metal ions which play a significant role in biological systems.

10.3 BRIEF INTRODUCTION TO BIO-INORGANI CHEMISTRY

 We know that in our body at least 29 elements are present. Out of 29 element 13 elements (C, H, O, N, S, P, Cl, F, Br, I, B, Si, Ar) are non- metals, and remaining 16 elements,(Ca, Mg,K,Na,Fe,Cu,Zn,Ni,Co,Mn, Al, Pb, Sn, Mo, V,Ti) are metals have been definitely established in biological systems. In 13 elements , C, H, O, N are derived in the body dietary carbohydrate, lipids , protein and found in substantial amount in every tissue and cells.Rest of the elements have been classified into essential and non- essential elements.

10.3.1 Essential elements:

Essential element in biological science is the chemical elements that have biological functions to sustain the life of living organisms such as plants or animals. The absence or deficiency of essential or trace elements will lead to create serious health problems or affect the normal biological function of plants and animals.

Essential elements like hydrogen, oxygen, carbon, and nitrogen are required for every living system or organism. They form 99 percent of the structure of plants and animals. Phosphorus and sulfur are common examples of essential elements that are required for the structure of nucleic acids (DNA, RNA), and most amino acids and proteins.

Criteria for essential elements

1) Removal of the element from the diet causes a physiological deficiency.

2) The deficiency is relieved by the addition of that element in the diet.

3) A specific biological function is associated with a particular element

Chemical elements essential to life forms can be categories into four major groups:

a)**Bulk elements-** H/H^+, C, N, O^{-2} O_2^- /O_2^{-2}/P, S/S^{-2})

b)**Macro minerals and ions-** Na/Na^+ , K/K^+ , Mg/Mg^{2+}, Ca/Ca^{2+}, Cl^- , PO_4^{3-}, SO_4^{2-}

c)**Trace elements-** Fe/Fe^{II} /Fe^{III} /Fe^{IV}, Zn/Zn^{II} , Cu/Cu^{I} /Cu^{II} /Cu^{III}

d)**Ultratrace elements-** non-metals (F/F^-, I/I^- , Se/Se^{2-} , Si/Si^{IV}, As, B) and metals

(Mn/Mn^{II} /Mn^{III}/Mn^{IV}, Mo/Mo^{IV} /Mo^V /Mo^{VI}, Co/Co^{II} /Co^{III}, Cr/Cr^{III} /Cr^{VI}, V/V^{III} /V^{IV}/V^V, Ni^I /Ni^{II} /Ni^{III} , Cd/Cd^{2+},Sn/Sn^{II} /Sn^{IV}, Pb/Pb^{2+}, Li/Li^+).

Essential element further classified into: a) Macro-elements   b) Micro-elements

a)**Macro –elements :** The essential macro-elements are:

   i)**Carbon, Hydrogen and Oxygen:**

These three elements are also called framework elements. Plants absorb them from air and soil in the form of carbon dioxide and water. Although these macronutrients elements are not minerals in the true sense, they are still included in the list and they   are essential for plant and human life.

   ii) **Sodium (Na):**

Sodium is the major component of extracellular fluid. It mainly exists as chloride and bicarbonate. It is the primary cation (positive ion) in extracellular fluids such as blood plasma of animals and humans.It is intimately involved in acid- base balance.In human body 10-20g of Na required in daily life. Sodium also regulates osmotic pressure of the body. **iii)Potassium (K):**

Potassium is found naturally in many foods and as a supplement. Its main role in the body is to help maintain normal levels of fluid inside our cells.Like Na it is extracellular fluid , regulates acid base equilibrium and controls osmotic pressure.

iv)Calcium (Ca):

Calcium is the major constituent of bone and teeth. It is also important in neuromuscular functions, interneuronal transmission, maintenance the cell membrane integrity, and blood coagulation.

v)Iron (Fe) :

Iron is a part of haemoglobin which is the pigment of red blood cells and myoglobin, the muscle pigment. Iron is a mineral that the body needs for growth and development. Human body uses iron to make hemoglobin, a protein in red blood cells that carries oxygen from the lungs to all parts of the body, and myoglobin, a protein that provides oxygen to muscles.

vi)Phosphorous:

It is present in every cell of the body in the inorganic as well as organic form.It is estimated that body contains about 700g phosphorus , 90% of which is found in the bones and teeth , in muscles, in the blood and brain.It is needed for the growth, maintenance, and repair of all tissues and cells, and for the production of the genetic building blocks, DNA and RNA.

b)Micro-elements : The essential micro-elements are:

i)Copper (Cu):

All human subjects contain 100-150 mg of copper.Copper is mainly stored in the liver and is an enzyme component that is part of many essential metabolic processes. As an enzyme activator,

Cu provides strong bones and joints and is involved in the utilization of iron and thus, the synthesis of hemoglobin.

ii) Zinc (Zn):

In adult has about 1.3g of Zn,and mainly stored in the liver, pancreas, bone, skin and hair. It is needed for the body's defensive (immune) system to properly work. It plays a role in cell division, cell growth, wound healing, and the breakdown of carbohydrates. Zinc is also needed for the senses of smell and taste.

iii)Manganese (Mn)

Our body contains about 10mg of Mn.Manganese is mainly stored in the bone, liver, kidney and pancreas.It works as an enzyme activator and is crucial for energy, protein- and fat metabolism. It also plays a role in fat and carbohydrate metabolism, calcium absorption, and blood sugar regulation.Deficiencies of manganese causes reduced growth, skeletal deformities, poor fertility and birth defects in newborn calves.

iv)Iodine (I)

Iodine is present in the thyroid glands in the form of monoiodo and diiodo- trysines and thyroid harmones.In the blood it is present in the form of protein- bound blood. Its only function is in the formation of thyroid harmones.Iodine deficiency leads to endemic goiter. **v)Cobalt (Co):**

Cobalt is present as a central atom of Vitamin B_{12} (Cobalamin). Vitamin B_{12} is necessary for a functioning energy and protein metabolism in the liver. The deficiency of cobalt in the human body owing to decreases in the production of red blood cells which causes anemia.

vi)Fluorine (F):

Fluorine occurs mostly in bone and teeth where fluoride ion partially substituted the hydroxide ion in hydroxyapatite. It prevents the decay of tooth enamel.Excess fluoride causes many diseases of bones and teeth.

10.3.2 None -Essential elements :

The remaining elements bromine , boron , silicon, arsenic, nickel, aluminium, lead, stannic, vanadium, and titanium are present in very small amount and have been detected in the ash of the

animal tissues.These elements have no definite function in the body and no deficiency disease pertaining to these element is known , hence it is difficult to say that presence of these elements are required at all by the body.

10.4 ROLE OF METAL ION PRESENT IN BIOLOGICALSYSTEMS

Metal ions are fundamental elements for the maintenance of the lifespan of plants, animals and humans. Their substantial role in biological systems was recognized a long time ago. They are essential for the maintenance of life and their absence can cause growth disorders, severe malfunction, carcinogenesis or death. They are protagonists as macro or microelements in several structural and functional roles, participating in many biochemical reactions, and arise in several forms.The role of some metal ions present in the biological systems are given below:

10.4.1.Metal ion with special reference of Na^+ , K^+ ions:

i) Function of Na^+ ions: Sodium cation is a major cation of extracellular fluids of   animals including human beings. The functions of Na^+ are:

a. Sodium ions(Na^+) are the maintenance of body fluids in humans and the functioning of neurons and transmission of nerve impulses.

b. Sodium ions(Na^+) are necessary for heart activities and certain metabolic functions.

c. Sodium ions(Na^+) plays and important part in the absorption of monosaccharide's and amino acid from the small intestines.

d. Na^+ ions are used in the human body to establish osmotic gradients, which in turn is crucial to control the water balance.

Diseases due to deficiency of sodium

Too much sodium in the blood is called hypernatremia . Too little sodium in the blood called hyponatremia. Deficiency of sodium may the desease

- Decrease blood pressure
- Decrease blood volume
- Muscle weakness, spasms or cramps
- Circulatory failure

- Nausea and vomiting
- Loss of energy, drowsiness and fatigue

Function of K$^+$ ions: Potassium is a mineral found in the foods you eat. It's also an electrolyte. Electrolytes conduct electrical impulses throughout the body. They assist in a range of essential body functions, including:

a) Potassium ion K$^+$ is essential for the synthesis of glycogen.

b) It is the main cation in the cell and play an important part in the regulation of the acid base balance in the cell.

c) Phosphate is one of the body's electrolytes, which are minerals that carry an electric charge when dissolved in body fluids such as blood.

d) In biological synthesis of protein by ribosome, the higher concentration of K$^+$ ion is necessary.

e) Potassium ion (K$^+$)act as co factors for certain enzyme such as pyruvate kinase.

Diseases due to deficiency of potassium

- Deficiencies of Potassium know as hypokalemia.
- Hypokalemia is likely to cause injury to myocardium and Kidenys.
- Constipation, nausea, or vomiting
- Irregular heartbeat

10.4.2 Metal ion with special reference of Mg^{+2} ions:

Magnesium ion are concentrated more in intracellular than extracellular fluids in animal bodies.The presence of Mg^{+2} ions is a necessary requirement for the activation of phosphate transfer enzymes.Which participate in the energy releasing biochemical process occurring in animal body.It is also required for carbohydrate metabolism. Biological importance of magnesium ions are:

a)Magnesium maintains the equilibrium between osmosis and electrolyte.

b) Mg^{+2} ions helps to maintain normal nerve and muscle function, supports a healthy immune system,and helps bones remain strong.

c) Mg^{+2} ions required as w- factor for oxidative phosphorylation.

d) Magnesium as an enzyme co-factor plays an important role in the breakage of glucose   and

   fat molecules, in the production of enzymes, proteins and regulation of cholesterol.

e) It is responsible for the stability and proper functioning of DNA.

Diseases due to deficiency of Magnesium:

Magnesium deficiency can lead to health problem including:

- High Blood pressure and heart disease

- Osteoporosis

- Diabetes

- Muscular tremors, Delirium

10.5 Na / K PUMP

The sodium–potassium pump was discovered in 1957 by the Danish scientist Jens Christian Skou, who was awarded a Nobel Prize for his work in 1997. Its discovery marked an important step forward in the understanding of how ions get into and out of cells, and it has particular significance for excitable cells such as nerve cells, which depend on this pump to respond to stimuli and transmit impulses.

The functioning of this pump is actually a biological process which goes on occurring in each and every cell of all animals. In sodium–potassium pump, transfers Na^+ ions from the intracellular fluids to the extracellular fluids with the help of 'carries proteins'. Simultaneously it transfer K^+ ions from the extracellular fluids to the intracellular fluids. Since each operation of the pump(each cycle of this biological process) , pumps out larger number of sodium ions from the cell than the number of K^+ ions that is pumps into the cell, the interior of the cell acquires an excess negative charge and the exterior of the cell acquires an excess positive charge.This results in the development of electrical potential gradient across the cell membrane which is responsible for the transmission of nerve signals in animals.The Na^+ / K^+ pump is reversible its reversibility depend upon the result of Na^+ / K^+ gradient and it also maintains the volume of the cell.

10.6 ROLE OF Mg^{+2} IONS IN ENERGY PRODUCTION AND CHLOROPHYLL

Metalloporphyrin along with protein globule performs several important biochemical functions in biological systems. Hemoglobin, cytochromes catalase, myoglobin, chlorophyll, and paroxidases are well known examples of metalloporphyrins. Porphyrin is a universal molecule present in almost all living organisms in one form or other. The basic unit of porphyrin consists of four pyrrol units linked together by four methine bridges. It is an 18-electron system and hence, exhibits stability and aromaticity.

The porphyrin ring provides a vacant site at the centre which is suited for metal incorporation (Figure 10.1). With very few exceptions, the porphyrinato dianion acts as a tetradentate ligand with metal ions. Thus, the minimum coordination number of the metal ion possible in a metalloporphyrin is four (Figure 10.2). The extensive electronic delocalisation in the porphyrinato ligand leads to a considerable planarity of the macrocycle and an essentially square planar environment for the metal ion in four-coordinate complexes. Coordination number greater than four is also possible through ligation of suitable moieties either neutral or anionic. The five coordination complexes have generally a square-pyramidal geometry with the single axial ligand occupying the apical position of the square pyramid. The two ligands of the sixcoordinated metalloporphyrins are present on the opposite sides of the porphynato plane forming complexes with tetragonal/octahedral geometries.
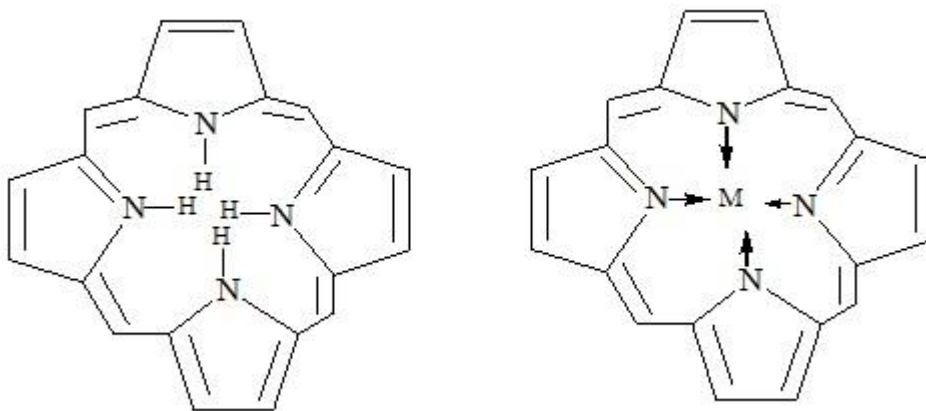
Figure. 10.1 Porphyrin   **Figure. 10.2 Metal complex with porphyrin ring**

Two types of the most widely used metallopophyrin ring systems can be defined as:

1.Heme: WhenFe in the +2 oxidation state is placed in the cavity of porphyrin ring then the metalloporphyrin obtained is known as Heme. The structure of two important metalloporphyrin heme and chlorophyll are being considered here: Heme Figure 10.3 contains iron (II) which is present in haemoglobin and myoglobin.
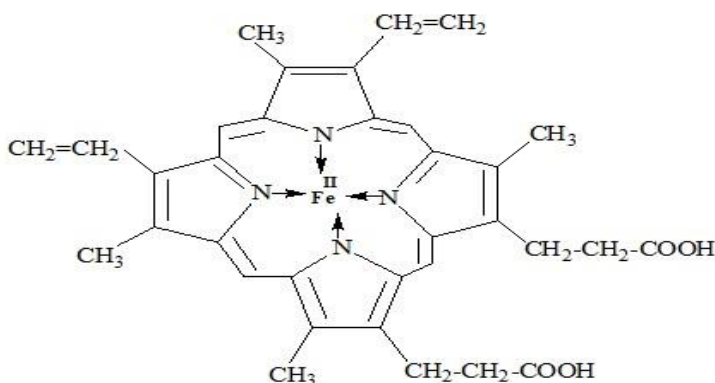
Figure. 10.3 Heme skeleton

When the heme skeleton combine with the globular protein than the macromolecule   (pigment) which is obtained is known as haemoglobin which acts as an oxygen carer within the human body.

2. Chlorophyll: when the metal in the +2 oxidation state is occupied in the cavity of porphyrin ring system then the metalloporphyrin which is obtained is knows as Chlorophyll (Figure 10.4). A simple diagrammatic representation for the chlorophyll metolloporphyrin can be given as
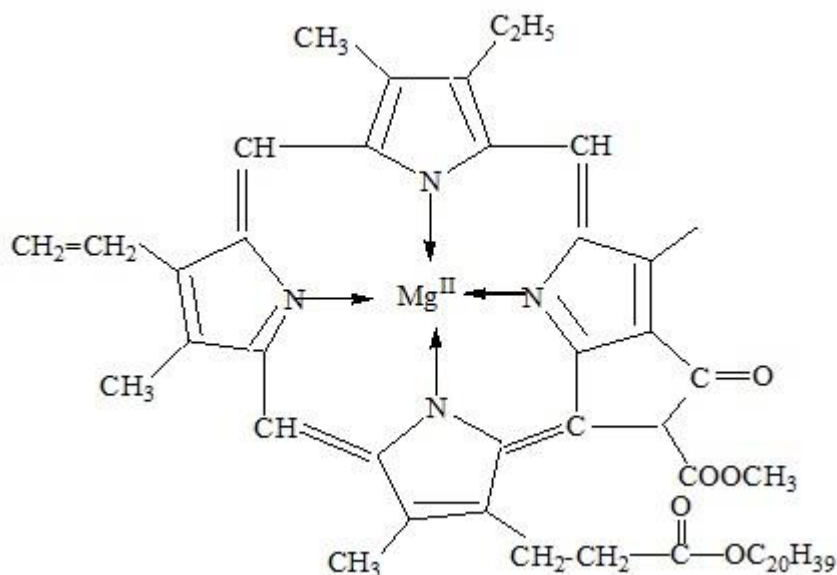
Figure. 10.4 Chlorophyll

Chlorophyll is present in the green plants and participates in the photosynthesis reaction in which CO_2 and moisture of atmosphere combined together in the presence of sunlight produce the glucose and O_2 gas. Glucose obtained from this process is further converts into polysaccharide like starch, cellulose.

$$6\,CO_2 \;+\; 6H_2O \;+\; \text{Solar energy} \xrightarrow{\text{Chlorophyll}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$
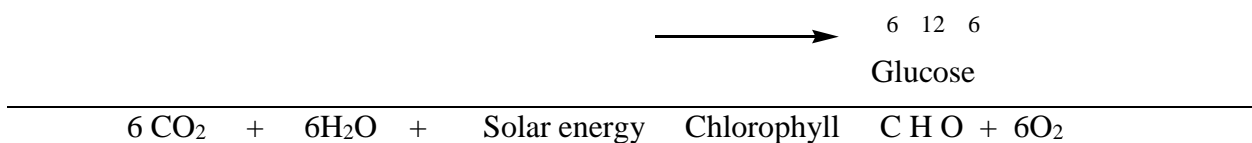
10.7 SUMMARY

This unit deals with the Bio-inorganic Chemistry which is the intermediate of inorganic chemistry and biochemistry.The principles of bioinorganic chemistry to explain the mutual relationship between the function of inorganic substances in living systems and in medicinal therapy and diagnosis.In this chepter studied elements like Copper, Magnesium,sodium , potassium Calcium, Cobalt, Iron, etc. play several important roles in biological functions also understand the function of Na^+ / K^+ pump, and Mg ion in chlorophyll.

10.8 TERMINAL QUESTIONS

1.Name the three macroelements, which constitute the living systems. Discuss the role of these element in biological system?

2.Name the three microelements, which constitute the living systems. Discuss the role of these element in biological system?

3.Write down the functions of following elements:

 a) Sodium ion   b) Potassium ion   c) Magnesium ion

4.Give an account for the disease caused due to the deficiency of , Na^+ , Mg^{+2} ions?

5.Write a short notes on Na^+ / K^+ pump?

6.Define metallopophyrin ring systems with suitable diagram?

7. What is porpyrin? Draw the structure of porpyrin with metal complex.

8. Explain diagrammatic representation of chlorophyll metolloporphyrin?

10.9 REFERENCES AND FURTHER STUDIES

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   76113- 6 (pbk.).

2.Stephen J. Lippard, Jeremy M. Berg, Principles of Bioinorganic Chemistry, University Science

   Books, 1994, ISBN 0-935702-72-5

3.Principles of Inorganic Chemistry: B. R. Puri, L.R. Sharma & K. C. Kalia,Milestone Publishers

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BLOCK-IV: REDOX REACTIONS AND CATALYSIS

UNIT 11: OXIDATION AND REDUCTION

CONTENTS:

11.1 Introduction

11.2 Objectives

11.3 Uses of redox potential data

11.1. INTRODUCTION

We all know that oxidation-reduction processes occur in our daily life. The various examples of oxidation-reduction reactions in our day-to-day life are rusting of iron, use of lead acid batteries

in inverters and other batteries used for different purposes, photosynthesis, respiration and combustion. In redox reactions, oxidation number of molecule, atom or ion (any species) changes by transfer of electrons (gain or loss of electrons).

The redox reactions involve two half reactions, a reduced half and an oxidized half and these two always occur together. The reduced half reaction gains electrons and called as oxidizing agent while the oxidation half is called as reducing agent. There are different definitions and phenomena given for oxidation and reduction reactions. Here, in this unit, we will discuss the different aspects of redox reactions.

Oxidation number

In case of ionic reactions, redox changes can be explained in terms of electron transfer. However, in the case of covalent compounds, the redox reactions can be explained on the basis of oxidation number. The oxidation number is a measure of extent of oxidation (charge which appears when the other atoms are removed) of an element and in its compounds.

Oxidation (De-electronation)

The process in which loss of electrons results in the increase in oxidation number of its atom / atoms is called oxidation reaction.

Oxidizing agent (O.A.)

It accepts electrons (electron acceptor) or oxidation number of whose atoms or ions decreases.

Reduction (Electronation)

Gain of electron or decrease in oxidation number of its atom / atoms is known as reduction.

Reducing agent (R.A.)

It donates electrons (electron donor) or oxidation number of whose atoms increases.

Here, oxidation of Fe and reduction of Cr takes place.

Oxidizing agent – $Cr_2O_7^{2-}$

Reducing agent – Fe^{2+}

Thus, a reduction-oxidation (redox) reaction is a chemical reaction which comprises transfer of electrons between two species viz. oxidizing agent and reducing agent.

Oxidation Number

It is the charge which an atom of an element has in its ion or appears to have when present in the combined state. It is also known as oxidation state.

Electrode potential (E)

In metal-metal ion electrode, metal (M) immersed in the solution containing metal ions (M^{n+} ions). In the electrode, there exists a separation of charges between the metal and its salt solution. The separation of charges results in the development of net (–)ve or (+)ve charge on the metal with respect to its solution. The (–)ve or (+)ve charge developed on the metal produces electrical potential difference between the metal and its solution. This electrical potential difference is called potential of the electrode or electrode potential. Electrode potential is a measure of the tendency of an electrode in a half-cell reaction to gain or lose electrons. It is denoted by E. Unit of electrode potential is volt (V). Volt is the potential, required to flow one coulomb of electric current per second, through a uniform thread of mercury 106.3 cm long, containing 14.4521 g of mercury at 0°C.

Standard electrode potential (E°)

When the concentration of the ions and the pressure of the gaseous species appearing in the electrode reaction (half-cell reaction) are 1mol dm^{-3} and 1 atmosphere, respectively at 25°C temperature, the electrode potential is called standard electrode potential. It is denoted by E°.

Types of electrode potential

Electrode potential may be of following types:-

Oxidation electrode potential (E°$_{ox}$)

Oxidation potential of an electrode is for the oxidation reaction taking place at the anode. Thus, oxidation electrode potential is the potential of the electrode at which oxidation takes place and

hence, is a measure of the tendency of the electrode in a half-cell to get oxidized or to lose electrons.   Zn(s) $\square$Zn^{2+} (aq) + 2e$^-$, E$^o_{ox}$ or E$^o_{Zn/Zn2+}$ = +0.76 V

Reduction electrode potential, (E$^o_{red}$)

Reduction potential of an electrode is for the reduction reaction taking place at the electrode. Thus reduction electrode potential is the potential of the electrode at which reduction takes place and hence is a measure of the tendency of the electrode in a half-cell to get reduced or to gain electrons.

e.g. –   Cu$^{2+}_{(aq)}$ + 2e$^-$ $\square$ Cu(s), E$^\circ_{red}$ or E$^\circ_{Cu}$$^{2+}_{/Cu}$ = +0.34 V Relation between oxidation potential and reduction potential of a given electrode

$$(E_{ox})_{elec.} = - (E_{red})_{elec.}$$

$$- (E_{ox})_{elec.} = (E_{red})_{elec.}$$

Similarly, for standard electrode potentials –

$$(E^o_{ox})_{elec.} = - (E^\circ_{red})_{elec.}$$

$$-(E^o_{ox})_{elec.} = (E^\circ_{red})_{elec.}$$

An important convention

According to the present convention, the value of electrode potential is expressed as reduction electrode potential. Thus, if we say that the value of standard electrode potential of zinc electrode is –0.76 volt, this means that the given value is the value of the standard reduction electrode potential of Zn electrode, i.e., E$_{Zn}$$^{2+}_{/Zn}$ = - 0.76 volt

11.2 OBJECTIVES

This unit deals with the oxidation-reduction processes, different terminologies involved and their application. When you study this unit, you will be able to identify, understand and answer the following terms and problems:

- Oxidation,
- Reduction,
- Oxidation number,

- Standard potential,
- Electrochemical series,
- Redox cycles,
- Latimer, Frost and Pourbaix diagram,
- Extraction of elements and redox reactions,

And you can also get acquainted with the following terms:

- Oxidizing agent,
- Reducing agent,
- Redox reactions,
- Redox Potential

11.2. INTRODUCTION

We all know that oxidation-reduction processes occur in our daily life. The various examples of oxidation-reduction reactions in our day-to-day life are rusting of iron, use of lead acid batteries in inverters and other batteries used for different purposes, photosynthesis, respiration and combustion. In redox reactions, oxidation number of molecule, atom or ion (any species) changes by transfer of electrons (gain or loss of electrons).

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Thus, a reduction-oxidation (redox) reaction is a chemical reaction which comprises transfer of electrons between two species viz. oxidizing agent and reducing agent.

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In metal-metal ion electrode, metal (M) immersed in the solution containing metal ions (M^{n+} ions). In the electrode, there exists a separation of charges between the metal and its salt solution. The separation of charges results in the development of net (–)ve or (+)ve charge on the metal with respect to its solution. The (–)ve or (+)ve charge developed on the metal produces electrical potential difference between the metal and its solution. This electrical potential difference is called

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Types of electrode potential

Electrode potential may be of following types:-

Oxidation electrode potential ($E°_{ox}$)

Oxidation potential of an electrode is for the oxidation reaction taking place at the anode. Thus, oxidation electrode potential is the potential of the electrode at which oxidation takes place and hence, is a measure of the tendency of the electrode in a half-cell to get oxidized or to lose electrons.

$$Zn(s) \square Zn^{2+} (aq) + 2e^-, E°_{ox} \text{ or } E°_{Zn/Zn2+} = +0.76 \text{ V}$$

Reduction electrode potential, ($E°_{red}$)

Reduction potential of an electrode is for the reduction reaction taking place at the electrode. Thus reduction electrode potential is the potential of the electrode at which reduction takes place and hence is a measure of the tendency of the electrode in a half-cell to get reduced or to gain electrons.

e.g. $- Cu^{2+}_{(aq)} + 2e^- \square Cu(s), E°_{red} \text{ or } E°_{Cu^{2+}/Cu} = +0.34 \text{ V}$

Relation between oxidation potential and reduction potential of a given electrode

$(E_{ox})_{elec.} = - (E_{red})_{elec.}$

$- (E_{ox})_{elec.} = (E_{red})_{elec.}$

Similarly, for standard electrode potentials –

$(E^o_{ox})_{elec.} = -(E^\circ_{red})_{elec.}$

$-(E^o_{ox})_{elec.} = (E^\circ_{red})_{elec.}$

An important convention

According to the present convention, the value of electrode potential is expressed as reduction electrode potential. Thus, if we say that the value of standard electrode potential of zinc electrode is –0.76 volt, this means that the given value is the value of the standard reduction electrode potential of Zn electrode, i.e., $E_{Zn^{2+}/Zn} = - 0.76$ volt

11.3 USE OF REDOX POTENTIAL DATA ELECTROCHEICAL SERIES

The values of standard reduction potentials of many electrodes have been determined at 25ºC or (25 + 273) = 298K. These values have been arranged in their increasing order, in the form of a series, which is called electrochemical series.

Reducing $\rightleftharpoons$ Oxidizing $+ e^-$ E^o (V)
agent   agent

$\rightleftharpoons$

Li $Li^+ + e^-$ –3.045

$\rightleftharpoons$

K $K^+ + e^-$ –2.925
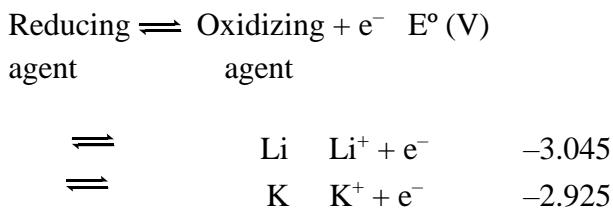
$$Ca \rightleftharpoons Ca^{2+} + 2e^- \qquad -2.866$$
$$Na \rightleftharpoons Na^+ + e^- \qquad -2.714$$
$$Mg \rightleftharpoons Mg^{2+} + 2e^- \qquad -2.363$$
$$Al \rightleftharpoons Al^{3+} + 3e^- \qquad -1.662$$
$$Mn \rightleftharpoons Mn^{2+} + 2e^- \qquad -1.180$$
$$Zn \rightleftharpoons Zn^{2+} + 2e^- \qquad -0.762$$
$$Cr \rightleftharpoons Cr^{3+} + 3e^- \qquad -0.744$$
$$\rightleftharpoons Cd\ Cd^{2+} + 2e^- \qquad -0.403$$
$$Fe \rightleftharpoons Fe^{2+} + 2e^- \qquad -0.400$$
$$\rightleftharpoons Co\ Co^{2+} + 2e^- \qquad -0.277$$
$$Ni \rightleftharpoons Ni^{2+} + 2e^- \qquad -0.250$$
$$\rightleftharpoons Pb\ Pb^{2+} + 2e^- \qquad -0.126$$
$$\rightleftharpoons H_2\ 2H^+ + 2e^- \qquad +0.000$$
$$\rightleftharpoons CH_4 \qquad C + 4H^+ + 4e^- \qquad +0.132$$
$$\rightleftharpoons Cu^+ \qquad Cu^{2+} + e^- \qquad +0.153$$
$$Cu \rightleftharpoons Cu^{2+} + 2e^- \qquad +0.337$$
$$\rightleftharpoons 2OH\ \tfrac{1}{2}O_2 + H_2O + 2e^-$$
$$\rightleftharpoons +0.401\ I^- \qquad \tfrac{1}{2} I_2 + e^-$$
$$\rightleftharpoons +0.536$$
$$^{2+}\rightleftharpoons Fe^{2+} \qquad Fe^{3+} + e^- \qquad +0.771$$
$$Ag \rightleftharpoons Ag^+ + e^- \qquad +0.799$$
$$Hg \rightleftharpoons Hg^{2+} + 2e^- \qquad +0.854$$
$$Hg_2 2Hg^{2+} + \rightleftharpoons 2e^- \qquad +0.908$$
$$Pd \rightleftharpoons Pd^{2+} + 2e^- \qquad +0.987$$
$$Br^- \rightleftharpoons \tfrac{1}{2}Br_2 + e^- \qquad +1.065$$
$$Pt \rightleftharpoons Pt^{2+} + 2e^- \qquad +1.200$$
$$Cl^- \rightleftharpoons \tfrac{1}{2} Cl_2 + e^- \qquad +1.359$$
$$\rightleftharpoons Au^+ \qquad Au^{3+} + 2e^- \qquad +1.402$$
$$Au \rightleftharpoons Au^{3+} + 3e^- \qquad +1.498$$
$$Pb^{2+} \qquad Pb^{4+} + 2e^- \qquad +1.800$$
$$Ag^+ \qquad Ag^{2+} + e^- \qquad +1.980$$
$$F^- \qquad \tfrac{1}{2} F_2 + e^- \qquad +2.870$$
$$HF_{(aq)} \qquad \tfrac{1}{2}F_2 + H^+ + e^- \qquad +3.060$$

(Reducing property — indicated by upward arrow along the series)

The potential data can be utilized for the following purposes:

11.3.1 To know the feasibility of a chemical reaction

With the help of potential data, we can determine the feasibility of a redox reaction. The electric pressure that makes current flow in a circuit is called as electromotive force.

Electromotive force (E.M.F.) = $E°_{cathode} - E°_{anode}$

$$= E°_{more} - E°_{less}$$

$$= E°_{right} - E°_{left}$$

Suppose, we want to know feasibility of the following redox reaction:

$Sn^{2+} + Cu \square Sn + Cu^{2+}$ $E°_{Sn2+/Sn}$= -0.136V and $E°_{Cu2+/Cu}$=0.34
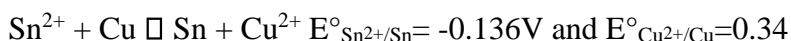
As reduction potential of $E°_{Cu2+/Cu}$ is higher as compared to $E°_{Sn2+/Sn}$ the oxidation potential, reduction will takes place at copper half cell. But in this reaction, the two reaction halves are:

$2e^- + Sn^{2+} \square Sn$ ($E_{Sn2+/Sn} = –0.136$ v) Cathode

$Cu \square Cu^{2+} + 2e^-$ ($E_{Cu/Cu}^{2+} = –0.34$) Anode
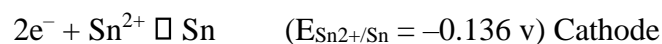
E.M.F. = $E_{cathode} - E_{anode}$

$= –0.136 – (+0.34)$

$= –0.476V$

Due to negative value of E.M.F. of the cell, it is not a feasible cell. Whereas if the cell reaction is

$Cu^{2+} + Sn \square Sn^{2+} + Cu$
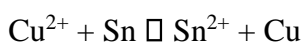
Than, it will be feasible to occur, because now E.M.F. will be positive.

$E°_{cell} = E°_{cathode} - E°_{anode}$

If we know $E°_{cathode}$ and $E°_{anode}$, we can easily calculate K. If K is very high, the reaction will proceed towards forward direction.

11.3.2 To calculate the redox potential and free energy change

There is the following relationship between E° and free energy change ($\square G°$):

$\square G° = –nE°F$

If E° is positive, the value of $\square G°$ will be negative and a reaction is generally thermodynamically feasible if value of $\square G°$ is negative.

11.3.3 To calculate the value of reduction electrode potential of a given electrode in nonstandard conditions

The value of $(E_{red})_{elec.}$ can be calculated by using the following Nernst Equation:

$$(E_{red})_{elec.} = (E^o{}_{red})_{elec.} - \frac{2.303\ RT}{nF} \log \frac{\text{Product of concentration of products}}{\text{Product of concentration of reactants}}$$

Here, $(E_{red})_{elec.}$ = Reduction electrode potential in non-standard conditions, $(E^o{}_{red})_{elec.}$ = Reduction electrode potential in standard conditions, i.e. $(E^o{}_{red})$ is the standard electrode potential, n = no. of electrons released in the electrode reduction reaction.

11.3.4 To calculate the value of potential (e.m.f.) of a given cell in standard conditions

The value of $E^o{}_{cell}$ can be calculated by using the equartion

$$E^o{}_{cell} = (E^o{}_{red})_{cathode} - (E^o{}_{red})_{anode}$$

11.3.5 To calculate the value of E_{cell} by using Nernst equation

$$E_{cell} = E^o{}_{cell} - \frac{2.303\ RT}{nF} \log \frac{\text{Product of concentration of products}}{\text{Product of concentration of reactants}}$$

11.3.6. To know oxidizing and reducing property of substances in aqueous solution

The substance which has a (+)ve value of $E^o{}_{red}$, has a tendency to gain electrons to undergo reduction and hence is capable of acting as an oxidizing agent in aqueous solution. The substance which has a (–)ve value of $E^o{}_{red}$, has a tendency to lose electrons to undergo oxidation and hence is capable of acting as an reducing agent in aqueous solution. Higher the value of $E^o{}_{red}$, higher the tendency of the substance to accept electrons to undergo reduction in aqueous solution and hence higher the oxidizing power of the substance. Higher the value of $E^o{}_{red}$, lower is the tendency of a substance to lose electrons to undergo oxidation in a aqueous solution and hence lower is the reducing power of the substance. Since, $E^o{}_{red}$ value increases down the electrochemical series (– ロ O ロ +), the oxidizing power of oxidizing agents also increases. Since, $E^o{}_{red}$ value increases down the electro-chemical series, the reducing power of the reducing agents decreases in the series.

11.3.7. To calculate redox potential and equilibrium constant

As redox reactions are reversible in nature, therefore, there is equilibrium between oxidizing and reducing agent. If we know the redox potential, we can calculate equilibrium constant for the reaction which can further decide the direction of the reaction forward / backward $Zn_{(S)}$+ $Cu^{2+}_{(aq)}$ ($\rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(S)}$).

(Equilibrium constant) $K = \dfrac{[Zn^{2+}]\,[Cu_{(S)}]}{[Zn_{(S)}]\,[Cu^{2+}]}$

As concentration of solids remains constant, $[Cu_{CS}]/[Zn_{CS}]$ will be constant (I) So,

$$K = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$$

K is related to E.M.F. of a cell by the following relation :

$E^{o}_{cell} = \dfrac{2.303RT}{nF}$ Log K and at 25ºC = 0.059/n log K.

11.4. REDOX STABILITY OF WATER

The compounds that are stable in water neither oxidize nor reduce or disproportionate in water (Figure 11.1). While, the substances, which are unstable in water, they can undergo the following reactions in aqueous medium:

11.4.1 The compound may release H_2 on reaction with water

In these reactions, water is reduced to H_2.

$$2H_2O + 2e^- \xrightarrow{\text{Reduction}} H^2 + 2OH^-$$

$+ e \qquad \tfrac{1}{2}H \qquad H^+_{(aq)} \longrightarrow \qquad 2(g)$
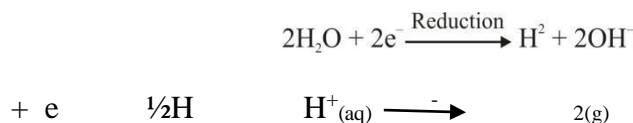
This reaction is shown by some alkali metals and elements of first series of transition elements like Sc, Ti, V, Cr, Mn, etc.

$$M + H_2O \rightarrow MOH + \tfrac{1}{2}H_2$$

$$Sc + 3H \rightarrow Sc^{3+} + 1\tfrac{1}{2}H_2$$

11.4.2 The compound can release O₂ on reaction with water Here,

water acts as an oxidizing agent:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad E^o_{ox} = -1.23V \text{ or } E^o_{red} = +1.23V$$

Most of the species with more than 1.23V E^o_{red} can oxidize water into O_2 such as F_2, Co^{3+}, Ce^{4+} etc.

$$4Co^{3+} + 2H_2O \rightarrow 4\,Co^{2+} + 4H^+ + O_2$$

$$4Co^{4+} + 2H_2O \rightarrow 4Co^{3+} + 4H^+ + O_2$$
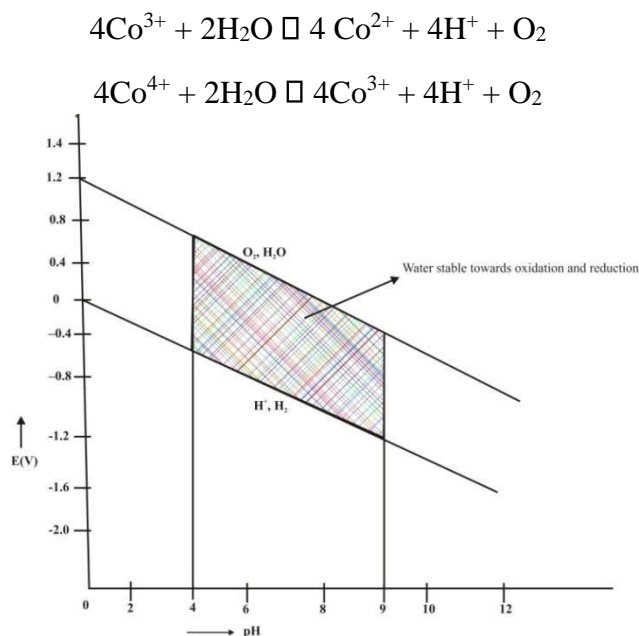
Figure 11.1: Redox stability of water

11.5 LATIMER, FROST AND POURBIX DIAGRAMS

11.5.1. Latimer diagram

Latimer diagram represents useful diagrammatic summaries of the relative stabilities of a series of species. The numerical value of standard potential is written over a horizontal line connecting species with the element in different oxidation states. The most highly oxidized form of the element is on the left, and to the right, the element is in successively lower oxidation states.

Latimer diagram of chlorine in an acidic solution

Unit 11: Oxidation and reduction

Use of redox potential data- analysis of redox cycles, redox stability in water-Frost, Latimer and Pourbaix. Principles involved in the extraction of the element.

$$2e^- + 2H^+ + ClO_4^- \xrightarrow{+1.20} ClO_3^- + H_2O \qquad E^o = 1.20v$$

$$2e^- + 2H^+ + 2HClO \xrightarrow{+1.67} Cl_2 + 2H_2O \qquad E^o = 1.67v$$
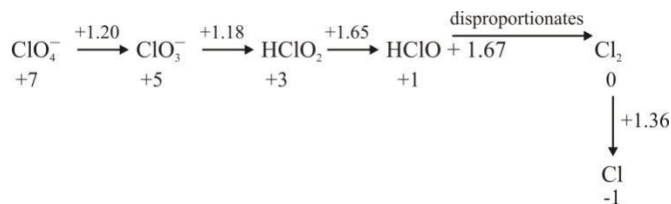
In basic medium (pH = 14), Latimer diagram of chlorine is
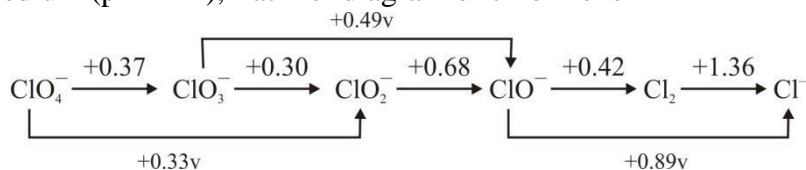
Potential around OCl^- do not decrease from left to right, and hence OCl^- is unstable with respect to disproportionation.

$$ClO_3^- \xrightarrow{0.49} ClO^- \xrightarrow{0.89} Cl^-$$

Potential around ClO_3^- and OCl^- do not decrease from left to right.

$$ClO_4^- \xrightarrow{0.37} ClO_3^- \xrightarrow{0.49} OCl^-$$

So, ClO_3^- should disproportionate into ClO_4^- and OCl^- and OCl^- should disproportionate to give Cl^- and ClO_3^-
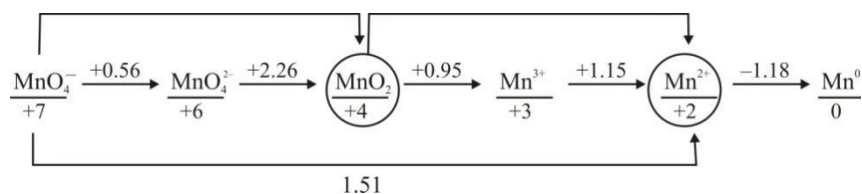
Latimer diagram of manganese (acidic medium)

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$
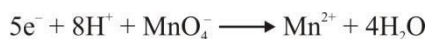
$E^o = 1.51$ V; $\Delta G = -5 \times 1.51$

$= -7.55$

▢ Oxidizing agents have large positive E^o values.

▢ Powerfully reducing agents ▢ large –ve E^o value (Mn^{2+} / Mn^0).

▢ Thermodynamically unstable species, generally, disproportionate.

If the sum of reduction and oxidation potentials is positive , then $\Box G = -ve$ and spontaneous disproportionation is possible.

$$MnO_4^- \xrightleftharpoons[\text{Oxidation}]{+0.56} MnO_4^{2-} \xrightarrow[\text{Reduction}]{+2.26} MnO_2$$

$(MnO_4{}^{2-} \Box MnO_4^- + e \; ; \quad E^o = -0.56V)$

$2e^- + 4H^+ + MnO_4{}^{2-} \Box MnO^{2} {}^{+} 2H_2O \xrightarrow[1.70V]{E^o = +2.26V}$
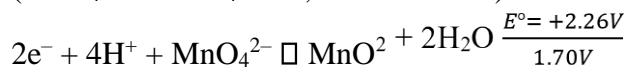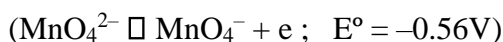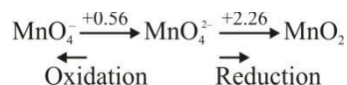
If the sum of reduction and oxidation potentials is positive, then the standard free energy change for the disproportionation will have a negative value and spontaneous disproportionation is possible.

Manganese redox reactions in alkaline solution are as follows:
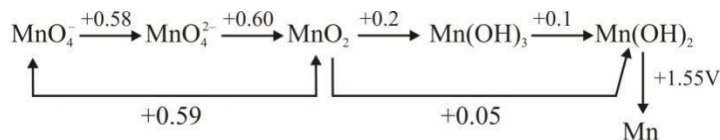
Latimer diagram for manganese in basic medium

Uses of Latimer diagrams

$$ClO_4^- \xrightarrow{+1.20V} ClO_3^- \xrightarrow{+1.18V} HClO_2 \xrightarrow{+1.65V} HClO \xrightarrow{+1.67V} Cl_2 \xrightarrow{+1.36V} Cl_2$$
$$\quad\quad +5 \quad\quad\quad +3 \quad\quad\quad +1 \quad\quad\quad 0 \quad\quad\quad -1$$
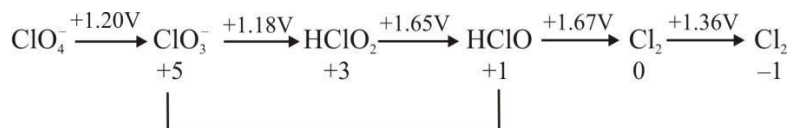
(i)   Predict feasibility of a reaction

$$M^{2+} \xrightarrow{E_1O} M^+ \xrightarrow{E^o_2} M^o$$
$$+2 \quad\quad +1 \quad\quad 0$$

$e^- + M^{2+} \longrightarrow M^+ \quad E^o_1$
$e^- + M^+ \longrightarrow M^o \quad E^o_2$ $\}$ difference
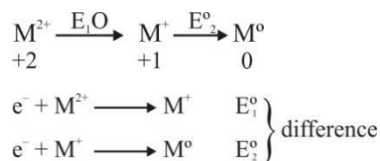
(ii) Predict disproportionation reaction (unstable species)

$$2M^+ \longrightarrow M^{2+} + M^+ \ (E^\circ_2 - E^\circ_1)$$

$$\Downarrow$$

$$E^\circ_2 > E^\circ_1 \quad \text{Positive value}$$
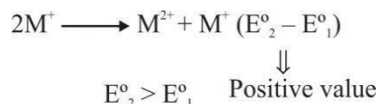
Hence, disproportionation occurs at HClO.

(iii) Calculate E° value for any non-adjacent couple

$$2e^+ ClO_3^- \longrightarrow HClO_2 \qquad (n_1 = 2)$$
$$2e^- HClO_2 \longrightarrow HClO \qquad (n_2 = 2)$$
$$\Delta G^\circ = \Delta G^\circ_1 + \Delta G^\circ_2$$

$$-(n_1 + n_2) FE^\circ = -n_1 FE^\circ_1 + (-n_2 FE^\circ_2)$$

$$E^\circ = \frac{n_1 E^\circ_1 + n_2 E^\circ_2}{(n_1 + n_2)} = \frac{2 \times 1.18 + 2 \times 1.65}{4}$$

11.5.2 Frost diagram

Plot of product of oxidation number (N) and reduction potential (E°) against oxidation number of the element (N) or plot between standard Gibbs energy against oxidation number (Figure 11.2).

(1) The most stable oxidation state will lie lowest in the frost diagram.

(2) The slope of the line joining any two points in the Frost diagram is equal to the standard potential of the couple formed by the two species represented by the joints. More positive the slope, the great the oxidizing power of the couple.
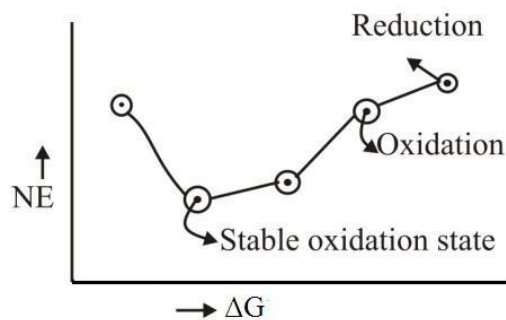
Figure 11.2: Frost diagram in general

A species in a Frost diagram is unstable with respect to disproportionation, if its point lies above the line connecting two adjacent species.

(3) N_2O_4 undergo disproportionation, Figure 11.3.

$2e^- + N_2O_4 \; \square \; 2NO_2$
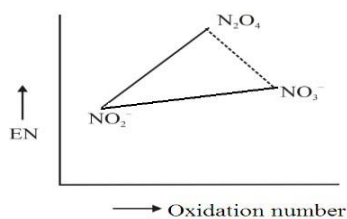
Figure 11.3: Frost diagram showing disproportionation of N₂O₄

Reverse of disproportionation is called comproportionation (Figure 11.4):

$2OH^- + NO + N_2O_4 \; \square \; 2NO_2^- + H_2O$

Two species will tend to comproportionate into an intermediate species that lies below the straight line joining the terminal species. Frost diagram showing comproportionation is given in Figure 11.4.
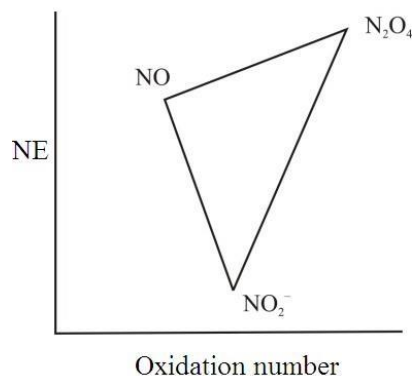
Figure 11.4: Frost diagram showing comproportionation
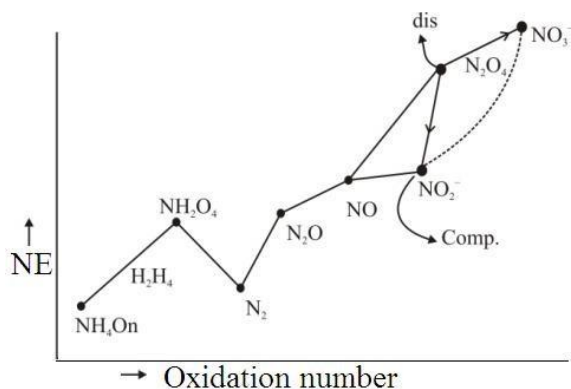
Figure 11.5: Frost diagram for nitrogen

Construction of Frost diagram from Latimer diagram (Figure11.5.)

$$Tl^{3+} \xrightarrow{+1.26V} Tl^{+} \xrightarrow{-0.34V} Tl$$

$$+0.73$$

$$Tl \square Tl^{+} + e^{-} \quad E^{0} = 0.34V$$

$$Tl \square Tl^{3+} + 3e^{-} \, NE°$$

$$= 2.19$$
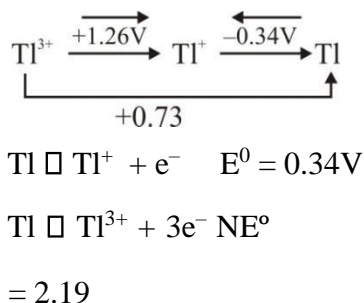
Thus, calculated NE along with oxidation can be plotted to get frost diagram.
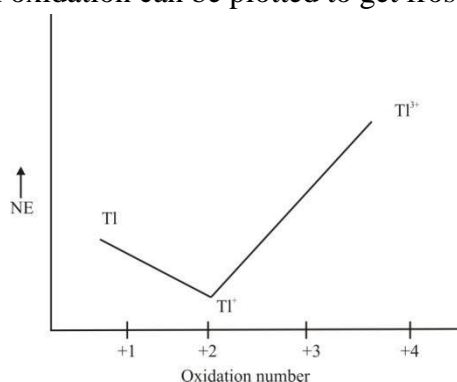
Figure 11.5: Construction of Frost diagram for thallium from Latimer diagram

Consider the Frost diagram for manganese in acidic medium (Figure 11.6). Mn(II) is the most stable oxidation state. Mn^{3+} and MnO_4^{2-} are unstable and undergo disproportionation because both Mn^{3+} and MnO_4^{2-} species lie above the line joining Mn^{2+} and MnO_2 and MnO_2 and MnO_4^{-}, respectively. Thus, disproportionate into the respective species (Figure 8.6). $2H_2O +$ $2Mn^{3+} \square MnO_2 + Mn^{2+} + 4H^{+}$

$$4H^{+} + 3MnO_4^{2-} \square MnO_2 + 2MnO^{-} + 2H_2O$$
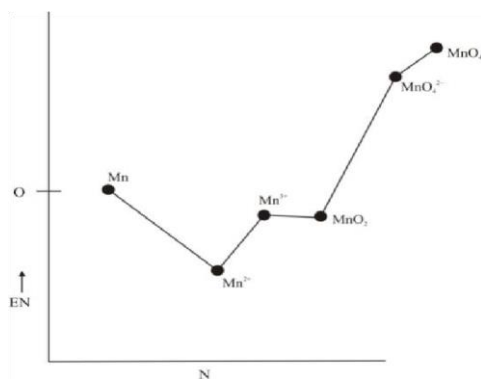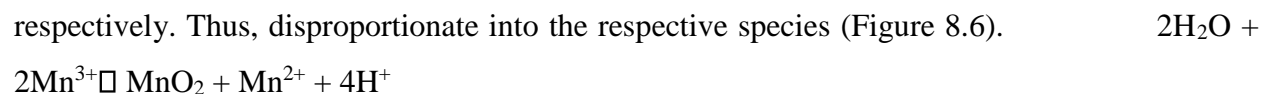
Figure 11.6: Frost diagram for manganese in acidic medium

11.5.3. Ebsworth diagram

Free energy is plotted along the vertical axis against oxidation states horizontal axis. The free energy changes between oxidation states are readily calculated from reduction potential. The lower oxidation state in the diagram is stable oxidation state. Mn^{3+} more stable than MnO_4^- but not than Mn^{2+} (Figure 11.7).
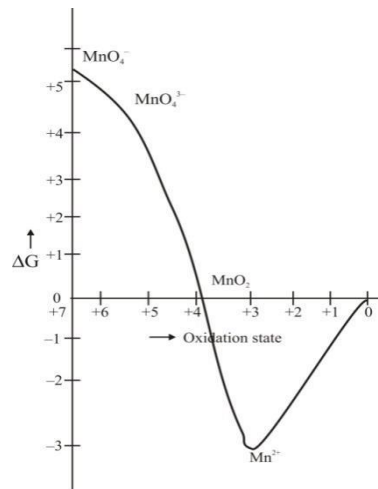
Figure 11.7. Ebsworth diagram of manganese: Free energies of oxidation states of manganese relative to oxidation state of the metal in aqueous solution at pH = 0.

11.5.4. Pourbaix diagram: Possible stable phases of an aqueous electrochemical system

Potential / pH diagrams are called as Pourbaix diagrams (Figure 11.8).

(1) $Fe^{3+} + e^- \rightarrow Fe^{2+}_{(aq)} - E° = +0.77V$ Not depend on pH (Horizontal line)

(2) $Fe^{3+}_{(aq)} + 3H_2O\ (R) \rightarrow Fe\ (OH)_3 + 3H^+_{(aq)}$ Not redox reaction, no change in oxidation number but depends upon pH.
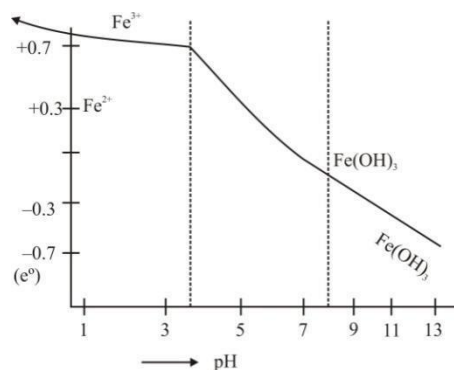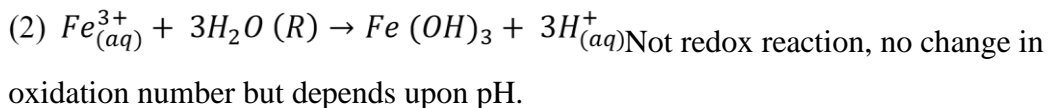
Figure 11.8: Pourbaix diagram of iron

(3) $Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$ pH increases,

potential will change negatively.

Disproportionation reactions

These are the redox reactions in which the oxidation number of a species can increase and decrease simultaneously.

$$2Cu^+ \rightarrow Cu^{2+} + Cu^0$$

$Cu^+ \xrightarrow{\text{oxidation half}} Cu^{2+} + e^-$ $E^o{}_{Cu+/Cu2+} = -0.16V$

$e^- + Cu^+ \xrightarrow{\text{Reduction half}} Cu^{\circ} + e^-$ $E^o{}_{Cu+/Cu^o} = +0.52V$

Overall reaction $2Cu^+ \rightarrow Cu^{2+} + Cu^o$; $E^o = +0.36V$ E^o
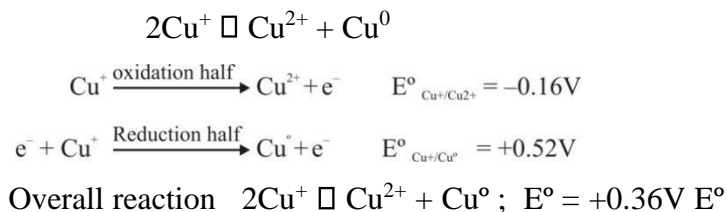
is positive, hence the reaction is feasible.

Redox stability of water depends upon pH value. The species with E^o values greater than [1.23V – (0.591pH) V] can oxidize H_2O to O_2 and the species whose E^o value is more negative than (–0.0591pH) V can reduce H^+ to H_2.

Comproportionation reaction

This reaction is opposite of disproportionation reaction and in this two oxidation states convert into only one oxidation state: $Cu^{2+} + Cu^o \rightarrow 2Cu^o$ (–0.37V)

Autooxidation

It is same as disproportionation reaction but it occurs slowly without the action of heat, light or electricity: $3HNO_2 \rightarrow HNO_3 + 2NO$

                    +3   +5   +2
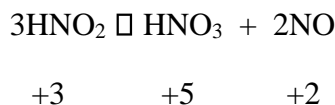
11.6 PRINCIPLES INVOLVED IN THE EXTRACTION OF ELEMENTS

Gibbs free energy change (ΔG), entropy change (ΔS) and ΔH of a reaction are related as follows:

$\Delta G = \Delta H - T\Delta S$

From this equation, you can observe that if ΔS is positive, $T\Delta S$ will also increase and the value ΔG will be negative ($\Delta H < T\Delta S$). Thus, the reaction in the forward direction will occurs spontaneously.Equilibrium constant (K) and $\Delta G°$ are related as:

$$\Delta G° = - RT \log K$$

From this equation, it can be concluded that higher the value of K, more negative will be the value of $\Delta G°$ and thus, the reaction will again proceed towards forward direction.When ΔG for a reaction is positive, it can be proceed spontaneously by coupling with another reaction with larger (in negative) ΔG value so that the resultant ΔG value should be negative. This type of coupling reactions can be better understood by Ellingham diagram.

11.6.1. Thermodynamic principle for the reduction of metal oxides to metal by carbon ($C_{(s)}$) or CO $_{(g)}$

Metal oxide on reduction with $C_{(s)}$ converts into $CO_{(s)}$ or $CO_{2(g)}$ as shown by the following redox reactions :

$$M_xO_{(s)} + C_{(s)} \longrightarrow xM_{(s)} + CO_{(g)}$$

$$M_xO_{(s)} + \tfrac{1}{2}C_{(s)} \longrightarrow xM_{(s)} + \tfrac{1}{2}CO_{2(g)}$$

Conversion of $C_{(s)}$ to $CO_{(g)}$ and $M_{(s)}$ to $M_xO_{(s)}$ are oxidation reactions :

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)}; \Delta G° = \Delta G°_{(C\rightarrow CO)} \ xM_{(s)}$$

$$+ \tfrac{1}{2}O_{2(g)} \rightarrow M_xO_{(g)}; \ \Delta G°= \Delta G°_{(M\rightarrow MxO)}$$
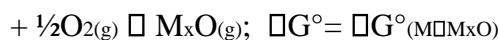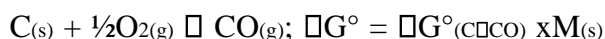
After subtracting these two equations, we get –

$$C_{(s)} + M_xO_{(s)} \rightarrow xM_{(s)} + CO_{(g)} ; \Delta G° = \Delta G°_{(C\rightarrow CO)} - \Delta G°_{(M-MxO)}$$
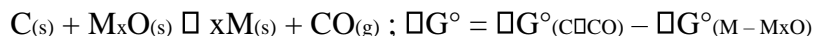
Hence, if $\Delta G°(C – CO)$ is more negative as compared to $\Delta G°_{(M\rightarrow M2O)}$, then only the reaction is feasible. The other reaction where $C_{(s)}$ can be converted to $CO_{2(g)}$, similarly the $\Delta G°_{(C\rightarrow CO2)}$ should be more negative as compared to $\Delta G°_{(M\rightarrow MxO)}$ for reaction to occur spontaneously. In the similar way, we can understand the reaction of M_xO to xM on reaction with CO.

$$M_xO + CO_{(s)} \; \square \; xM + CO_{2(g)} \text{ (Redox reaction)}$$

The two oxidation reactions of $CO_{(g)}$ and M are

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \; \square \; CO_{2(g)}; \; \square G^\circ = \square G^\circ_{(CO\square CO2)} \; xM_{(s)}$$

$$+ \tfrac{1}{2}O_{2(g)} \; \square \; M_xO_{(g)}; \; \square G^\circ = \square G^\circ_{(xM\square MxO)}$$
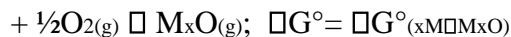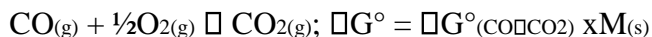
The overall free energy change will be

$$\Delta G^\circ_{(CO \rightarrow CO_2)} - \Delta G^\circ_{(M \rightarrow MxO)}$$

If $\Delta G^\circ_{(CO \rightarrow CO2)} \square G^\circ_{(CO\square CO2)}$ will be more negative than $\square G^\circ_{(M\square MxO)}$, the overall free energy change will also be negative and reduction of $M_x \square M$ with CO will be feasible.

11.6.2. Reduction of a metal oxide by another metal

$$\begin{array}{cc} X + YO \longrightarrow XO + Y \\ \text{(metal)} \quad \text{(Metal oxide)} \end{array}$$
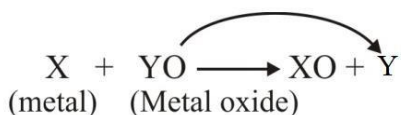
In the above reaction, X and Y are two different metals, while YO and XO are oxides of these metals.

Change in free energy = free energy change of products – free energy change of reactants

Change in free energy of reaction = $\square G^\circ_{(X \square XO)} - \square G^\circ_{(YO \square Y)}$

As X and Y are elemental form, the change in free energy of reaction becomes:

$$\square G^\circ_{(XO)} - \square G^\circ_{(YO)}$$

The $\square G^\circ_{(XO)}$ value should be negative so that the overall free energy change is negative.

11.7 SUMMARY

In this Unit, you have studied that

- Oxidation and reduction reactions occur simultaneously and are called redox reactions.
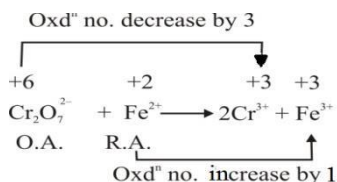
Here Fe^{2+} has been oxidized to Fe^{3+} while $Cr_2O_7^{2-}$ has been reduced to Cr^{3+}.

- Oxidation state or oxidation number of an element or an atom is the charge that appears when the particular element is present in the combined state.

- In oxidation reaction, loss of electron(s) or in the increase in oxidation number takes place.

- Oxidizing agent is the species that accepts electron/s and reduce itself.

- Reduction reaction is the process where either gain of electron/s or decrease in oxidation number is observed.

- Reducing agent is a species which donates electron/s and oxidize itself during the course of a redox reaction.

- The tendency of cathode to gain the electron/s is called reduction potential while the tendency of the other half electrode (anode) to lose the electron/s is called as oxidation potential. Reduction potential is denoted by E_{red} and oxidation potential by E_{ox}. If reduction / oxidation potential of a compound is measured under standards conditions, then it is called as standard reduction ($E°_{red}$)/standard oxidation potential ($E°_{ox}$).

- Electrochemical series is arrangement of standard oxidation potentials in their increasing order.

- The potential data can be utilized to know feasibility of a chemical reaction, to calculate redox potential and free energy change, to calculate the value of reduction potential of a given electrode at non standard conditions, to calculate e.m.f. of a given cell at standard conditions, to calculate the value of E_{cell}, to know the oxidizing and reducing property of substances in aqueous solution and to calculate equilibrium constant.

- Oxidation cycle of alkali metals and reduction cycle of halogens explain pattern of their reduction potential data.

- Redox stability of water explains stability or instability of certain species in water.

- Latimer diagrams show the standard reduction potentials connecting various oxidation states of an element in a horizontal line with the most oxidized form on the left and the

elements with successive lower oxidation states on the right. Latimer diagram of chlorine in basic medium is given below:

$$ClO_4^- \xrightarrow{+0.37} ClO_3^- \xrightarrow{+0.30} ClO_2^- \xrightarrow{+0.68} ClO^- \xrightarrow{+0.42} Cl_2 \xrightarrow{+1.36} Cl^-$$

with +0.49v spanning ClO_3^- to ClO^-, +0.33v spanning ClO_4^- to ClO_2^-, and +0.89v spanning ClO^- to Cl^-.
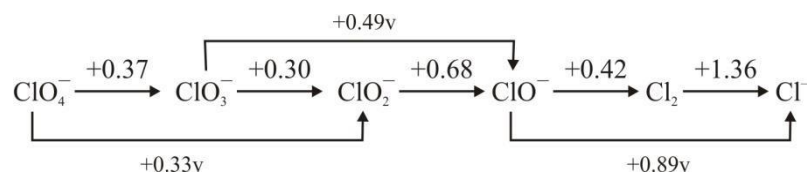
- Latimer diagram is useful to predict feasibility of a redox reaction, unstable species and help in calculating $E°$ value for any non-adjacent couple.

- Frost diagrams are plot between $NE°$ and oxidation state of an element. This diagram is helpful in predicting the most stable oxidation state of the element, unstable species and oxidizing power of coupled reactions. It also tells about the species which can comproportionate.

- Ebsworth diagrams are the plots between oxidation state and free energy.

- Pourbaix diagrams are plotted between potential and pH.

- Disproportionation reactions are redox reactions in which the oxidation number of a species increases and decreases simultaneously.

- Comproportionation reactions are opposite of disproportionation reactions in which two oxidation states converts into a single oxidation state.

- Autooxidation reaction is similar to disproportionation reaction but occurs without any external support like heat, light or electricity.

- Free energy change, entropy change and enthalpy change of a chemical reaction control extraction of elements during their metallurgy.

11.8 TERMINAL QUESTIONS

A) Fill in the blanks:

i. The redox reactions involve two half reactions, a ………….. half and an ………….. half and these two always occur together.

ii. Charge that appears when the other atoms are removed is called as

…………………………

iii.   The reaction in which, loss of electrons results in the increase in oxidation number of its atom / atoms is called ………………… reaction.

iv.   Gain of electron or decrease in oxidation number of its atom / atoms is known as …………………...

v.   …………………………….. is also known as oxidation state.

vi.   Electrode potential is a measure of the tendency of an electrode in a half-cell to ……………. or ………………… electrons.

vii.   ……………………………………… potential is the potential of the electrode at which oxidation takes place and hence, is a measure of the tendency of the electrode in a half-cell to get oxidized or to lose electrons.

viii.   The values of ……………….. Potentials have been arranged in their increasing order, in the form of a series, which is called electrochemical series.

ix.   Relationship between redox   potential and free   energy change   is …………………..

x.   In ……………………. diagrams numerical value of the standard potential is written over a horizontal line connecting species with the element in different oxidation state.

xi.   If sum of the reduction and oxidation potential is positive, then the standard free energy change for the ……………………. will have a negative value and spontaneous ………………………….. is possible.

xii.   In ………………… diagram, free energy is plotted along the vertical axis against oxidation states horizontal axis.

xiii.   ………………… diagram is plot between potential and pH.

xiv.   Plot of product of oxidation state (N) and reduction potential (E^o) against oxidation number of the element (N) or plot between standard Gibbs energy against oxidation number is ……………………… diagram.

xv.   …………………………. reaction is opposite of disproportionation reaction.

xvi. It is same as disproportionation reaction but it occurs slowly without the

action of heat, light or electricity is…………………………………... **B)**

State True (T) or False (F).

i. Rusting of iron, use of lead acid batteries in inverters and other batteries used for different purposes, photosynthesis, respiration and combustion are the examples of oxidation-reduction reactions.

ii. The reduction half reaction gains electrons and called as reducing agent while the oxidation half is called as oxidizing agent.

iii. Redox reactions are reduction reactions.

iv. Loss of electrons results in the increase in oxidation number of its atom / atoms is called oxidation reaction.

v. Gain of electron or decrease in oxidation number of its atom / atoms is known as electronation. vi. In metal-metal ion electrode, metal (M) immersed in the solution containing metal ions (M^{n+} ions).

vii. Unit of electrode potential is volt per meter (V/m). viii.

Standard electrode potential is denoted by E.

ix. The tendency of the electrode in a half-cell to get reduced over to gain electrons is reduction electrode potential.

x. If E^o is positive, the reaction will be thermodynamically feasible if value of $\Box G^o$ is negative.

xi. Nernst equation is

(E red) elec = (E^o red) elec – 2.303RI log Conc. of reactants

$$\frac{}{np} \qquad \frac{}{\text{Conc. of products}}$$

xii. The substance which has a (+) ve value of E^o_{red} has a tendency to gain electrons to undergo reduction and hence is capable of acting as an oxidizing agent in aqueous solution.

xiii. Since E^o_{red} value increases down the electro-chemical series, the reducing power of the reducing agents increases in the series.

xiv. Redox reactions are irreversible in nature.

xv. In Latimer diagram, the most highly reduced form of an element is written on the left and the most highly oxidized species written on the right side of the horizontal line.

xvi. The most stable oxidation state lies lowest in the Frost diagram.

C) Long answer questions

i. What is electrochemical series? Discuss its applications.

ii. Define the terms disproportionation, comproportionation and auto-oxidation with example. iii. Explain the main features of Latimer diagram. Also, discuss the usefulness of Latimer diagram.

iv. Discuss oxidation and reduction cycle with examples.

v. What do you mean by redox stability of water ?

vi. Discuss different principles involved in the extraction of elements. vii. Given that

$$Sn^{4+} + 2e \rightleftharpoons Sn^{2+} \quad E^\circ = 0.154V$$

$$Fe^{3+} + e \rightleftharpoons Fe^{2+} \quad E^\circ = 0.771 V$$

Determine E° cell?

viii. Will it be possible to oxidize Cl^- and Co^{2+} with acidic $Cr_2O_7^{2-}$? Given that E° ($Cl_2/2Cl^-$) = 1.3595V, $E^\circ(Co^{3+}/Co^{2+})$ = 1.81 V and E° ($Cr_2O_7^{2-}/2Cr^{3+}$) = 1.33V. ix. Will permanganate ion oxidize H_2O to evolve O_2 in acidic medium? Given that

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-} \quad E^\circ = 0.56V$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O(e) \quad E^\circ = 1.23V$$

x. The Latimer diagram for americium is:

$$AmO_2^{2+} \xrightarrow{+1.70} AmO_2^+ \xrightarrow{+0.86} Am^{4+} \xrightarrow{2.62} Am^{3+} \xrightarrow{0:207} Am$$

with 1.724 and 1.726 couplings shown below.

Predict the species which disproportionate into which species?

$$Am_{4+}Am_{3+}$$

$$AmO_{2+}$$

$$AmO_2Am_{3+}$$

$$AmO_{22+}$$

xi. The reduction potentials are:

$$Cu^{2+} + 2e \rightarrow Cu^+ \qquad\qquad E^\circ = 0.15V$$

$$Cu^+ + e^- \rightarrow Cu \qquad\qquad E^\circ = 0.50V$$

Calculate the value for $Cu^{2+} \rightarrow Cu$ and draw Latimer diagram

$$Cu^{2+} \xrightarrow{\;0.15\;} Cu^+ \xrightarrow{\;0.50\;} Cu \quad E_{Cu2+\rightarrow Cu} \underline{\quad\quad\quad} \frac{2\times0.15+1\times0.50}{3} = \frac{0.45+0.50}{3} = \frac{0.95}{3} = 0.31V$$
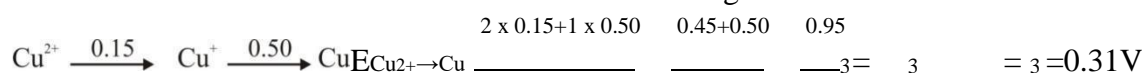
xii. Latimer Diagram of iron is:

$$Fe^{3+} \xrightarrow{\;0.771V\;} Fe^{2+} \xrightarrow{\;0.44V\;} Fe$$

$$0.04V$$
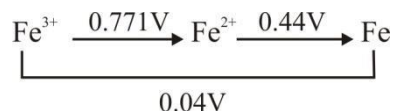
How would you derive the potential for iron?

$$e^- + Fe^{3+} \rightarrow Fe^{2+}$$

$$Fe^{2+} + 2e^- \rightarrow Fe \quad \frac{(+1 \times 0.771)+ (+2 \times 0.44)}{3} = \frac{0.771+0.88}{3} = \frac{1.651}{3} = 0.550V$$
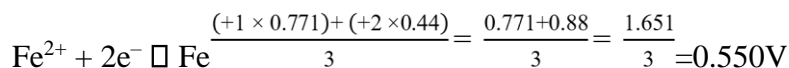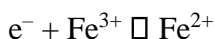
xiii. The Latimer diagram for manganese system is:-

$$MnO_4^- \xrightarrow{\;0.56\;} MnO_4^{2-} \xrightarrow{\;2.26\;} MnO_2 \xrightarrow{\;0.95\;} Mn^{3+} \xrightarrow{\;0.51\;} Mn^{2+}$$

$$2e^- + MnO_4^{2-} \rightarrow MnO_2 \; e^-$$

$$+ MNO_2 \rightarrow Mn^{3+}$$

$$e^- + Mn^{3+} \rightarrow Mn^{2+} \frac{(2.26 \times 2)+ (0.95 \times 1)+ (0.51 \times 1)}{4} = \frac{4.52+0.95+0.51}{4} = \frac{5.98}{4} = 1.49V$$
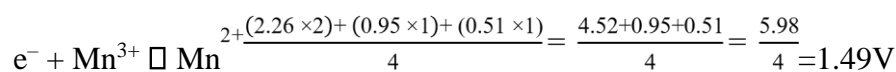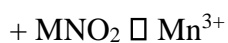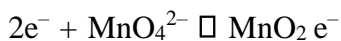
xiv. Show that disproporionation of H_2O_2 into O_2 and H_2O is spontaneous under acidic conditions. Given that:

$$O_2 \xrightarrow{\;+0.70\;} H_2O_2 \xrightarrow{\;+1.76\;} H_2O$$

$$2e^- + 2H^+ + O_2 \rightarrow H_2O_2; \qquad E^\circ = 0.70V$$

$$2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O; \; E^\circ = +1.76V$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \; E^\circ = 1.06V$$
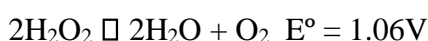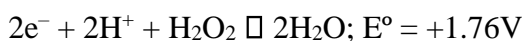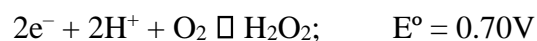
ANSWERS

A) Fill in the blanks

i. reduced, oxidized ii. oxidation number

iii. oxidation iv. reduction

v. oxidation number

vi. gain, lose

vii. oxidation electrode

viii. reduction ix. $\Delta G^{\circ} = -nE^{\circ}F$

x. Latimer

xi. Disproportionation

xii. Ebsworth xiii. Pourbaix xiv. Frost

xv. Comproportionation

xvi. autooxidation

B) True (T) or False (F)

i. T

ii. F iii. F iv. T v. T vi. F vii. F viii. F ix. T x. T xi. F xii. T

xiii. F xiv. F xv. F

xvi. T

11.9 REFERENCES AND FURTHER STUDIES

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UNIT 12: CATALYSIS

CONTENTS:

12.1 INTRODUCTION

There are certain reactions which do not proceed to completion even when carried out for indefinite periods of time. These reactions get completed very soon when small quantity of a foreign substance is added. Berzelius in 1836 realised that there are substances which increase the rate of a reaction without themselves being consumed. These substances are called catalyst. A catalyst is defined as a substance which increases the rate of the chemical reaction without undergoing any change and can be recovered as such at the completion of the reaction. The phenomenon of increase in the rate of a reaction with the help of the catalyst is known as catalysis.Usually a catalyst accelerates a reaction as was originally thought by Berzelius. But a number of cases are now known where the catalyst definitely retards the progress of a reaction.

Thus a catalyst is a substance which alters the rate of a chemical reaction, itself remaining unchanged chemically at the end of the reaction. The process is called as catalysis.

Now it is evident from the above definition a catalyst may increase or decrease the rate of a reaction. A catalyst which increases the rate of a reaction is called positive catalyst and the process positive catalysis or simply catalysis. A catalyst which retards the rate of a reaction is called negative catalyst and the process negative catalysis.

The decomposition of potassium chlorate takes place much more rapidly and at a much lower temperature if a little of manganese dioxide is added to it. Manganese dioxide is not used up at all and can be recovered unchanged.

The combination of hydrogen and oxygen to form water which is slow at ordinary temperature proceeds more rapidly in the presence of platinum.

While studying chemical kinetics you have studied that when a catalyst is added a new reaction path with a lower energy barrier is provided

Fig. 7. The concept of energy barrier in chemical reactions
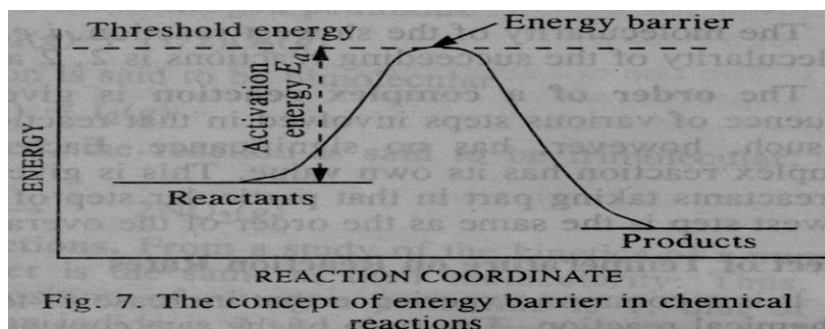
Fig-12.1

Since energy barrier is reduced in magnitude a large number of molecules of the reactants can get over it. This increases the rate of the reaction. In this case the catalyst does not alter the position of the equilibrium in a reversible reaction. It simply hastens the approach of the equilibrium by speeding up both the forward and the backward reactions. How the catalyst works you will study in this chapter later.

12.2 OBJECTIVE

It is an interesting aspect of chemistry that certain reactions which do not proceed to completion even when carried out for indefinite periods of time, get completed within a matter of few minutes when small quantity of a foreign substances added. This substance is known as catalyst. Because of this property it is important to study this topic in detail particularly for many industrial processes.

Autocatalysis:

In certain reactions, one of the product acts as a catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate becomes much more rapid due to the presence of manganese (II) ions which are formed in the reaction.

This type of reaction in which one of the products itself acts as a catalyst is known as autocatalysis.

12.3 CHARACTERISTIC OF CATALYTIC REACTIONS

As you have studied that a catalyst remains unchanged during the chemical reaction although there are different type of catalytic reactions, the following characteristics are common to most of them. These features are often referred as the criteria of catalysis.

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction. However the catalyst may undergo a physical change. Thus granular manganese dioxide used as a catalyst in the thermal decomposition of potassium chlorate is left in a fine powder at the end of the reaction.

2. A small quantity of catalyst is generally needed to produce almost unlimited reaction. Sometime a trace of metal catalyst is required to affect very large amounts of reactants. For example one ten-millionth of its mass of finely divided platinum is all that needed to catalyse the decomposition of hydrogen peroxide.

   On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl + [AlCl_3]$$
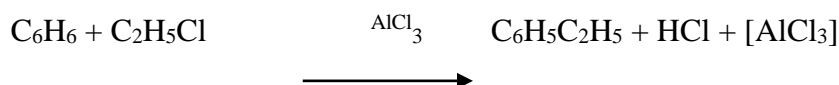
Anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene.

3. A catalyst is more effective when finely divided in heterogeneous catalysis; the solid catalyst is more effective when in a state of fine subdivision that it is used in bulk. Finely divided nickel is more effective as catalyst than lump of solid nickel.

4. A catalyst is specific in action. While a particular catalyst works for one reaction it will not necessarily work for another reaction. Different catalysts can bring about completely different reactions for the same reaction. For example ethanol gives ethene when passed over hot aluminum oxide.

$$C_2H_5OH + [Al_2O_3] \longrightarrow C_2H_4 + H_2O + [Al_2O_3]$$
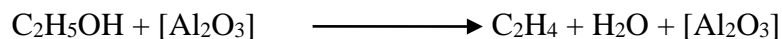
But with hot copper it gives ethanol (CH_3CHO).

$$C_2H_5OH + [Cu] \longrightarrow CH_3CHO + H_2 + [Cu]$$

5. A catalyst cannot in general initiate a reaction.As you have studied earlier that in most cases a catalyst speeds up a reaction already in progress and does not start the reaction but there are certain reactions where the reactants do not combine for very long time.

For example a mixture of hydrogen and oxygen which remains   unchanged almost indefinitely at room temperature can be brought to reaction by the catalyst platinum black in a few seconds.

$$H_2 + O_2 \quad\quad \text{room temp.} \quad\text{No reaction}$$

$$2H_2 + O_2 \quad \underrightarrow{\text{Pt black}} \quad\quad 2H_2O$$
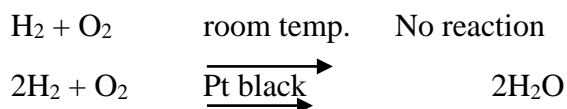
This is because the reacting molecules do not possess minimum   kinetic energies for successful collsion.The molecules rebound from collisions without reacting at all. But in the presence of the catalyst   they   get sufficient energies after reacting with catalyst and are now in a position to give products after further collision with other molecules.

6. A catalyst does not affect the final position of equilibrium although it   shortens the time required to establish the equilibrium. It means that in a reversible reaction the catalyst accelerates the forward and reverse reactions equally. Thus the ratio of the rates of two opposing reactions i.e. equilibrium constant remains unchanged.

The effect of a catalyst on the time required for equilibrium to be established for the reaction

$$A + B \rightleftharpoons C + D$$
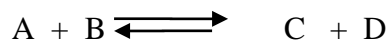
is shown in fig-12.2
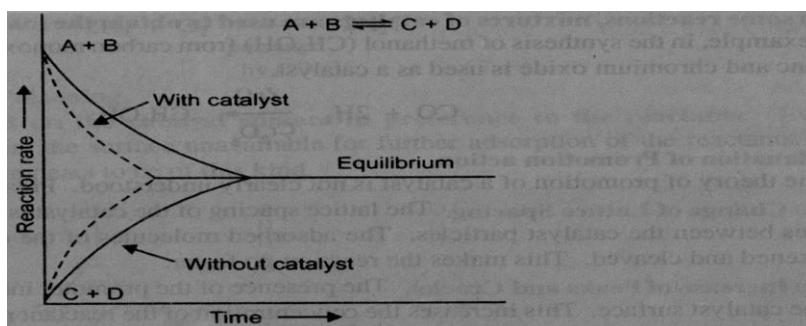
Fig-12.2

To start with the concentration of A and B are at the maximum and hence rate of forward reaction is maximum. As the time passes the rate of reaction decreases till the equilibrium is established. For the reverse reaction the initial concentration of C and D are zero and the rate of reaction is lowest. As the time passed the rate of reaction increases till the equilibrium is established. Similar

curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are altered equally but the equilibrium is established in a much shorter time.

7. The catalyst cannot alter the nature of products of the reaction. The combination of hydrogen and nitrogen under suitable conditions results invariably in the formation of ammonia whether a catalyst is added or not.

8. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction with a catalyst. You have already studied in your earlier classes the effect of temperature on reversible reactions under Le Chatelier's Principle, which says that *"If equilibrium is subjected to a stress, the equilibrium shifts in such a way as to reduce the stress".*

Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise of temperature may cause their coagulation. In such a case the rate of reaction increases up to certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature called the *optimum temperature.*

12.4 CLASSIFICATION OF CATALYSIS

There are two types of catalysis:
(a) Homogenous catalysis

(b) Heterogeneous catalysis

A third type of catalysis known as enzyme catalysis which is largely of biological interest, you will study in this chapter later on.

12.4.1 Homogenous catalysis

When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis. Following are some *examples of homogeneous catalysis: Gas phase:*

(i)   Oxidation of sulpher dioxide (SO_2) into sulphurtrioxide (SO_3) with nitric oxide (NO) as catalyst.

$$2SO_2 + O_2 + [NO] \longrightarrow 2SO_3 + [NO]$$

gas   gas   gas   gas

(ii)   Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst

$$CH_3CHO + [I_2] \longrightarrow CH_4 + CO + [I_2]$$

vapour vapour   gas   gas *example of*
homogeneous catalysis in solution phase:

Many reactions in solutions are catalysed by acids (H^+) and bases (OH^-).

(i)   Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6 +$$

[H_2SO_4] cane sugar   glucose   fructose

(ii)   Hydrolysis of an ester in the presence of acid or alkali

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H+/OH} CH_3COOH +$$

C_2H_5OH ethyl acetate   acetic acid

ehtenol

12.4.2 Heterogeneous catalysis

The catalysis in which the catalyst is in a different physical state from the reactants is termed as heterogeneous catalysis. The most important of such reactions are those in which reactants are in the gas phase while the catalyst in solid phase. This form of catalysis has great industrial importance, as you will study later in this chapter.

Example of heterogeneous catalysis

(i)   Oxidation of ammonia to nitric oxide in the presence of a platinum gauze.

$$4NH_3 + 5O_2 + [Pt] \longrightarrow 4NO + 6H_2O + [Pt]$$

gas   gas solid

(ii)   Combination of hydrogen and nitrogen to form ammonia in the presence of finely divided iron (Haber's process for ammonia).

$$N_2 + 3H_2 + [Fe] \longrightarrow 2NH_3 + [Fe]$$

gas gas solid

(iii) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_2, (Contact process for sulphuric acid).

$$2SO_2 + O_2 + [Pt] \longrightarrow 2SO_3 + [Pt]$$

gas   gas   solid
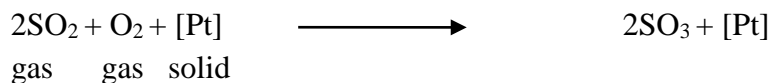
(iv) Hydrogination reaction of unsaturated organic compounds are catalysed by finely divided nickel

$$H_2C = CH_2 + H_2 + [Ni] \longrightarrow H_3C\text{-}CH_3 + [Ni]$$
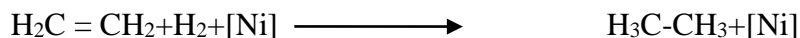
(v) Decomposition of hydrogen peroxide in aqueous solution is catalysed by gold and platinum in colloidal form as well as by mercury and oxides of metals like lead, manganese cobalt, nickel etc.

$$2H_2O_2 + [Pt] \longrightarrow 2H_2O + O_2 + [Pt]$$
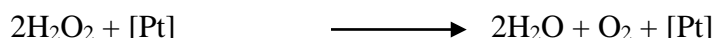
(vi) The decomposition of potassium chlorate is catalysed by manganese dioxide is shown below

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

The above reaction is heterogeneous, though both reactants are in the same phase (solid), because every solid forms a new phase.

12.4.3 Promoters

It has been observed in a number of cases that the activity of a catalyst is considerably increased by the addition of a second substance which by itself has no catalytic property. Such a substance which promotes the activity of catalyst is called promoter. Thus molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \xrightarrow[+Mo]{Fe} 2\,NH_3$$
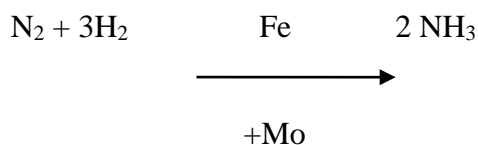
In the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc oxide and chromium oxide is used as catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$
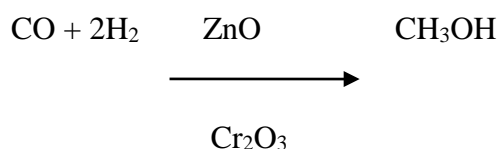
Explanation of promoter action

The action of promoter is not clearly known, this action may be because of the following points:

(1) Change of lattice spacing:

The lattice spacing of the catalyst is changed. Thus enhancing the spaces between catalyst particles. The adsorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes the reaction go faster (fig 12.3).
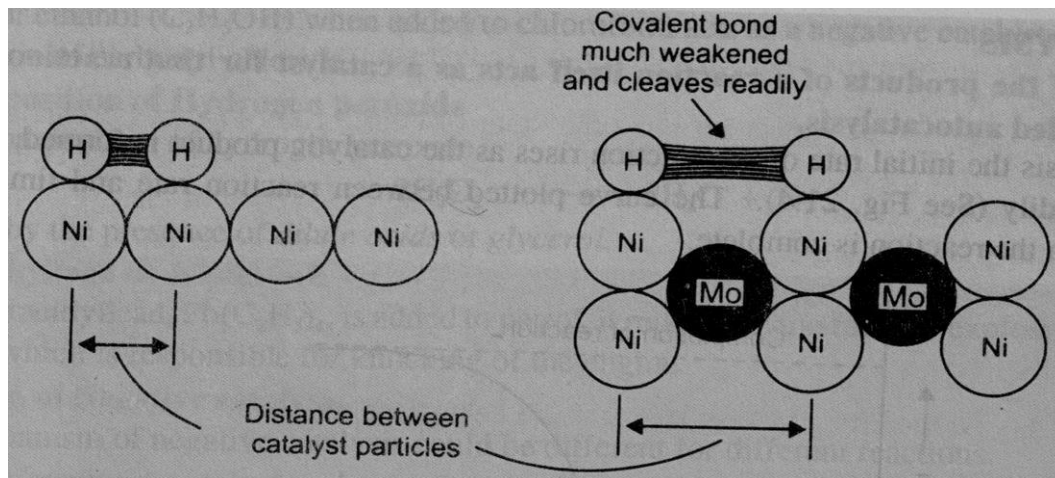
Fig-12.3

(2) Increased peaks and cracks:

The presence of promoter increases the peaks and cracks on the catalyst surface.This increases the concentration of the reactant molecules and hence the rate of reaction.

12.4.4 Catalytic poisoning

A substance which destroys the activity of the catalyst to accelerate a reaction is called a poison and the process and the process is called catalytic poisoning.

Example of catalytic poisoning

(i)   The platinum catalyst used in the oxidation of sulphurdioxide is poisoned by arsenic oxide (AS_2O_3).

$$SO_2 + O_2 \quad \xrightarrow{Pt} \quad 2SO_3$$

Poisoned By As_2O_3
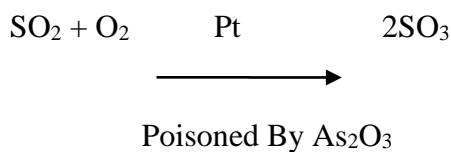
(ii)   The iron catalyst used in the synthesis of ammonia is poisoned by H_2S

$$N_2 + 2H_2 \quad \xrightarrow{Fe} \quad 2NH_3$$
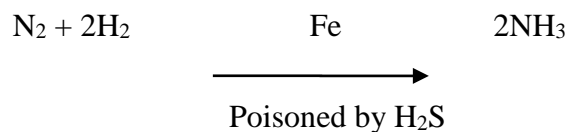
Poisoned by H_2S

(iii)   The platinum catalyst used in the oxidation of hydrogen is poisoned   by   carbon monoxide.

$$2H_2 + O_2 \xrightarrow{\quad Pt \quad} 2H_2O$$

Poisoned by CO
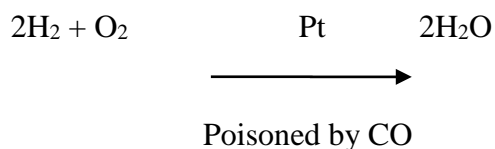
Explanation of catalytic poisoning

(i) The poison is adsorbed on the catalyst surface is presence of the reactants. It has been found that even a monolayer renders the surface unavailable for further adsorption of the reactants. The poisoning by As_2O_3 or CO appears to be of this kind.
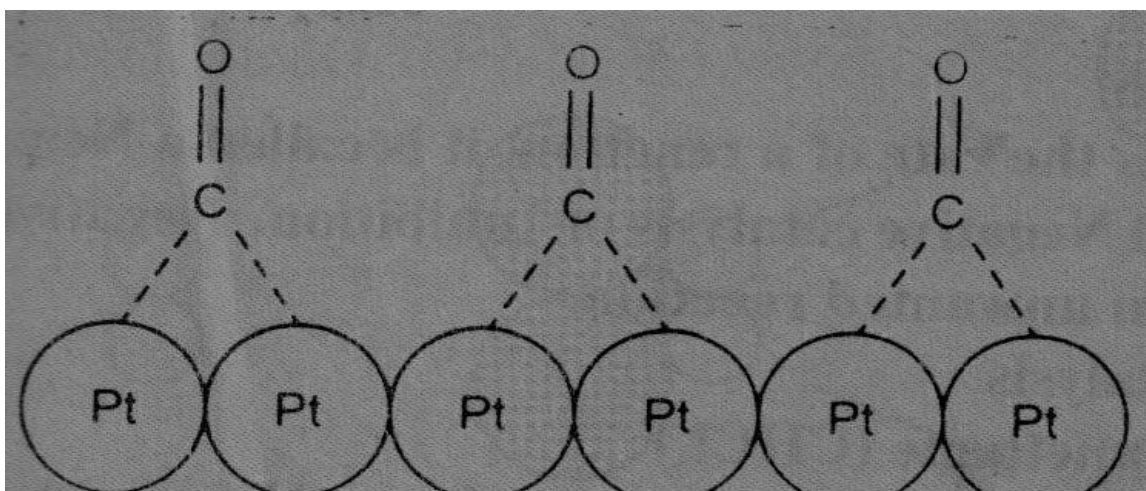
Fig -12.4

(ii)   The catalyst may combine chemically with the impurity.

The poisoning of iron catalyst by H_2S falls in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

12.4.5 Negative catalysis

In some cases it has been found that a catalyst instead of speeding up a reaction may actually retard it. Such substances are called negative catalysts   or inhibitors. The negative catalysts are of great use when it is desired to   slow down altogether a particular reaction.

(i) In the decomposition of hydrogen peroxide a small amount of acetanilide or glycerine when added slow down the reaction.

(ii) When tetraethyl lead $Pb(C_2H_5)_4$ is added to petrol it retards the too rapid or explosive combustion of the fuel which is responsible for knocking of the engine. **Explanation of negative catalysis**

Negative action of substances to catalyst could be different for different reactions.

(i) By poisoning the catalyst:

The negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture. For example the traces of alkali dissolved from the glass of a container, catalyse the decomposition of hydrogen peroxide (H_2O_2). But the addition of an acid would destroy the alkali catalyst thus prevents decomposition.

(ii) By breaking the chain reaction:

In some cases negative catalysis are believed to operate by breaking the chain of reaction. For example, the combination of hydrogen (H_2) and chlorine (Cl_2) which is a chain reaction is negatively catalysed by nitrogen trichloride (NCl_3).

$$Cl_2 \longrightarrow Cl^* + Cl^*$$

$$H_2 + Cl^* \longrightarrow HCl + H^*$$

$$H^* + Cl_2 \longrightarrow HCl + Cl^*$$
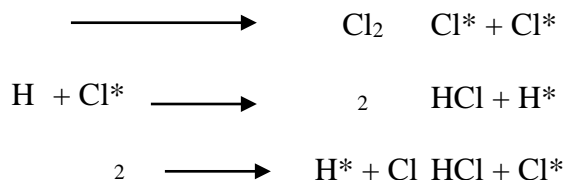
NCl_3 breaks the chain of reactions by absorbing the propagating species (Cl^*) and the reaction stops.

$$NCl_3 + Cl^* \longrightarrow \frac{1}{2} N_2 + 2Cl_2$$
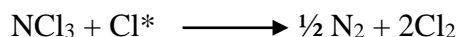
12.4.6 Enzyme catalysis (biochemical catalysis)

Definition

Enzymes are complex nitrogeneous organic compounds. They are produced in living cells of plants and animals. When dissolved in water they produce colloidal solution, hence they behave as very active catalysts in certain biochemical reactions. They are thus known as biochemical catalysts and the phenomenon itself is known as biochemical catalysis.

Enzyme is proteins having high molar mass of the order of 10,000 or even more. Each enzyme can catalyse a specific reaction.

Characteristics of enzyme catalysis

(i)   Enzymes form a colloidal solution in water and hence they are very active catalysts.

(ii) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.

(iii) They are highly specific in nature, i.e. , one catalyst cannot catalyse more than one reaction.

(iv)   They are highly specific to temperature. The optimum temperature of their activity is 35^0C to 40^0C. They are deactivated at 70^0C.

(v)   Their activity is increased in the presence of certain substances known as co- enzymes.

(vi)   A small quantity of enzyme catalyst is sufficient for a large change.

(vii)   They are destroyed by U.V. rays.

(viii) Their efficiency is decreased in the presence of electrolytes.

Examples of enzyme catalysis

(i)   Conversion of starch into maltose sugar:

The enzyme diastate produced in the germinated barley seeds converts starch into maltose sugar.

$$2 (C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{diastase}} nC_{12}H_{22}O_{11}$$
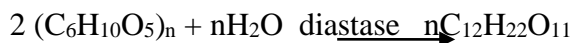
(ii)   The enzyme zymase produced by living yeast cells converts glucose into ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

Glucose   ethyl alcohol
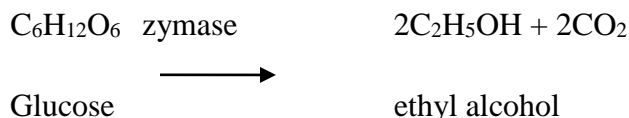
(iii)   The enzyme urease present in soyabean hydrolyses urea into ammonia.

$$NH_2 CONH_2 + H2 \xrightarrow{\text{urease}} 2NH_3 + CO_2$$

urea   ammonia
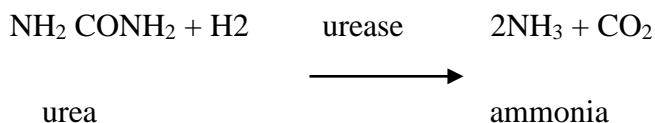
(iv)   Canesugar converted into glucose and fructose by the enzyme invertase.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

canesugar   glucose   fructose

The catalytic activity of enzymes is due to their capacity to lower the activation energy for a particular reaction.

E=Enzyme   S= substrat (reactant) ES = activated complex   P=product

12.5 INDUSTRIAL APPLICATION OF CATALYSIS

The following are a few important examples of heterogeneous catalytic reactions of industrial importance.

1. Haber's process for manufacture of ammonia

$$N_2 + 2H_2 \xrightarrow{\text{Fe/MO}} 2NH_3$$

Finely divided iron and molybdenum (as promoter) 200 atm. pressure and temperature range is $400^0C - 500^0C$ are applied in this process.

2. The manufacture of chlorine by Deacon's process.

$$4HCl + O_2 \xrightarrow{\text{CuCl}_2} 2H_2O + 2Cl_2$$
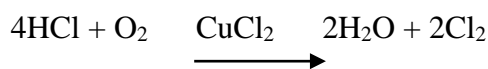
In this case cupric chloride is catalyst and excess of air functions as promoter. The temperature should be 500^0C.

3. Ostwald's process for the manufacture of HNO_3.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
$$2NO + O_2 \; 2NO_2 \longrightarrow$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$
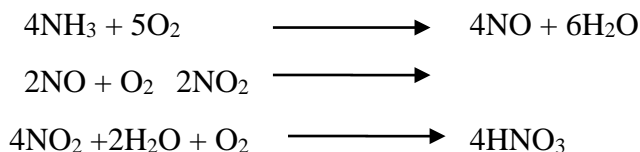
Conditions for better yield are platinised asbestos as catalyst + excess of air (as promoter) and temperature 300^0C.

4. Manufacture of hydrogen by Bosch's process.
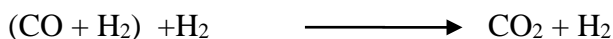
$$(CO + H_2) + H_2 \longrightarrow CO_2 + H_2$$
water gas

In this process ferric oxide acts as catalyst, chromic oxide as promoter and temperature is maintained between $400^0C - 600^0C$.

5. In the manufacture of methyl alcohol from water gas

$$(CO + H_2) + H_2 \longrightarrow CH_3OH$$
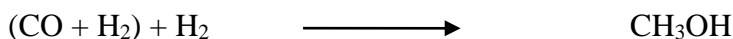
water gas

Zinc oxide is used as catalyst, chromic oxide as promoter pressure 200 atms. and temperature 450^0C.

6. In Chamber process for manufacture of H_2SO_4, nitric oxide is used as   catalyst.

$$2SO_2 + O_2 + [NO] \longrightarrow 2SO_3 + [NO]$$

catalyst

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
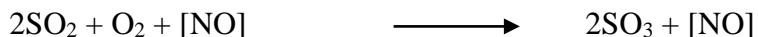
7. In the manufacture of acetic acid from acetaldehyde.

$$2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$$
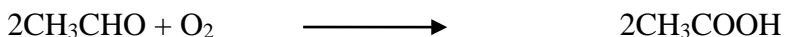
Vanadium oxide (V_2O_5) is used as catalyst.

12.6 SUMMARY

It is indeed, a fascinating aspect of chemistry that certain reactions which do not proceed to completion even when carried out for indefinite period of time, that completed within a matter of few minutes when small Quantity of a catalyst is added. A catalyst provides for the reaction another path that has a lower energy of activation E_a. A Better explanation is offered by the activated complex theory on the basis of the decrease in free energy of activation. The presence of catalyst is very useful in many industrially important reactions which are either very slow or takes place at a very high temperature. Hence to decrease the cost of production it is essential to make use of a suitable catalyst.

In this chapter you have studied classification of catalysis, types of catalysis, catalytic promoters, negative catalysis enzyme catalysis and industrial application of catalysis.

12.7 TERMINAL QUESTIONS

(A) **Multiple choice questions:**

Q.1 In the hydrogenation of oils the catalyst used is:

(a) Iron   (b) Platinum

(c) Nickel   (d) Molybdenum   ans (c)

Q.2 Which of the following statement is universally correct?

(a) A catalyst remains unchanged at the end of the reaction.

(b) A catalyst physically changes at the end of the reaction.

(c) A catalyst take part in a chemical reaction.

(d) A catalyst can induce chemical reaction.   ans (a)

A catalyst

Q.3

(a) may be in the same phase with the reactants or in a different phase.

(b) may accelerate a reaction.

(c) affect a reaction without being consumed in the process.

(d) all of the above.

                              ans(d)

Q.4 Which one the following statements about enzyme catalysis is

ncorrect? (a)Enzymes are mostly proteinous in nature (b) Enzyme

action is specific.

(c) Enzyme are denaturized by UV rays at high temperatures.

(d) Enzyme are least reactive at an optimum temperature.   ans(d)

Q.5   Substance that decreases the activity of a catalyst is known as:

(a)Promoters

(b)Poisons

(c)Controllers

(d)Initiators   ans(b)

(B) Short answer and very short answer type questions:

1. Define catalyst and catalysis.

2. Explain how a catalyst increases the rate of a reaction.

3. Define the terms

(i)   catalytic promoter

(ii)catalytic poison

4. Explain the term homogeneous catalysis and heterogeneous catalysis.

5. Explain with examples what is negative catalyst.

6. Where are the following used as catalyst?

(i)   Finely divided nickel

(ii) Platinum gauge

(iii) Ferric oxide

(iv) Manganese dioxide.

(C) Essay type or long answer questions:

1.   Write a brief account of the theories of catalysis. Explain the function of active centres.

2.   Write an essay on catalysis.

3.   Give a brief account of adsorption theory. How does this theory explain the characteristics of contact catalysis?

4. Explain the important characteristics of enzyme catalysis with examples.

5. (a) Describe the theory of homogeneous and heterogeneous catalysis.

    (b) Give an example each for enzyme catalysis and acid base catalysis.

12.8 REFERENCES AND FURTHER STUDIES

1.R. L. Madan, *Chemistry for degree students, B.Sc. II year*, S. Chand & Company Ltd., New Delhi, 2011.

2. S. Prakash, G. D. Tuli, S. K. Basu, and R. D. Madan. *Advanced Inorganic Chemistry*,   Vol. I, S. Chand & Company Ltd., New Delhi, 2007.

3. Br. R. Puri, L. R. Sharma and K. C Kalia. *Principles of Inorganic Chemistry*, Milestone Publishers & Distributors, Meerut, 2013.

BLOCK-V: LABORATORY HAZARDS AND SAFETY

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 Introduction

13.2 Objective

13.3 Purpose of laboratory & chemical safety

13.4 Types of hazards in the laboratory and their prevention

13.5 Laboratory safety

13.6 Assess and minimize the risk of the hazards

13.7 Summary

13.8 References and further studies

13.1 INTRODUCTION

In the laboratory it is require great care and attention in order to avoid safety hazards occures due to delicate lab instrument, open flames, hazardus chemicals etc. Negligent handling of dangerous/harmful chemicals can result in both short-term (acute) and long-term (Chronic) health issues. Burns, eye injuries, lung diseases, asphyxiation, and suffocation are some of these potential issues. Chemicals cause adverse reactions in the body through ingestion, inhalation, skin contact, and percutaneous exposure. No matter how much is being used or how it is used, a substance, operation, or activity has intrinsic hazardous characteristics or properties. Various risks to human health and physical injury can be posed by chemicals given below:

Health Hazards	Physical Hazards
Toxic	Combustible
Carcinogenic	Flammable
Mutagenic	Explosive

Reproductive toxins	Reactive or pyrophoric
Sensitizers	Oxidizers
Irritants and Corrosives	Corrosive
Asphyxiants	Compressed Gas and Liquid

The chemistry practical could involve a minor incident. Inform your teacher or the lab attendant right away, remain calm, do not panic, and use the first aid provided in the laboratory.

However, if any of these symptoms occur, you should immediately stop working, take off your personal protective equipment, wash your hands, and contact your healthcare provider.

- Unusual taste or odor,
- Respiratory irritation, coughing, choking, or shortness of breath,
- Sudden headache, dizziness, blurred vision, or loss of consciousness,
- Burning or painful sensation,
- Swelling, reddening, or itching skin.

13.2 OBJECTIVE

After completing this unit learners will be able

- To known 'What is a laboratory hazard'? The physical hazards and the chemical hazards in the laboratory.
- How to prevent chemical hazards in the laboratory.
- To know the effect of laboratory incidents on learner's health, such as heat burns, glass cuts, and the inhalation of gas.
- To assess and reduce the risks associated with chemical hazards in the laboratory.

13.3 PURPOSE OF LABORATORY & CHEMICAL SAFETY

- To promote safety awareness and encourage safe working practices in the laboratory.
- Safety guidelines should serve as a reminder of things you can do to work more safely and are applicable to all users of the laboratory.
- All learners are expected to adhere to safety guidelines and maintain safety standard strictly.

13.4 TYPES OF HAZARDS IN THE LABORATORY AND THEIR PREVENTION

Chemical and physical hazards in the laboratory fall into five major categories. Now discuss each category in details with their prevention in the laboratory.

- Chemical burns
- Heat burns
- Eyes injuries
- Injury from glassware
- Inhaling dangerous gases

13.4.1 Chemical burns

Acids, bases, etching solutions and solvents are commonly used in chemistry lab and classified as corrosive substance, and also present a serious health hazards such as chemical burns, tissue damage, organ damage, asphyxiation, corneal damage, which can lead to blindness and genetic damage if used improperly.

(Burns are a common type of hazard when dealing with harmful substances).

- Wear the gloves when working in lab.

- If the skin burn with acid , wash it with ammonium hydroxide, while in case of concentrated H_2SO_4 wash affected part with Barium chloride solution and then with cold water and apply burnol.

- If the skin burn due to the concentrated/ stong alkali (base), washed it with acetic acidand finally with cold water and apply burnol. If the injury is deep then immediately contact with the health consultant/doctor.

13.4.2 Heat burns

Burners and other heating devices are frequently used in laboratories to expedite chemical reactions and processes. As with any activity that involves fire, it is important to be aware of the potential risks associated with heat-related injuries. If exposed to temperatures higher than 70°C, it is likely that a burn will occur, even if the skin is only exposed for a split second.

It is essential to maintain a safe distance away from open flames and heating devices in order to reduce the likelihood of heat-related burn injuries in the laboratory.

- Skin clothing and protective equipment should be kept away from any other combustible materials in the vicinity. Furthermore, it is imperative to ensure that burners are not left on after use.

- If a heat-related burn occurs while in the laboratory, it is recommended to immediately put the affected area in cold running water and hold it for a few minutes before allowing the burning sensation to subside. After that apply coconut oil or burnol on the burnt part.

(The heat generated by Bunsen burners can create a range of serious physical hazards for laboratory learner who are using the equipment)

13.4.3 Eye injuries

In the laboratory at the time of working, you need to be aware of the chemicals that can be harmful to your eyes. You can be exposed to chemicals if you accidentally release liquids or gases that can damage your eyes. The severity of your injury depends on hazardus properties of chemical are and how much you have been exposed to it. For instance, if you get a mild eye injury from exposure to a chemical, it could just cause redness and irritation. But if you get a really bad eye injury, it could lead to permanent blindness. To prevent eye injuries in the lab, you need to wear the right protective eyewear.

- If the eyes injuries occur due to the some pungent vapours in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still eatvhing persists consult an eye doctor immediately.

- If chemical solution or dust particle enter into eye thenwash your eye with cold water untill you feel relief.

- If acid has been entered into eye then eye must be washed with a dilute solution of alkali sodium bicarbonate solution few timesand after that with cold water till you feel relief. an eye doctor

- If base/alkali has been entered into eye then eye must be washed with dilute boric acid solution and finally washed with cold water till irritation persists. If still problem exist immediately consult an eye doctor.

13.4.4 Injury from glassware

The use of laboratory glassware for the storage and mixing of hazardous chemicals is a common practice; however, there is a risk of laboratory glassware breaking. If the glass is broken, it can expose sharp edges, particularly if it is very thin, which can cause severe eye and skin damage. Therefore, it is important to take steps to reduce the risk of glass breaking in laboratories.

- In order to prevent cuts from glassware, it is important to handle the glassware with caution. It is recommended to hold the glassware in a secure grip and to avoid handling the glassware with wet or wet hands.

- It is important to ensure that when glassware is not in use, it is stored in a safe and secure place where there is no potential for it to fall and shatter. If glassware is not stored in an accessible cupboard with a well-maintained and even surface, it is likely to fall and break, potentially exposing to physical injury.

- If the is due to the breakage of some glassware, glass apparatus, wound washed with sprit and then aqueous alum solution because alum is antiseptic in nature and can also help in stop bleeding by coagulation.

- It is essential to take prompt action in the case of a glass cut in order to avoid the development of an infection. If a cut is sustained from glassware, the first aid officer/doctor should be contacted so that they will dress the wound.

13.4.5 Inhaling dangerous gases

A wide variety of hazardous chemicals emit toxic vapors and gases that pose a risk to human life. The health consequences associated with exposure to these hazardous vapors can be classified as acute, chronic, or both. Acute consequences are those that occur immediately after exposure to the vapors. Chronic consequences are those that do not occur immediately but occur months and even years after exposure. Heath effects of gas inhalation can include symptoms such as:

Irritation to mucous membranes in the nose, throat, respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing etc.

- If you feel any symptoms occurs due to the inhalation of gaes first go away from the working place (lab) in the open place. If still feel some problems consult with doctor immediately.

13.5 LABORATORY SAFETY

In the laboratory following safety will be taken while working in the lab.

(i) Laboratory hygiene

(ii) Fire safety

(iii)Chemical safety

(iv) Personal safety

(i) Laboratory hygiene

- Scrub hands thoroughly when finished.
- Avoid cross contamination
- Do not touch self, faucets, doorknobs, notebooks, pens etc. with gloves on.
- Keep a pen or two in your drawer for lab use only.
- Clean and disinfect your workspace **(ii) Fire safety**
- Never leave flames unattended.
- Do not use flammables near ignition sources.
- Fire Extinguishers
- Fire Blanket
- Fire alarm pulls

(iii) Chemical Safety

- Wear gloves and glasses where appropriate.
- Follow instructor's directions.
- Dispose of waste properly-Do Not pour down the drain. **(iv) Personal Safety**
- Lab coat to be worn all the time.
- Safety goggles must be worn all the time while working in the lab.
- Wear sensible clothing and Wear shoes.
- Appropriate gloves while handling chemicals.
- Working of alone student is not allowed

13.6 ASSESS AND MINIMIZE THE RISK OF THE HAZARDS

When you are working in a chemical lab, there is a risk associated with every chemical and glassware you use. Once you have evaluated the risks, your next step is to consider how you can reduce exposures. There are following step to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant steps you can take to reduce the risk in any laboratory environment. While incidents can occur even in the well-prepared environment, meticulous attention to detail can reduce the risk.

I.   Know what you are working with. It is important to always recognize the substance that is being used and to consider how to reduce the exposure to that substance during the experiment. For example, sodium hydroxide is commonly known as lye or caustic soda. If you are unsure, look for the Chemical.

II.   Ensure that the proper concentrations are prepared. In laboratory should not routinely work with basic (NaOH) or acidic (HCl) solutions at concentrations greater than 1 M.

III.   Ensure that all chemical bottles are properly labeled. For example sodium hydroxide, the bottle should have the chemical name ("sodium hydroxide") spelled out, not just the formula ("NaOH"), and the concentration of the solution should also be listed.

- The signal words "Danger", "Warning", and "Caution" are used to describe the level of the hazard.

- Words such as "Caustic", "Corrosive", and "Flammable" are used to describe specific hazards.

IV.   Write down all the chemicals you are going to use and how much you will need for the experiment.

V.   Consider the physical arrangement and the facilities available in your laboratory.

13.6.2 During an experiment

It is essential that learners are monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students throughout.

I.   Use the lowest concentrations and smallest volumes possible for all chemicals. Do not allow learners to handle solids that are classified as fatal or toxic if swallowed.

II.   Wear appropriate eye protection that offers both impact and splash protection. This is not only for your safety but also as a precaution in the event that an accident is caused by someone else in the laboratory.

III.   Wear appropriate protective clothing (laboratory apron, coat, and gloves).

IV.   Long hair must be pulled back, and clothing must be tucked in.

V. After transferring a chemical (solid or liquid) from a reagent bottle into a secondary container, be certain that the reagent bottle and the container are properly closed.

VI. Students should take only the amount required of each reagent. If there is excess, it must be disposed of properly and not returned to the reagent container.

VII. No mixing of chemicals should be allowed, other than that specified in an experimental procedure.

13.6.3 What if an emergency occurs?

I. If the chemical is in the eye: Flush water using an eyewash station for at least 15 minutes. Medical attention must be summoned as soon as possible.

II. If the chemical is swallowed or ingested: Do not induce vomiting unless the SDS recommends vomiting. Medical attention must be summoned as soon as possible.

III. If the chemical comes into contact with skin: Rinse the affected area for 15 minutes with tap water. It may be necessary to use a safety shower. If the safety shower is used, all contaminated clothing should be removed while the person is under the safety shower, and medical attention must be summoned as soon as possible.

13.6.4 After an experiment

I. Return any chemicals (excess reagent, product, or waste) to the appropriate location, or dispose of them as instructed.

II. Clean any used glassware and return the items to the appropriate location.

III. Ensure that all chemicals are properly stored. Make sure that the caps on the reagent bottles are tightly secured.

IV. Ensure that benches are clean before the next class comes in. One of the major causes of accidents is carelessness on the part of someone else.

V. All gas outlets are closed; especially burners were used during the experiment.

13.7 SUMMARY

- Keep tabletops clean. Return all equipment to its original location before leaving the lab.

- Report all accidents, no matter how minor, to the instructor. If you break something made of glass, be sure to use dustpan and hand broom to sweep it up and dispose of it in the glass waste receptacle.

- In case of an emergency where we have to evacuate, proceed out the nearest exit.

- Both the door should remain open all the time while working in the lab.

- Never put anything in your mouth while in the lab (including chemicals, solutions, food and drink)

- All food and drinks should be restricted to sitting area only.

13.8 REFERENCES AND FURTHER STUDIES

1. Guidelines for Chemical Laboratory Safety in Secondary Schools. American Chemical Society 1155 Sixteenth Street, NW Washington, DC 20036, 2016.

2. Mobin Shaikh, Laboratory & Chemical Safety Guidelines, Indian Institute of Technology (IIT), Indore.

3. Sudha Goyel, Chemistry Practical-I, Krishna Publication Media (P) Ltd. Meerut, 2017.

BLOCK -2: EXPERIMENT UNIT 14: COMPOUND IDENTIFICATION

CONTENTS:

14.1 INTRODUCTION

Qualitative analysis of an organic compound refers to the detection of the elements present in a compound. The most common elements present in an organic compound are carbon, hydrogen, oxygen, nitrogen, halogen and sulphur. Sometimes, elements such as phosphorus and some metals may also be present. Therefore, qualitative analysis is limited to the detection of only a small number of elements usually present in organic compounds.

14.2 OBJECTIVES

In this chapter students learn the following objectives.

- To detect nitrogen, sulphur and halogen in given mixture.
- To identify functional groups with known samples

14.3 DETECTION OF N, S AND HALOGENS

In organic compounds the most commonly occurring elements are nitrogen (N), sulphur (S) and halogens along with carbon (C), hydrogen (H) and oxygen (O). In the identification of an organic compound N, S and halogens are detected before the functional groups are to be looked for. This
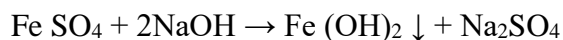
is done by **Lassaigne's Test** in which these elements are converted into ionisable inorganic substances. This is because these elements along with the others are covalently linked in the organic compounds and do not respond to ionic reactions. This may be accomplished by fusing the substance with metallic sodium in an ignition tube. Thus N, S and halogens are converted to sodium cyanide, suphide and halides respectively. If N and S both are present in the same compound these are converted into   NaCNS (thiocyanate).

 In the Lassaigne's test, sodium extract is first prepared as follows: A sodium metal piece is dried by pressing between the folds of a filter paper. It is then introduced into a clean ignition tube and covered by pouring the given substance into the tube. The ignition tube is first heated very gently in the flame holding it by means of a pair of tongs, taken it away from the flame and heated again. This process is repeated three to four times till the bottom of tube becomes red hot and reaction begins. The red hot ignition tube is plunged into a beaker or porcelain dish containing about 10 to 15 ml. distilled water. The contents are stirred and allowed the remaining sodium to react with water. The mixture is boiled for five minutes and filtered. This filtrate is known as Lassaigne's solution or sodium extract which should be colourless and transparent. Otherwise the fusion is repeated with larger piece of sodium and sodium extract is prepared as above. The conversion of the elements into ionic form occurs as follows:

$$Na + C + N \rightarrow NaCN \rightleftharpoons Na^+ + CN^-$$

$$2Na + S \rightarrow Na_2S \rightleftharpoons 2Na^+ + S^{2-}$$

$$2Na + X_2 \rightarrow 2NaX \rightleftharpoons 2Na^+ + 2X^- \ (X = Cl, Br, I)$$

(1) Detection of Nitrogen.

About 2 ml. of sodium extract is treated with 3-4 drops of fresh and saturated solution of $FeSO_4$ followed by 2-3 drops of NaOH. The contents are boiled for two minutes. Then the solution is cooled and 2 ml. of dil. H_2SO_4 are added to it to dissolve the precipitate of ferrous hydroxide if formed and make the solution acidic. Then added 2-3 drops of $FeCl_3$ solution. Formation of Prussian blue or greenish blue precipitate or colouration indicates the presence of nitrogen. The reactions involved are given below:

$$Fe\ SO_4 + 2NaOH \rightarrow Fe\ (OH)_2 \downarrow + Na_2SO_4$$

Fe SO_4 + 6NaCN → Na_4 [Fe(CN)$_6$] + 2NaOH

$3Na_4$ [Fe(CN)$_6$] + $4FeCl_3$ →Fe_4 [Fe(CN)$_6$]$_3$(Prussian blue) +12NaCl

In the presence of N and S both in the compound, the above test gives blood red colour as follows:

Na + C + N + S → Na CNS

3Na CNS + Fe Cl_3 → Fe (CNS)$_3$ (blood red) + 3NaCl
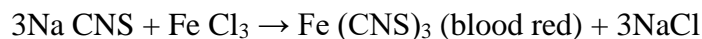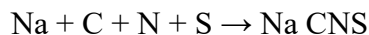
<div align="center">Ferric sulphocyanide</div>

(2) Detection of Sulphur.

(1) 2ml. of freshly prepared sodium nitropursside solution (colourless) are added to 1ml. of sodium extract. A violet or purple colour is developed confirming the presence of sulphur, Na_2S + Na_2 [Fe(CN)$_5$ NO]→Na_4 [Fe(CN)$_5$ NOS] (violet colour).

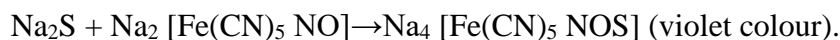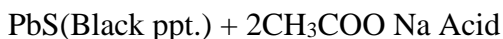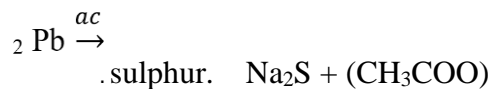**(2)** Alternately, to 2ml. of sodium extract acidified with acetic acid is added 2ml. of lead acetate solution, a black precipitate of PbS if formed, it also indicates the presence of

$$_2 \text{ Pb} \xrightarrow{ac}$$
$$. \text{sulphur.} \quad Na_2S + (CH_3COO)$$

PbS(Black ppt.) + $2CH_3$COO Na Acid

(3) Detection of Halogens.

The halogens (Cl, Br, I) present in an organic compound are detected in two ways:

(i) By silver nitrate test. - This is done as follows: 2ml. of sodium extract is boiled with 1ml. conc. HNO_3 and then $AgNO_3$ is added to it:

(a) White curdy precipitate is formed; soluble in NH_4OH-Cl is present.

(b) Pale (light) yellow precipitate appears; partially soluble in NH_4OH-Br is present.

(c) Yellow precipitate is formed, insoluble in NH_4OH-I is present.

<div align="center">Na Cl + Ag NO_3 →Ag Cl ↓ (White ppt.) + $NaNO_3$</div>

<div align="center">Ag Cl + $2NH_4OH$ → [Ag (NH$_3$)$_2$]Cl (soluble) + $2H_2O$</div>

<div align="center">Na Br + Ag NO_3 → Ag Br ↓ (light yellow ppt.) + $NaNO_3$</div>

<div align="center">Ag Br + $2NH_4$ OH → [Ag (NH$_3$)$_2$ Br] (partially soluble) + $2H_2O$</div>

<div align="center">NaI + Ag NO_3 → Ag I ↓ (Yellow ppt) + $NaNO_3$</div>

<div align="center">AgI + NH_4 OH → insoluble</div>
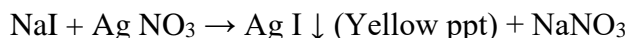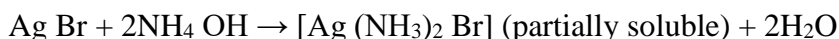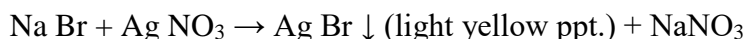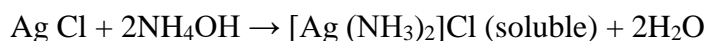
(ii) By chloroform test. - 2ml. of sodium extract are acidified with dil. HNO_3, then added 2-3 drops of chloroform or CCl_4, followed by chlorine water shaking first gently and then vigorously, if chloroform layer turns pale-brown-bromine is present but if it turns purple or violet iodine is present.

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

$$Br_2 + CHCl_3 \rightarrow \text{Pale- brown colour.}$$

$$2\ Nai + Cl_2 \rightarrow 2NaCl + I_2$$

$$I_2 + CHCl_3 \rightarrow \text{purple or violet colour.}$$
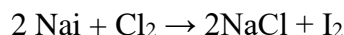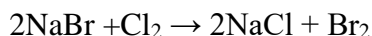
14.4 IDENTIFICATION OF FUNCTIONAL GROUPS

Organic compounds may be regarded as the derivatives of hydrocarbons having different functional groups in place of one or more hydrogen atoms. Their characteristic properties and reactions are largely due to the presence of functional groups present in them. Correct detection of functional groups in the organic compounds leads to a very reasonable and accurate identification of those compounds.

For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds.

Type I : Compounds containing C and H with or without oxygen.

S.N.	Experiment	Observation	Inference
1.(a)	On treatment of the compound with $NaHCO_3$ solution	Brisk effervescence appears	Acids
(b)	On treating of the compound with blue litmus,	Blue litmus turns red	Acids
2.	On adding ceric ammonium nitrate solution to the compound,	Red colouration is observed	Alcohols
3.(a)	Two drops of $FeCl_3$ are added to an aqueous of alcoholic solution of the compound, Phthalein test is performed,	Typical colour changes are observed	Phenols

(b)		Positive result is observed	Phenols
4.	The compound is heated with Fehling's solution or Benedict's solution,	Red priapitate is formed	Aldehydes or reducing sugars
5.	The compound is treated with Schiff's solution.	Pink colouration is observed.	Aldehydes
6.	On Shaking the compound with sodium bisulphite solution,	White precipitate is formed.	Aldehydes or Ketones
7.	The compound is treated with alkaline sodium nitroprusside solution,	Red colouration appears	Methyl Ketones
8.	Molisch's test is performed,	Result is positive	Sugars
9.	On heating the compound with dil. NaOH solution containing a drop of phenolphthalein	Pink colour is slowly discharged	Esters
10.	On heating the compound with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated hydrocarbons Saturated aliphatic hydrocarbons or ethers

Type II: Compounds containing C, H and halogens with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	On boiling the compound with alcoholic $AgNO_3$,	(i) White ppt. soluble in NH_4OH (ii) Ligth yellow ppt. Partially soluble in NH_4OH (iii) Deep yellow ppt. insoluble in NH_4OH	Chloro compounds Bromo compounds Iodo compounds

2.	If the compound is heated with fuming H_2SO_4,	(i) Soluble	Aromatic or unsaturated alkyl halides
		(ii) Insoluble	Saturated aliphatic alkyl halides

Type III. : Compounds containing C, H and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	The compound is boiled with aq. NaOH,	Smell of ammonia is noticed	Amides
2.	The compound is treated with dil. HCl followed by $NaNO_2$ drowse in cold,	(i) Brisk effervescence occurs (ii) Brown or green ppt. is formed (iii) Blue colouration appears	Amides, amino acids, primary amines or urea
3.	On treating the above contents with alkaline β - naphthol solution ,	Bright orange-red dye in formed	Aromatic primary amines
4.	The compound is boiled with water,	Yellow colouration	Nitro phenols or nitro compounds
5.	The compound is boiled with zinc dust and aq. NH_4Cl, filtered and filtrate is treated with Tollen's regent,	Grey precipitate is formed	Nitro compounds

Type IV (A) : Compounds containing C, H and S with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	To the aq. solution of the substance is added few drops of $FeCl_3$ solution,	Violet or red colour is observed	Sulphonic acids of phenols or hydrdro carbons

2.	Equal quantities of substance and animal charcoal are mixed and filled one third of the ignition tube with it and heated,	Disagreeable garlic like odour is noticed	Sulphones

(B): Compounds containing C, H, S and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	2ml. of NaOH solution are added to a trace of the substance in a test tube, heated to boiling, cooled and added 2 drops of aq. lead acetate,	Brown or black colour or precipitate appears	Thioureas
2.	A trace of the substance is dissolved in 2ml. of water by boiling in a test tube and a piece of blue litmus paper is introduced in it,	(i) If colour changes to red. (ii) If no change in colour	Test (a) given below is performed Test (b) is performed as given below
(a)	A trace of the substance is dissolved in 3ml. of dil. HCl, cooled in ice cold water and added 3ml. of 2% sodium nitrite solution and then 4ml. of alkaline β naphthol solution	Red colouration appears	Amino sulphonic acids
(b)	5 drops of conc. H_2SO_4 are added to a trace of substance and heated gently for few minutes, cooled and diluted with 2ml. water. Then added flakes of NaOH and a piece of moistened red litmus paper is brought near the mouth of the test tube,	Colour changes to blue and smell of NH_3 is noticed	Sulphonamide or saccharin

Confirmation of Functional Groups.

The functional groups are then confirmed by normal and sometimes by performing some special test.

1. Carboxylic acid group (-COOH).

(i) *Litmus paper test.*   If the blue litmus paper or solution is added to the aq. solution or suspension of the compound, it turns red.

(ii) *Sodium bicarbonate test*.   If a small amount of the compound is added to about 3ml. of saturated sodium bicarbonate solution, brisk effervescence is noticed.

(iii) *Fluorescence test.*   0.2gm. of organic compound is heated gently with 0.5gm. of resorcinol and few drops of conc. H_2SO_4 in a hard test tube for two minutes, cooled and poured the contents into a beaker containing NaOH diluted largly with water. Intense green fluorescence is formed indicating the presence of 1,2 or ortho dicarboxylic group (i.e. phthalic acid)

(iv) *Ester formation.*   A small quantity of the substance is heated with ethyl alcohol and a little conc. H_2SO_4, cooled and poured in a tube containing water. A fruity smell due to the formation of an ester indicates the presence of carboxylic group.

(v) *Ferric chloride test.*   0.5gm. of the acid is neutralised with excess of ammonia in a boiling test tube, the solution is boiled to remove excess of ammonia, cooled and added few drops of neutral $FeCl_3$ solution:

If reddish brown precipitate is formed: aliphatic carboxylic acids; Buff ppt. is formed: Aromatic acids and certain dibasic acids; If violet colour appears: Aromatic hydroxy acids

Note. Phenols and α-naphthylamine also produce colour with $FeCl_3$.

2. Alcoholic –OH group.

(i) *Ceric ammonium nitrate test.* 2drops of the organic substance are treated with 0.5ml. of ceric ammonium nitrate solution, then diluted with 2ml. water. A red colouration is observed.

(ii) *Sodium test.*   About 2ml. of the compound are taken in a test tube, added to it a piece of anhyd. $CaCl_2$ to absorb any water if present. The clear liquid is transferred to another dry test tube and added to it a dry piece of sodium. The effervescence appears due to liberation of hydrogen.

Distinction among primary, secondary and tertiary alcohols.

If 2ml. of the compound is treated with about 5ml. of Lucas reagent (8 gm of anhyd, $Zn\ Cl_2$ in 5ml. conc. HCl) and shaken, an insoluble layer at once is formed by a tertiary alcohol, cloudiness within 4-5 minutes appears in case of a secondary alcohol and the solution remains clear for a primary alcohol.

3. Phenolic –OH group.

(i) *Ferric chloride test.* On adding 2-3 drops of ferric chloride to 2ml. of aqueous or alcoholic solution of the compound, a green, blue or violet colour shows the presence of phenolic –OH group but nitro phenols do not show this test.

Exceptions. α-naphthylamine and benzoic acid also respond to this test as follows:

α - naphthylamine   -   blue colour

Benzoic acid -   buff coloured ppt.

(ii) *Liebermann's test.* A little amount of the compound is fused with a crystal of sodium nitrite in a tube, the mixture is cooled and to it added 1ml. conc. H_2SO_4, a deep green to blue solution is formed which turns red when poured in large excess of water. The red aqueous solution again becomes deep green or blue if made alkaline with NaOH.

(iii)*Azo-dye formation.*   2drops of aniline are treated with 0.5ml. conc. HCl in a test tube, diluted with water and cooled in a freezing bath, then added dil. $NaNO_2$ solution while shaking. This diazotized solution is poured to that of phenol in excess of 2N-NaOH solution. Formation of a dye or orange or red colour indicates the phenolic group.

(iv)*Phthalein test.* 0.5gm. of compound is heated with 1gm. phthalic anhydride and 2drops of conc. H_2SO_4 for 1minute, cooled and made alkaline with dil. NaOH solution. If few drops of this alkaline liquid are poured in 20ml. water, characteristic colour appears due to phenolic group:

Phenol, O-Cresol   -   red colour

Catechol, m-Cresol   -   blue colour

Resorcinol   -   fluorescent green

p-Cresol   -   no colouration

Hydroquinone   -   deep blue

α – Naphthol   -   green

β – Naphthol   -   light green

2. Aldehyde group (-CHO)

(i) *Test with Schiff's reagent.* 5-6 drops of liquid or (0.1gm) of compound are added to 2ml. of the reagent, contents are shaken vigorously, a deep red or violet colour after waiting for 2-3 minutes. (no heating)

(ii) *Test with Tollen's regent.* 0.1gm. of solid or 0.1ml. of liquid compound is added to 2ml. of Tollen's reagent, warmed and allowed to stand for 2-3 minutes when a silver mirror or a grey precipitate is formed.

(iii) *Test with Fehling's solution.* 0.1gm. of soid or 0.2ml. of liquid compound is added to 5ml. of fehling's solution and the mixture is boiled when red precipitate is formed.

(iv) *Test with Benedict's solution.* 0.1gm. of the compound is boiled with 2-3ml. of Benedict's solution for few minutes while a red yellow precipitate appears. The compounds can be quickly guessed by the following points:

(a) Smell of bitter almonds – benzaldehyde

(b) If bad pungent odour is there, NaOH is added to the liquid compound and shaken

(i)   Brown resin formed – acetaldehyde

(ii)   No such change – formaldehyde

3. Ketone group (>C = O).

(i) *2,4- Dinitrophenyl hydrazine test.* 2drops of the substance are added to about 2ml. of the reagent solution, shaken vigorously and heated if necessary, when a yellow or orange red precipitate separates out.

(ii) *Sodium bisulphite test.* 0.2gm. or 0.3ml of the compound is added to 1ml. of saturated sodium bisulphite solution and shaken vigorously, a white precipitate is formed.

(iii) *Sodium nitroprusside test.* 0.1gm. of solid or 0.2ml. of liquid compound is added to 2ml. of aq. sodium nitroprusside solution and contents are made alkaline with 2-3 drops of sodium hydroxide, a red or purple colour appears (benzophenone does not respond to this test).

Note: The first two tests, i.e. with 2,4 dinitrophenyl hydrazine and sodium bisulphite, are also given by aldehydes but the difference is that ketones do not respond to the tests with Tollen's reagent, Fehling's solution, Schiff's solution, etc.

4. Ester group (RCOOR').

All the esters possess fruity smell.

(i) *Phenolphthalein test.* To 3ml. of the compound are added 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heated gently, the pink colour is gradually discharged (due to hydrolysis of ester).

5. Carbohydrate.

(i) *Molisch's test.* To 1ml. aqueous suspension of compound are added 2drops of 10% alcoholic solution of α – naphthol and shaken well. Now added carefully 2ml. of conc. H_2SO_4 along the side of the test tube, a reddish-violet ring is formed at the junction of two layers in case of carbohydrate. In the Molisch's test 8ml. conc. HCl is added in place of conc. H_2SO_4 and the solution is boiled, a violet colour is produced immediately for sucrose or fructose but glucose gives this colour after 1-2 minutes of continuous boiling.

(ii) *Sulphuric acid test.* A small amount of the powdered compound is treated with 1ml. cold conc. H_2SO_4, colour varying from yellow, brown and black appears.

(iii) *Test with Tollen's reagent.* 0.1gm. of the compound is added to 2ml. of Tollen's reagent and heated gently, a silver mirror is obtained inside the wall of the vessel.

(iv) *Test with Fehling's solution or Benedict's solution.* 1ml. of the aq. solution of the compound is boiled with 2ml. of Fehling's solution or Benedict's solution for two minutes, red precipitate is formed in case of reducing sugars. If the mixture with Benedict's solution remains blue or only slight turbidity appears then sucrose is present.

6. Hydrocarbon and Ether.

If the compound does not respond to any above test, it may be suspected to be either a hydrocarbon or ether. Ethers are soluble in phosphoric acid while hydrocarbons are rendered insoluble. All ethers are sweet smelling. Liquid benzene and toluene have characteristic sweet petrol like odour.

i. *Feigl's test for ethers.* 1-2ml. of ether are taken in a boiling tube and its mouth is covered with a filter paper moistened with a mixture of cupric acetate and benzidine hydrochloride solution. On heating to boiling, a deep blue colour appears on filter paper due to the formation of benzidine blue due to the ether group.

ii. To 0.5 ml. of the compound is added 1ml. of iodine solution in CS_2 and shaken well the purple colour of CS_2 layer changes due to ether group.

iii. 1ml. of compound is mixed with 4ml. of glacial acetic acid and 1ml. conc. H_2SO_4, heated under reflux condenser for about 5 minutes, cooled well and extracted with benzene purple colour

appears due to ether group (This test can be applied only when ester group is absent, otherwise not). If the above tests are negative, then the compound is a hydrocarbon.

7.   **Halogen containing compound.**

  i.   *Alcoholic silver nitrate test.* A little amount of the compound is heated with 2ml. of alcoholic silver nitrate solution for a few minutes and the observed the following: (a) Formation of a precipitate indicates the presence of aliphatic or reactive halogen. (b) No precipitate indicates the presence of halogen atom attached to benzene nucleus   (but 1-chloro-2, 4-dinitro benzene does not respond to this test).

  Quick guess.

(a) If the Cl-containing compound is solid, aliphatic and crystalline containing –CHO group, it is chloral-hydrate.

(b) Cl-containing compound is aromatic solid, colourless and crystalline with characteristic smell, it is p-dichlorobenzene.

8.   **Amide group (-CONH₂)**

  (i) *Sodium hydroxide test.* 0.2gm. of the compound is heated with 4ml. of aq. NaOH, ammonia gas is evolved due to amide group.

  (ii) *Nitrous acid group.* To 0.2gm. of substance is added 2ml. dil. HCl followed by 2ml. of 2% aq. NaNO₂ and shaken, brisk effervescence due to the evolution of nitrogen indicates amide group.

  (iii)   *Hydroxylamine hydrochloride test.* In a test tube 0.2gm of the compound, 0.2gm of hydroxylamine hydrochloride and 2ml. ethyl alcohol are taken, boiled for five minutes, cooled and added few drops of $FeCl_3$. Blue-red colour appears indicating an aliphatic amide.

  (iv) To the aq. solution of the compound are added 7-8 drops of 6% H_2O_2 and heated nearly to boiling, cooled and added 1-2 drops of 5% $FeCl_3$ solution, Bluish red colour appears in cold within 2mintues or a brown colour on warming shows the presence of an aromatic amide.

  (**Quick test**: Compound is dissolved in water by heating cooled and added 1ml. conc. HNO_3

  (a)   Crystalline ppt formed   -   urea

  (b)   No ppt. and aliphatic - acetamide (c) No ppt. and aromatic   - benzamide)

9.   **Amine groups (-NH₂, > NH and≡ N).**

  (a)   Primary amine.

(i)   *Nitrous acid test.* 0.2gm. of the compound is dissolved in 10ml. dil. HCl and cooled.

Now added 10% aq. $NaNO_2$ solution, brisk effervescence appears-aliphatic primary amine.

(ii)   *Carbylamine test.* A mixture of 2 drops of the compound, 2drops of chloroform and 2ml. of alcoholic caustic potash (KOH) is boiled. An intolerable offensive odour of carbylamine indicates a primary amine.

(iii)   *Diazotisation test.* About 0.2gm. of the compound is dissolved in dil. HCl, cooled and added to it 10% aq. $NaNO_2$ This is poured into a beaker containing 10% alkaline β – naphthol, a bright orange-red dye appears-aromatic primary amine

(iv)   *Rimini test.* To about 0.3gm. of the compound taken in a test tube are added 5ml. water, 1ml. acetone and a few drops of sodium nitroprusside, allowed to stand for 2minutes: a violet red colour appears for aliphatic primary amines.

(b)   Secondary amine.

(i) *Nitrous acid test.* Ice cold dil. HCl is added to a solution of 1% aq. $NaNO_2$. This solution is added gradually to the solution of compound in HCl (0.5gm. in l0ml. HCl). An oily dark coloured liquid or low melting solid is formed due to aliphatic or aromatic secondary amine.

(ii) *Libermann's nitroso test.* In the above test, if 1ml. conc. H_2SO_4 is added cautiously to the reaction mixture, a blue colouration which changes to red on dilution with water and blue or green with aq. alkali confirms the secondary amine.

(c)   Tertiary amine.

(i) *Nitrous acid test*. Ice cold dil. HCl is added to 1% aq. $NaNO_2$. To this solution is added gradually 0.2gm. of the compound in 10ml. dil. HCl: (a) If there is no reaction-tertiary aliphatic amine.

(b)   If green or brown coloured salt is produced-aromatic tertiary amine.

10.   Nitro group (-NO2).

Almost all nitro compounds are light yellow or yellow in colour.

(i) *Sodium hydroxide test.* A small amount of the compound is shaken with 2ml. of NaOH solution, yellow, intense yellow or orange colour is produced due to nitro group.

(ii) *Zinc-ammonium chloride test.* A small amount of the substance is boiled with 5ml. of 5% alcohol, 0.2gm. each of NH_4Cl and zinc dust, cooled, filtered and added to the filtrate 2 ml. of Tollen's reagent. On heating, a black grey precipitate is formed due to nitro compounds.

(iii) *Azo-dye test.* 0.1gm. of the substance is heated with 0.5ml. conc. HCl and 2-3 small pieces of metallic tin for 3-4 minutes, filtered, cooled and added 3ml. of aq. $NaNO_2$ solution.

This is poured into a beaker containing alkaline β naphthol solution. An orange red dye is formed.

11. Sulphonic acid group (-SO₃H).

The compound having sulphonic acid group gives positive test for S element.

(i) *Sodium bicarbonate test.* A little amount of the compound is added to a few ml. of aq. $NaHCO_3$ and the contents are stirred. Brisk effervescence of CO_2 and positive test of element S confirms the sulphonic acid group.

(ii) *Fusion test.* Equal amounts of the compound and solid NaOH/KOH are fused and treated with dilute mineral acid. A penetrating smell of SO_2 is noticed. The gas if passed into acidic $K_2Cr_2O_7$ solution, green colour is developed.

14.5 SUMMARY

Detection of nitrogen (N), sulphur (S), and halogens (X) is done by Lassaigne's Test in which these elements are converted into ionisable inorganic substances. This can be done by fusing the substance with metallic sodium in an ignition tube. On fusion with sodium N, S, and halogens are converted to sodium cyanide, sulphide and halides respectively. If N and S both are present in the same compound these are converted into NaCNS (thiocyanate). Functional groups are specific atoms, ions, or groups of atoms having consistent properties. For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds. The functional groups are then confirmed by normal and sometimes by performing some special test.

14.6 REFERENCES AND FURTHER STUDIES

1.Sudha Goyel, Chemistry Practical-I, Krishna Publication Media (P) Ltd. Meerut, 2017.

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UNIT 15: TITRATION AND CHROMATOGRAPHY

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15.2 Objectives

15.3 Titration

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15.3.2 Titration of weak acid (CH_3COOH) with strong base (NaOH)

15.4 Determination of the strength of a given unknown solution of hydrochloric acid by pH titration of the hydrochloric acid with sodium hydroxide

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15.1 INTRODUCTION

A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the know solution) is added from a buret to a known quantity of the analyte (the unknown solution) until the reaction is complete. There are many types of titrations with different procedures and goals. The most common   typesof qualitative titration are acid–base titrations and redox titrations. Acid–base titrations depend on the neutralization between an acid and a base when mixed in solution. In addition to the sample, an appropriate pH indicator is added to the titration chamber, representing the pH range of the equivalence point.

Redox Titration is a laboratory method of determining the concentration of a given analyte by causing a redox reaction between the titrant and the analyte. These types of titrations sometimes require the use of a potentiometer or a redox indicator.

15.2 OBJECTIVES

After completing this unit you should be able to

1. Calculate pH for various combinations of strong and weak acid-base pairs.

2. Locate the end point from the graph of pH of solution versus volume of base added.

3. Determine the strength of an acid by potentiometric titrations.

4. This unit are to make aware the readers about separation technique basically chromatyography like thin layer chromatography, paper chromatography etc.

The other aim of this unit is separation and identification of the sugars present in the given mixture of glucose, fructose and sucrose etc. using paper and thin layer chromatography and determination of Rf value.
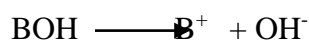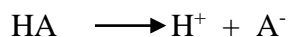
15.3 TITRATION

A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the know solution) is added from a buret to a known quantity of the analyte (the unknown solution) until the reaction is complete.

There are many types of titrations with different procedures and goals. The most common typesof qualitative titration are acid–base titrations and redox titrations. Acid–base titrations depend on the neutralization between an acid and a base when mixed in solution. In addition to the sample, an appropriate pH indicator is added to the titration chamber, representing the pH range of the equivalence point.

Redox Titration is a laboratory method of determining the concentration of a given analyte by causing a redox reaction between the titrant and the analyte. These types of titrations sometimes require the use of a potentiometer or a redox indicator.

Acid base titrations are basically neutralization titrations. Acids and bases ionize in water.

$$HA \longrightarrow H^+ + A^-$$

$$BOH \longrightarrow B^+ + OH^-$$

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

The extent of hydrolysis of the salt BA formed from neutralization between the acid and base decides the pH of the solution at equivalence point. The pH of a solution is given as $pH = - \log [H^+]$ pH titration is the process of adding either base from the burette to a known volume of acid (alkalimetry) in a beaker and measuring the pH of the solution at each addition or vice versa (acidimetry). In a titration of an acid with a base, the pH of the solution before titration is low. On addition of aliquots of base to the acid, the pH starts increasing. Near the end point a sharp increase in pH occurs. When a plot of pH versus volume of base is constructed you obtain a pH curve. After the end point, addition of the base does not change pH and results in a plateau in the curve. The pH curves for strong acid-strong base, strong acid-weak base, weak acid-strong base and weak acid-weak base are depicted in Fig 15. However, it is difficult to locate the end point in weak acid-weak base titrations by potentiometric method.

15.3.1 Titration of strong acid (HCl) with strong base (NaOH)

In titration of a strong acid (HCl) with a strong base (NaOH) the salt formed by neutralization reaction does not hydrolyse in water. Hence the solution at the equivalent point is neutral.

Initially the pH keeps increasing slowly as the base is added. After the end point the concentration of the base (NaOH) is in excess and a sharp increase in pH is noted.

$[H^+] = [HCl]$ The

pH is given by pH

$= 14 - pOH$

In the case of a strong acid versus strong base, at equivalence point $[H^+] = [OH^-]$

The ionic product of water $= K_w = [H^+][OH^-] = 10^{-14}$

$K_w = [H_+]_2$

$(K_w)^{1/2} = [H^+][H^+]$

$= [HCl]$

$pH = -\log[H^+] = -\log(K_w)^{1/2} = -\frac{1}{2}\log K_w = -\frac{1}{2}\log 10^{-14} = \frac{1}{2} \times 14 \times \log 10 = 7$
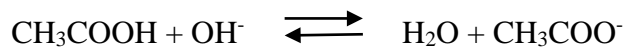
$(\log 10 = 1)$
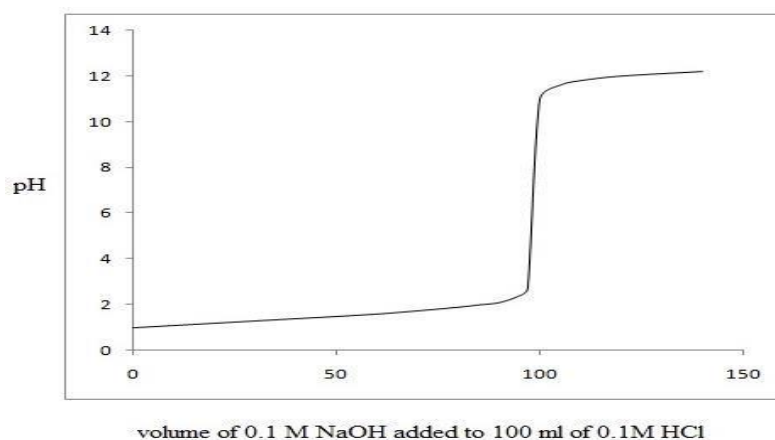
Figure 15.1. (a) pH titration curve of strong acid (HCl) vs strong base (NaOH)

15.3.2 Titration of weak acid (CH$_3$COOH) vs strong base (NaOH)

In case of weak acid

$[H^+] = \{K_a \, [\text{acetic acid}]\}^{1/2}$

$$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$$

Addition of NaOH converts a portion of acetic acid to its conjugate base. This solution of a weak acid and its conjugate base forms a buffer for which the pH of the solution is calculated by Hendersen equation .

At equivalence pH is more than 7 pH = pKa +

log [Conjugate base] / [Weak acid]

After the equivalence point, NaOH is present in excess and pH rises to about 12..
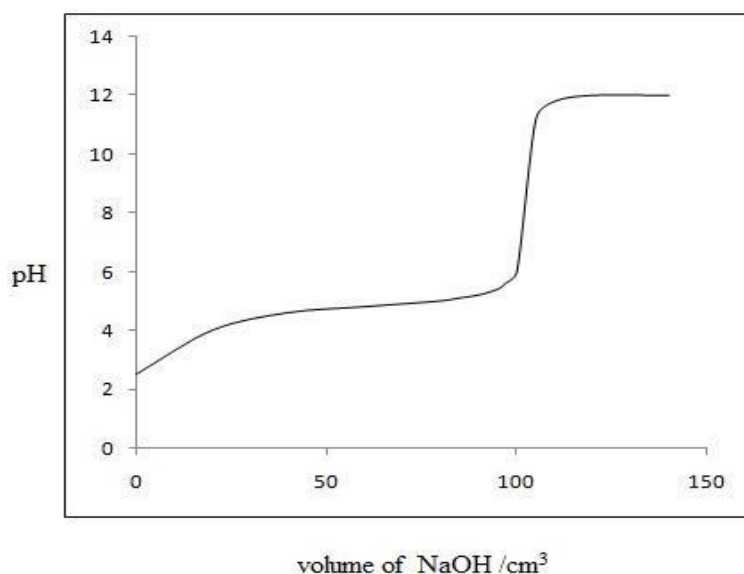
Figure. 15.1. (b) pH titration curve of weak acid (CH$_3$COOH) vs strong base (NaOH)

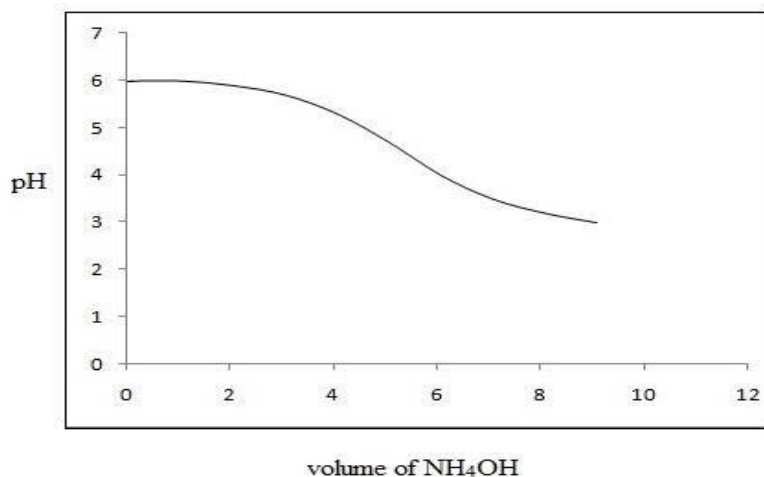*Figure 15.1. (c) pH titration curve of weak acid (CH₃COOH) vs weak base (NH₄OH)*

15.4 DETERMINATION OF THE STRENGTH OF A GIVEN UNKNOWN SOLUTION OF HYDROCHLORIC ACID BY PH TITRATION OF THE HYDROCHLORIC ACID WITH SODIUM HYDROXIDE

15.4.1 Chemicals and apparatus required

HCl, NaOH and distilled water,: Beaker (250 cm^3), burette (50 cm^3), burette stand, pH meter and pH electrode.

15.4.2 Principle

In titration of a strong acid (HCl) with a strong base (NaOH) the salt formed by neutralization reaction does not hydrolyse in water. Hence the solution at the equivalence point is neutral.

Initially the pH keeps increasing as the base is added. After the end point the concentration of the base (NaOH) is in excess.

$[H^+]$ = $[HCl]$ The

pH is given by pH

= 14 − pOH

In the case of a strong acid versus strong base, at equivalence point $[H^+] = [OH^-]$

The ionic product of water $= K_w = [H^+] [OH^-] = 10^{-14}$

$K_w = [H_+]_2$

$(K_w)^{1/2} = [H^+] [H^+]$

$= [HCl]$

$pH = -\log [H^+] = -\log (K_w)^{1/2} = -\dfrac{1}{2} \log K_w = -\dfrac{1}{2} \log 10^{-14} = \dfrac{1}{2x\ 14\ x\ \log 10} = 7$

$(\log 10 = 1)$

15.4.3 Procedure

1.Prepare 1M NaOH by weighing 4 g of NaOH and dissolving it in 100 cm^3 of distilled water.
2.Fill the burette with standardized 1M NaOH solution.

3.Standardize the pH meter (Follow the specific instructions for the pH meter that you have in your laboratory)

4.Now pour 50 cm^3 of given solution of HCl in a 250 cm^3 beaker. Dip the pH probe in the solution and measure and record the pH of the solution before any NaOH has been added.

5.Proceed to add aliquots of 1cm^3 standardized 1M NaOH. Take the burette reading and also record the pH reading after each addition.

6.When you notice that the pH starts to change rapidly, reduce the aliquots of the additions of NaOH to 0.5 cm^3 and then to single drops. Continue adding NaOH till the pH reaches 12.

7.Tabulate your data as given in Table 1 and construct a graph of pH versus volume of NaOH solution added from the burette (Fig15.2). Locate the end point from inflexion point.

8. Incorporate the volume of NaOH consumed for neutralizing the acid in the formula $V_1 N_1 = V_2 N_2$ to determine the normality of hydrochloric acid.
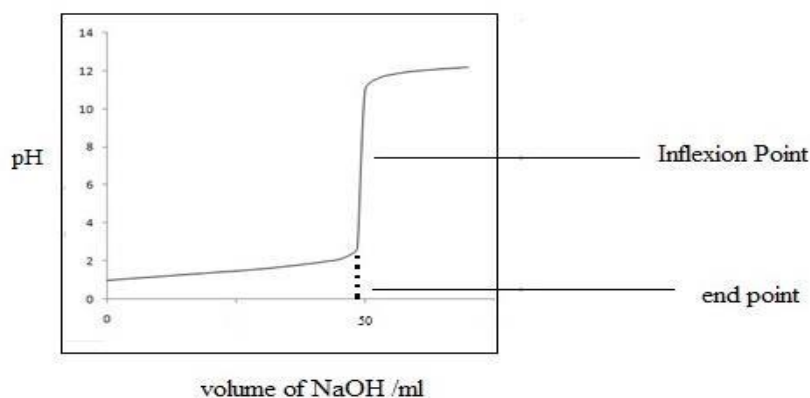
Figure 15.2. pH titration curve of strong acid (1M HCl) vs strong base (1M NaOH)

15.4.4 Observations

Table 1. Titre values for HCl versus NaOH titration

S. N.	Burette Reading/ cm³		Volume of NaOH /cm³
	Initial	Burette	

15.4.5 Calculation

$V_1 N_1 = V_2 N_2$

V_1 = volume of NaOH

N_1 = normality of NaOH

V_2 = volume of HCl

N_2 = normality of HCl

Strength of HCl = Normality of HCl (N_2) × Equivalent weight of HCl (36)

15.4.6 Results

The strength of given solution of hydrochloric acid is ……………… g/litre

15.5 INTRODUCTION OF CHROMATOGRAPHY

The term chromatography wae coined by M. Tswett a Russian botanist in the year 1901 during his research on plant pigments. M. Tswett used the technique to separate various plant pigments such as chlorophylls, xanthophylls and carotenoids. Because of the appearance of colored band during the separation of pigment he named the technique chromatography (chrom = colour, graphy. = writing) because of it's mimically resemblance with with colour writing. The technique is also used for the separation of colorless mixtures in todays science hence is also known as separation technique. Based on the above facts chromatography is defined as "The separation technique used for separation, purification, quantification, identification, analysis etc. due to differential migration of the components in a mixture between two immiscible phases, the stationary and mobile phase." Based on interactions of solute with stationary and moblile phase involved in chromatography is adsorption and partition type. Paper chromatography is partition type while thin layer chromatography is adsorption type. Paper chromatography can be developed by Ascending mode. Fig 15.3
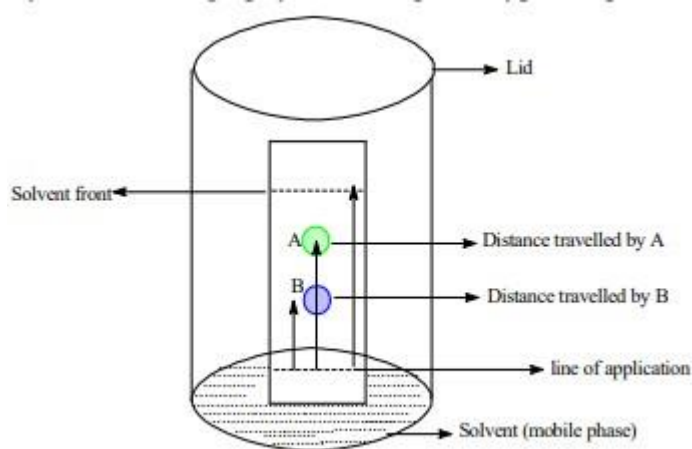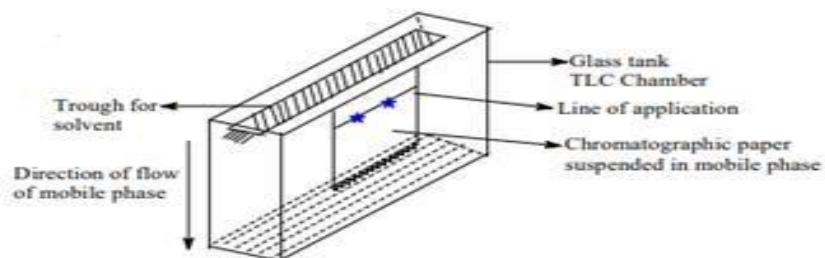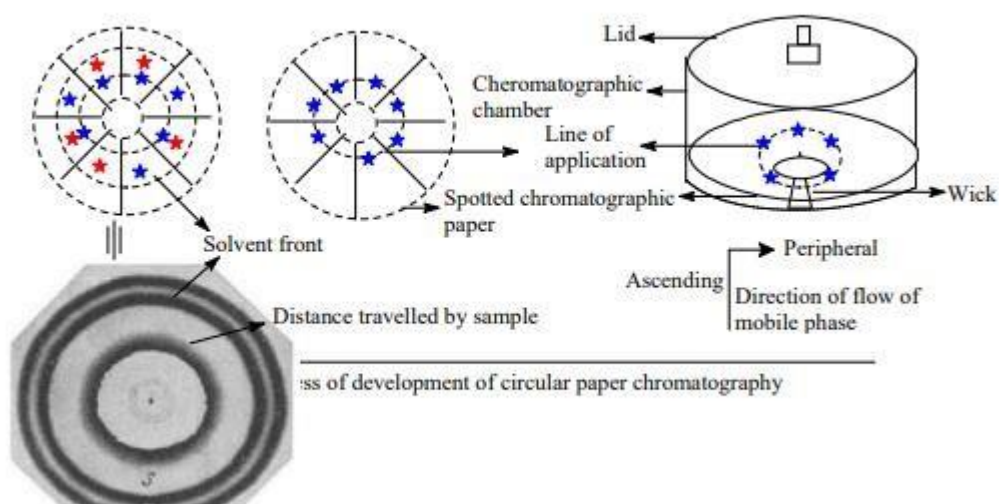

Fig 15.3 Ascending paper chromatography

Descending paper chromatography

Circular paper chromatography

The analysis/ identification of components in paper chromatography is done by matching the Rf (retardation factor. i.e the force that drag back the components towards line of application aginst propelling force due to capillary action) values of component separated with Rf of standard components co-spoted. The Rf is calculated as follow Fig 15.4.
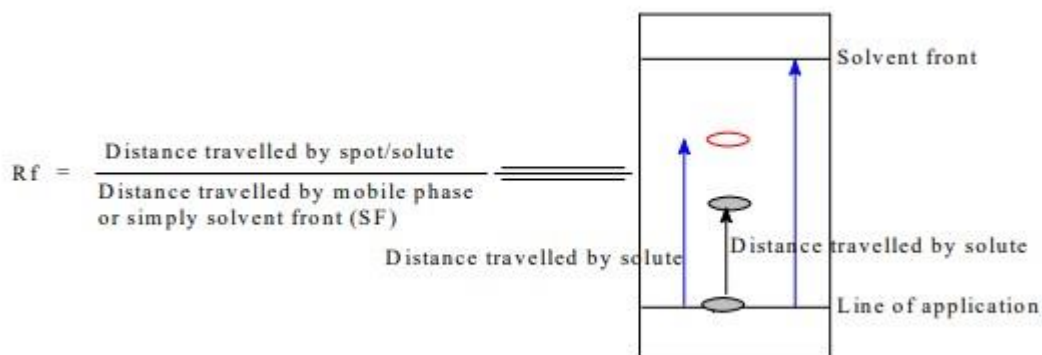
Fig 15.4 Measurment of R_f value

15.6: SEPARATION GLUCOSE, FRUCTOSE AND SUCROSE ETC. IN THE GIVEN MIXTURE OF SUGARS

Principle: "The differential migration of components of a mixture between ststionary and mobile phase as a result of attainment of equlibrioum is known as chromatography". In present experiment the glucose and fructose in a mixture can be separated by chromatographic methods like paper chromatography or TLC. In order to separate the mixture by paper chromatography the following procedure is followed. Requirement: To separate glucose and fructose by TLC and paper chromatography the following materials are required: Stationary phase: Silica gel-G for TLC, Chromatographic paper for paper chromatography Mobile phase: The following cocktails are used as mobile phase [A] H2O + saturated phenol +1% NH4OH

[B] n- CH3CH2CH2CH2OH : CH3COOH: H2O [4:1:5 v/v] (upper layer)

[C] isopropanol :pyridine : H2O : CH3COOH [8:8:4:1 v/v]

TLC/Paper chromatographic chamber Spray reagent: As a result of development visualization of spots is required to calculate Rf values for further analysis. For visualizing the developed paper/TLC plate the following reagents are required: 1. A. Ammoniacal silver nitrate: To prepare ammonical AgNO3 solution add equal volumes of NH4OH to a saturated solution of AgNO3 and dilute with methanol to give a final concentration of 0.3M.After spraying the developed chromatograms,place it in an oven for 5-10 minutes, when the reducing sugars appear as brown spots. 2. Alkaline

permanganate: Prepare aqueous solution of KMNO4 (1%) containing 2 % Na2CO3.After spraying with this mixture, the chromatograms are kept at 100 °C for a few minutes, when the sugar spots appear as yellow spots in purple background. 3. Aniline diphenylamine reagent: Mix 5 volumes of 1% aniline and 5 volumes of 1% diphenylamine in acetone with 1 volume of 85% phosphoric acid. After spraying the dried chromatograms with this solution the spots are visualized by heating the paper at 100 °C for a few minutes. 4. Resorcinol reagent: Mix 1% ethanolic solution of resorcinol and 0.2N HCl (1:1 v/v).Spray the dried chromatograms and visualize spots by heating at 90 °C. 5. Con.sulphuric acid: Spraying the chromatogram with H2SO4 solution black spots are appeared due to charring of sugers.
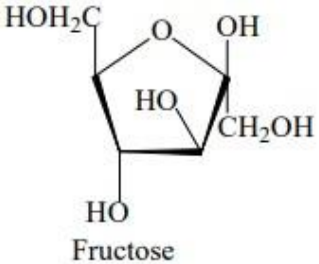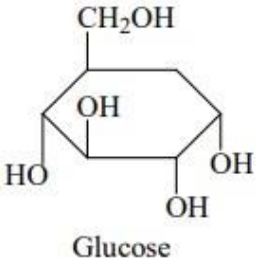
Procedure: Put sufficient solvent (mobile phase) into the bottom of the Paper chromatographic/TLC chamber. Cover the lid and allow the chamber to be saturated with the vapours of mobile phase. Now take a sheet of whattman no. 1 chromatography paper (about 9 × 10 cm) or a TLC plate and place it on a piece of clean paper on a working table/bench. Draw a fine line with a pencil along the width of the paper and about 1.5cm from the lower edge. Do not mark TLC with pencil otherwise the silica will be removed mark on the side of TLC in order to ensure the line of application/spotting. Along this line place four equally spaced (about 2cm apart) small circles with a pencil (in paper only). Label the paper at the top with the name of each of the sugars and label the last unknown. Use a fine capillary to place the drops of the solutions of the sugars, glucose, fructose etc and the mixture. After spotting, dry the paper with hot air dryer for one minute, repeat this step again. Spotted TLC plate is dried by keeping it for few minutes at room temperature. Do not dry with air dryer in case of TLC. Place the spotted paper/ TLC plate in the solvent saturated chromatographic chamber and make the development by using the ascending technique. Close the tank with lid, allow the solvent to flow for about 30-45 minutes. Remove the paper/ TLC plate and immediately mark the position of the solvent front with a pencil. After the chromatogram has dried, spray the paper/TLC plate with the visualizing reagent. Put the paper on the hot plate at low temperature or expose it to the hot air dryer, untilthe colored spots appear.TLC plates can be dried in oven. The colors are stable for some weeks if kept in the dark and away from acid vapors. Circle the position of each spot with pencil. Calculate the Rf value for each spot and also for the spots the mixture contained by using the formula as given in Fig.5.4.

15.7 RF VALUE AND ITS DETERMINATION

When chromatographic paper or TLC plate is develoved by allowing the mobile phase to run over stationary phase two forces comes in play. The propelling force, which drag the mobile phase against gravitational force due to capillary action and the second force force that pull back the mobile phase towards the line of application is known as retardation force. The retardation force is calculated by using the the following formula as also depicted in Fig 5.4.

$$R_f = \frac{\text{Distance travelled by spot/solute}}{\text{Distance travelled by mobile phase or simply solvent front (SF)}}$$

Observation: The following pattern of Rf value in different solvents can be achieved fig 15.5

Sugars	R_f values in different solvent system (Mobile Phase)		
	Solvent A	Solvent B	Solvent C
Fructose	0.51	0.25	0.68
Glucose	0.39	0.18	0.68

BASICS OF CHEMISTRY

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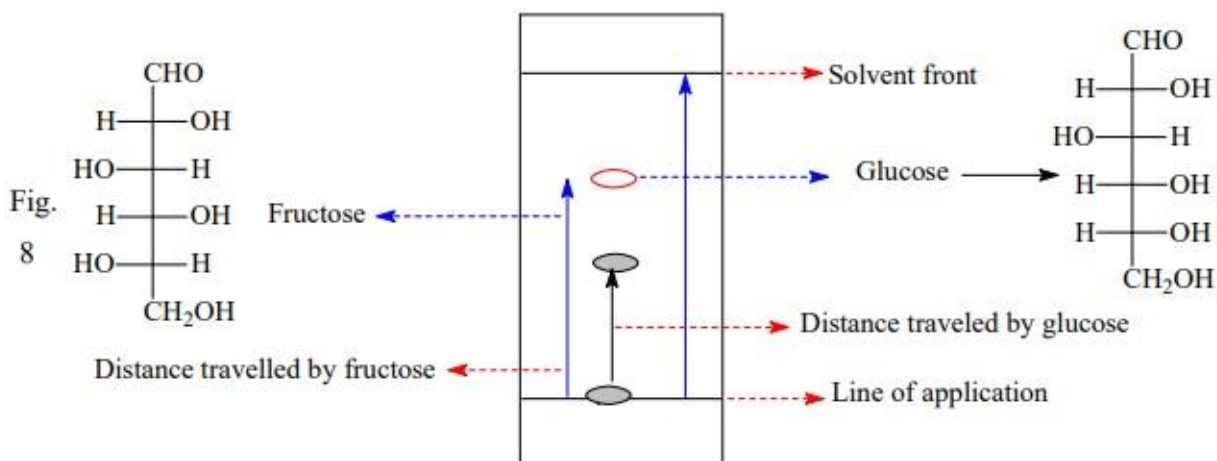GYAN VIHAR
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Fig 15.5 Separation pattern of glucose and fructose

Result: The R_f values of glucose and fructose in given mixture of monosaccharide are------------- ----respectively in different solvent systems/ mobile phases.

15.8 SUMMARY

Quantitative analysis by potentiometric titration method for an acid base neutralization reaction involves recording the pH after each addition of a standard solution of a base to a known volume of an acid of unknown strength. The pH of the solution depends on the ionisability of the acid and base in water and the extent of hydrolysis of the salt formed from the neutralization of the acid by the base. A graph of pH versus volume of base added to the acid is constructed. The end point is located from the point of inflexion which is a point where the pH of the solution changes rapidly. A perpendicular drawn from point of inflexion to X axis gives the volume of base required to neutralize the volume of acid taken in the beaker. This value is incorporated in the equation $V_1N_1=V_2N_2$ to determine the normality of the acid . The strength of the acid is calculated by the formula, Strength of acid =Normality of Acid x Equivalent weight of acid.

The procedure for TLC has also been discussed in detail explain in this unit. R_f value and its determination is also being described in this unit. Analytical and preparative alongwith 2D- TLC will make aware the students that in which t these techniques . The Detailed experimental condition

we can selec procedure for the separation of mixture of monosaccharides glucose and fructose by paper chromatography/ TLC .

15.9 TERMINAL QUESTIONS

1. Define acidimetry and alkalimetry.
2. What is a standard solution?
3. Give two examples of a primary standard.
4. What is equivalence point in an acid base titration?
5. How do you express acidity of a base and basicity of an acid?
6. What factors affect the form of a pH curve?
7. When will be the pH $=0, < 7$ and > 7 at equivalent point in an acid base reaction?
8. How do you express the pH of acetic acid?
9. Calculate the weight of NaOH required neutralizing 25 cm^3 of 1N HCl.
10. In an experiment 50 cm^3 of 0.1N HCl is titrated against 0.1N NaOH. Calculate the pH of the solution after addition of 40 cm^3 of NaOH.
11. What is chromatography? How it is classified? Discuss briefly
12. How will you differentiate among the term Chromatograph, Chromatogram, Chromatography and Chromatographer? Discuss briefly.
13. Why TLC chamber is saturated with mobile phase?
14. What is partition coefficient? What are different sequential steps involved in paper chromatography?
15. How alanytical chromatography differs from preparative chromatography? **Answers**

1. The process of addition of a standard acid from a burette to a known volume of base in a conical flask is called acidimetry. The process of addition of a standard base from a burette to a known volume of acid in a conical flask is called acidimetry.
2. A standard solution is a reagent of known concentration.
3. Oxalic acid and sodium carbonate.

4. Equivalence point is a stage where the reaction between acid and base undergoes completion theoretically.

5. Acidity of a base = Molecular weight / Equivalent weight
   Basicity of an acid=Molecular weight / Equivalent weight

6. The following factors affects the shape of pH curve

   i.   The extent of ionization of acid or base.

   ii.   The molalities of the solution used in the titration and

   iii. Acidity of the base and basicity of the acid.

7. In an acid base titration if the salt formed between strong acid and strong base does not hydrolyse then pH =0 at equivalence point.

   In an acid base titration if the salt formed between strong acid and weak base, the salt hydrolyses to give an acidic solution then pH < 7 at equivalence point.

   In an acid base titration if the salt formed between weak acid and strong base, the salt hydrolyses to give a basic solution then pH > 7 at equivalence point.

8. $pH = pK_a + \log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$

9. Let w = weight NaOH in gm

   Equivalent weight of NaOH = Molecular weight of NaOH = 40 $\dfrac{w}{E}$

   x 1000 = $V_{HCl}N_{HCl}$

   $\dfrac{}{x\ 1000}$ E w = $V_{HCl}N_{HCl}$

   w = 25 x 1 x $\dfrac{40}{1000}$= 1g

10. Given

    V = 50 ml, N_{HCl} = 0.1N, N_{NaOH} = 0.1N

    Apply the formula $V_{NaOH} N_{NaOH} = V_{HCl} N_{HCl}$

    V_{NaOH} = ($V_{HCl} N_{HCl}$) / N_{NaOH}

    V_{NaOH} = (50 x 0.1)/ 0.1

Let y = 40 ml

When volume of NaOH (y ml) is less than that required at equivalence point, then

[Excess acid]= [(V x N_A) - (y x N_g)] / (V + y)
= 50 x 0.1 – 40 x 0.1/ 50+40 = 0.011 pH

= -log[excess HCl]

$= -\log [1.1 \times 10^{-2}]$

$= 2 - \log 1.1$ pH

= 2- 0.04 = 1.96

15.10 REFERENCES AND FURTHER STUDIES

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